STRUCTURES OF
LANTHANIDE - EDTA
COMPLEXES

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BY

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ABSTRACT

The structures of six lanthanide-edta complexes were elucidated by X-ray diffraction, so as to ascertain exactly at which point the change from the nine-coordinate $[Ln(edta)(H_2O)_3]^-$ complex to the eight-coordinate $[Ln(edta)(H_2O)_2]^-$ complex occurs. The transition was found to occur at Erbium.

The structures of the complexes $K^+[Ln(edta)(H_2O)_3].5H_2O$ for Ln = Praseodymium, Europium, Gadolinium and Holmium were elucidated and found to be isomorphous crystallizing in the orthorhombic space group *Fdd2* with $Z = 16$. In each case, the central metal ion has a coordination number of nine, being bonded to the hexadentate edta ligand and three water molecules. For each structure, anomalous dispersion corrections were applied since *Fdd2* is a polar space group. The molecules of water of crystallization were seen to be partially disordered.

The structures of the complexes $K^+[Ln(edta)(H_2O)_2].4H_2O$ for Ln = Erbium and Ytterbium were elucidated and found to be isomorphous. A space group problem arose with these two structures as there was a problem of pseudo-symmetry, in that the molecules were arranged in a $P2_1/n$ pattern, but the motif in fact resembled that of $C2/c$ or Cc. The structures were finally refined in the centrosymmetric, monoclinic space group $C2/c$ with $Z = 4$, but were found to be disordered. In fact, in each case, two independent structures were identified, one 'good' and one 'lesser' structure. A study of the 'good' structure in each case showed that the central metal ion has a coordination number of eight, being bonded to the hexadentate edta ligand and two water molecules.

The technique of thermogravimetric analysis was employed in the study of the molecules of water of crystallization.

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CHAPTER 1

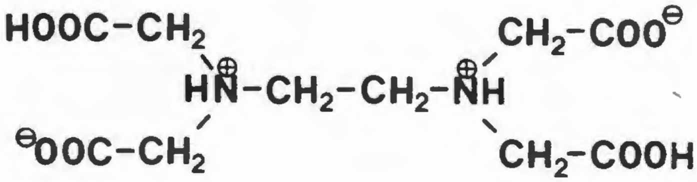
CHAPTER 1

INTRODUCTION

1.1 GENERAL

Ethylenediaminetetraacetic acid, (or edta; ethylenedinitrilotetraacetic acid; $C_{10}H_{16}N_2O_8$; H_4Y) can be represented in the zwitterion form as follows:

FIGURE 1.1



Edta is one of the most widely used reagents in titrimetric analysis and it owes its importance to the facts that:

(i) it forms complexes with nearly all the metals;

(ii) the stoicheiometry is nearly always 1:1, thus facilitating the simultaneous determination of mixtures of metals and metals in different oxidation states;

(iii) the titrimetric end-points are sharp and can be detected by a wide variety of different techniques[1]. Many anions can also be determined in direct compleximetric procedures[2].

The order of stabilities of the various metal-edta complexes can be seen from the summary in Table 1.1 from which it is possible to draw certain

TABLE 1.1 Stability Constants of Metal-edta Complexes

Li^{+}	Be^{2+}												
.79	9.2												
Na^{+}	Mg^{2+}	Al^{3+}											
.66	8.79	16.3											
				V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}		
K^{+}	Ca^{2+}	Sc^{3+}	Ti^{3+}	12.7	(13.6)	13.87	14.32	16.31	18.62	18.80	16.50		
.8	10.69	23.1	(21.3)^{b}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	-	-	-	Ga^{3+}	
				(26.0)^{b}	(23.4)^{b}	(25.3)^{b}	25.1	40.7^{a}				20.3	
	Sr^{2+}	Y^{3+}	Zn^{4+}	Nb	Mo	Tc	Ru	Rh	Pd^{2+}	Ag^{+}	Cd^{2+}	In^{3+}	Sn^{2+}
	8.73	18.09	29.5	-	-	-	-	-	(18.5)^{d}	7.32	16.46	25.0	18.3^{e}
												Tl^{+}	
	Ba^{2+}	La^{3+} *	Hf^{4+}	Ta	W	Re	Os	Ir	Pt	Au	Hg^{2+}	6.54	Pb^{2+}
											21.7	Tl^{3+}	18.04
	7.86	15.50	29.5^{a}	-	-	-	-	-	-	-		(35.3)^{b}	
	Ra^{2+}	Ac^{3+} **											
	7.1	-											

* LANTHONS (Z = 58-71)

Ce^{3+} 15.98; Pr^{3+} 16.40; Nd^{3+} 16.61; Pm^{3+} 17.0; Sm^{3+} 17.14; Eu^{3+} 17.35; Gd^{3+} 17.37
Tb^{+} 17.93; Dy^{3+} 18.30; Ho^{3+} 18.62; Er^{3+} 18.85; Tm^{3+} 19.32; Yb^{3+} 19.51; Lu^{3+} 19.83

** ACTINONS (Z = 90-103)

Th^{4+}	Pa;	U^{4+};	Np^{4+};	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}
23.2	-	25.8	24.6^{a}	18.1	(17.8)^{b}	(18.1)^{b}	(18.5)^{b}	(18.7)^{b}
			NpO_2^{+}	7.33^{b}				

[a] 25° and I = 1.0 M [b] 25° and I = 0.1 M [c] 20° and I = 0.2 M [d] 25° and I = 0.2 M [e] 20° and I = 1.0 M. Data from Critical Stability Constants, Vol 1, A.E. Martell and R.M. Smith, Plenum Press, 1974.

generalisations.

Firstly, it can be seen that the stability of the complex MY^{n-4} increases as the charge on the cation M^{n+} increases (i.e. in the order n=1<2<3<4). That is, when an element exists in more than one oxidation state, the cation with the higher oxidation state will exist as the more stable complex. For example:

$$\underline{K}_{Fe(II)Y} = \frac{[FeY^{2-}]}{[Fe^{2+}][Y^{4-}]} = 10^{14.32}$$

$$\underline{K}_{Fe(III)Y} = \frac{[FeY^{-}]}{[Fe^{3+}][Y^{4-}]} = 10^{25.1}$$

Secondly, divalent transition metals form complexes that are far more stable than the divalent alkaline earth metals. Metals carrying a unit positive charge, such as the alkali metals, do not complex readily with edta.

Thirdly, as a general rule, within a series of similar ions the stabilities of the complexes increase as the radii of the ions decrease. Correlations between $\log\underline{K}_{MY}$ and the functions such as $\underline{r}^{-1}$ and $\underline{r}^{-2}$, where $\underline{r}$ is the ionic radius of the cation, have been pointed out by many authors. This can be seen in the case of the first row transition series, i.e.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\log \underline{K}_{MY}$:	13.87	14.32	16.31	18.62	18.80	16.50
r(Å) :	0.80	0.76	0.74	0.72	0.69	0.74

This is in fact the Irving-Williams stability series.

The edta ligand is potentially hexadentate as it has the ability to bond to the central metal ion via the oxygen atoms of the four acetate groups, and the two nitrogen atoms. Therefore the stability of the edta complexes is ascribed to the formation of five chelate rings, each having the most favourable ring size of five members.

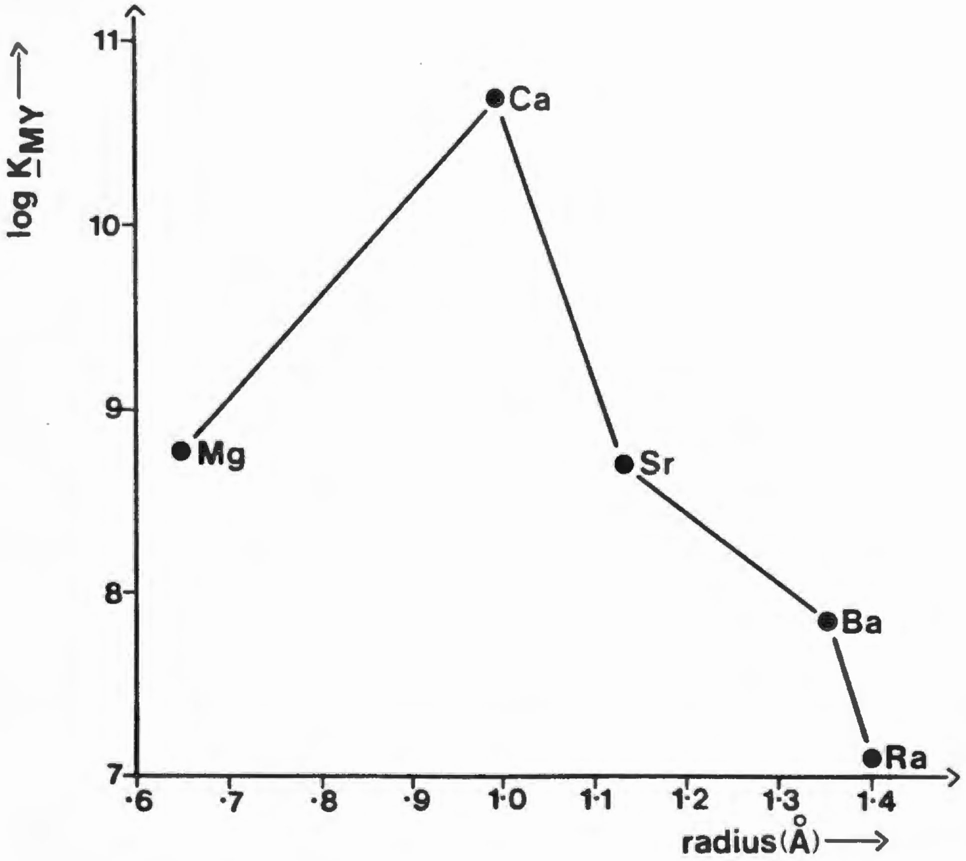
1.2 COMPLEXES OF THE GROUP IIA ELEMENTS

An interesting exception to the third general rule discussed above occurs in the case of the alkaline earths, i.e.

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
log $\underline{K}_{MY}$:	8.79	10.69	8.73	7.86	7.10
r(Å) :	0.65	0.99	1.13	1.35	1.40

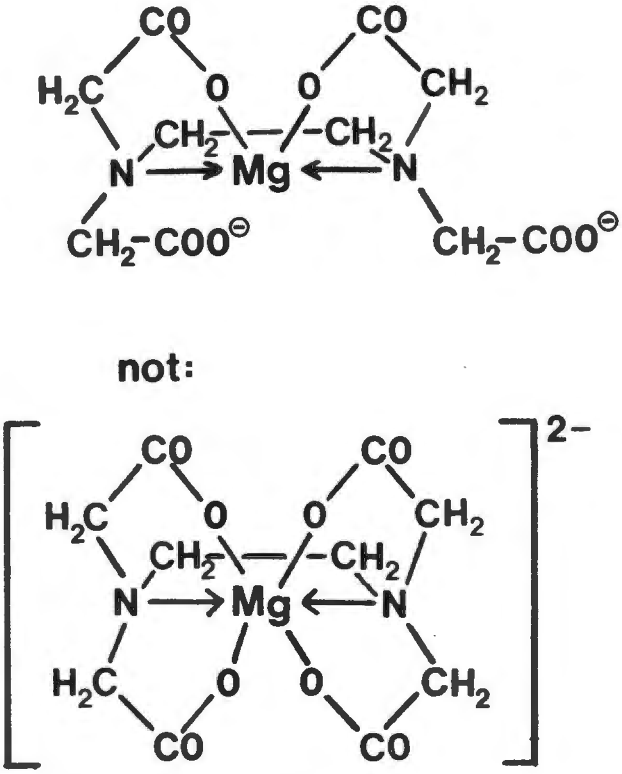
In this case the trend is interrupted by virtue of the fact that the Mg^{2+}-edta complex is less stable than the Ca^{2+} complex. (i.e. see Figure 1.2)

FIGURE 1.2



Originally a number of authors tried to explain the lower stability of the Mg^{2+} complex in terms of a lower degree of coordination, i.e. as a four-coordinate complex rather than a six-coordinate complex, thereby having fewer chelate rings. (see Figure 1.3)

FIGURE 1.3



This phenomenon of lower stability could be more quantitatively and better understood when the thermodynamic data in Table 1.2 was taken into account. It can be seen that Mg^{2+} is unique in forming the edta complex endothermically so that the net effect of the enthalpic and entropic contributions to the free energy change is responsible for the phenomenon, since:

$$\begin{aligned}\log \underline{K}_{ML} &= -\Delta G/2.303RT \\ &= (T\Delta S - \Delta H)/2.303RT\end{aligned}$$

TABLE 1.2

Thermodynamic data for complexes of edta with the alkali earths[3].

		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
${}^{a}\Delta S$/cal.mol^{-1}.deg^{-1}	:	52	26	26	19
$-T\Delta S$/kcal.mol^{-1}	:	-15.5	-7.8	-7.8	-5.7
${}^{b}\Delta H$/kcal.mol^{-1}	:	+3.5	-6.6	-4.1	-4.9
$-\Delta G$/kcal.mol^{-1}	:	12.0	14.4	11.9	10.6
log $\underline{K}_{MY}$	:	8.79	10.69	8.73	7.86

${}^{a}25^{\circ}C$ and $\underline{I} = 0.1\underline{M}$

${}^{b}20^{\circ}C$ and $\underline{I} = 0.1\underline{M}$

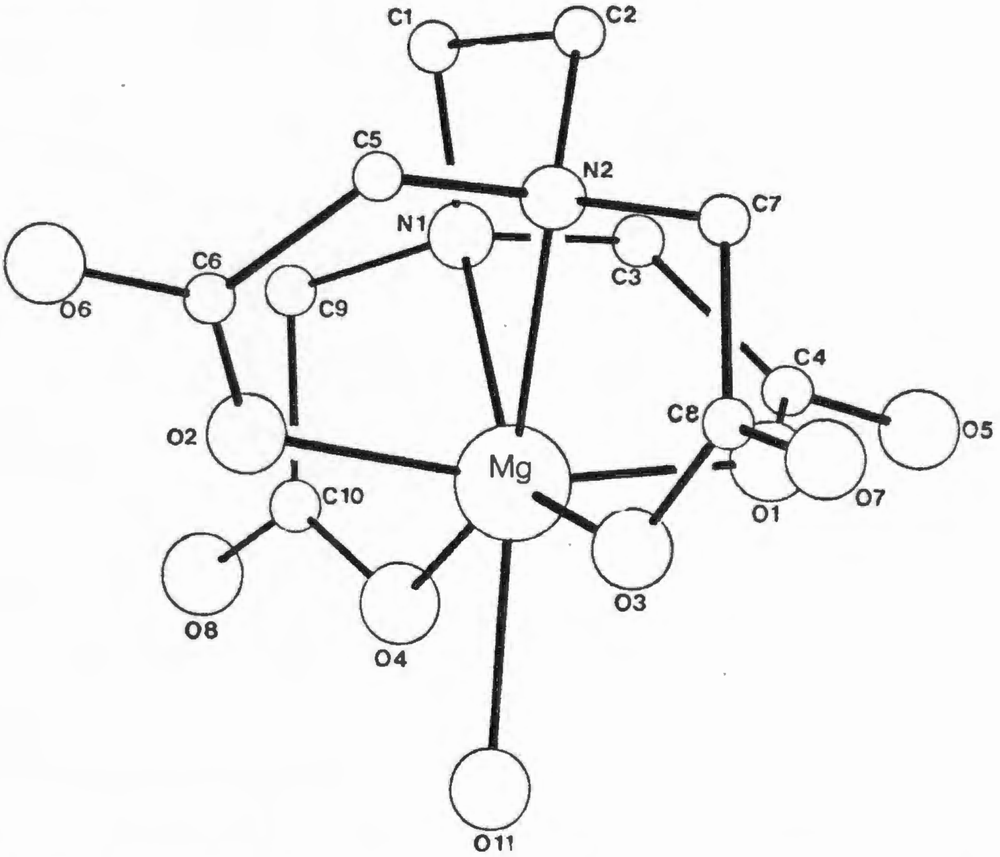
Note:

Critical thermodynamic values are reported in the literature in kcals and are quoted throughout in these units rather than in kJ.

However this is not a full explanation of the phenomenon since it gives no reason why the Mg^{2+} complex should be formed endothermically while the other alkaline earths are formed exothermically. Since the net enthalpy change must reflect the energy change in breaking six Mg-O bonds in the ion $Mg(H_2O)_6{}^{2+}$ and the formation of the Mg-N and Mg-O bonds to the edta ligand, the sum of the latter terms must be dependent primarily on the number of bonds involved (i.e. a coordination number of 4 would explain the positive value for the enthalpy). Factors reflecting the strain in the chelate rings and the interatomic repulsions would also play a part in the lower stability of the proposed four-coordinate structure.

It was therefore totally unexpected when it was discovered by Stezowski, Countryman and Hoard from X-ray crystallographic studies on the complex $Na[Mg(edta)].6H_2O$ that the Mg^{2+} ion was seven-coordinate with six-fold coordination from the hexadentate edta ligand and an additional molecule of water[4]. This seven-coordinate Mg^{2+} complex has since been confirmed by many other authors[5,6,7]. (see Figure 1.4)

FIGURE 1.4



The anion includes five rings which are located on one side of a plane passing through the Mg^{2+} ion, while the other side is occupied only by the coordinated water molecule[5].

Stezowski *et al.* explain the abnormally low value for the stability constant of the Mg^{2+} complex by the fact that the seven-coordinate structure must experience substantial stereochemical disability[4]. The coordination polyhedron is seen to be a geometric hybrid between the monocapped trigonal prism and the pentagonal bipyramid. For the geometry to be precisely that of monocapped trigonal prism it would require the ethylenediamine ring system to be planar which is physically impossible. Alternatively for the geometry to be exactly pentagonal-bipyramidal the water molecule, the two nitrogen atoms and two of the four carboxylate atoms would need to form an exactly planar girdle around the metal atom and this is also impossible.

Furthermore the averaged M-O and M-N distances in seven-coordinate species are known to be significantly larger than the value anticipated for standard octahedral coordination. However in the case of the Mg^{2+} complex these values are grossly larger thus indicating a decrease in the strength of these bonds which would consequently lower the stability of the complex. This is a result of the small size of the Mg^{2+} ion.

The reason for the preference for seven-coordination exhibited by the Mg^{2+} ion, in spite of the low stability of the resulting complex, is explained by Stezowski *et al.* as being partly attributable to the low affinity of the Mg^{2+} ion for the amino nitrogens relative to its affinity for the carboxylate oxygens[4].

The Ca^{2+}-edta complex, on the other hand, has been found to be an eight-coordinate complex with edta acting as a hexadentate ligand and the two additional coordination sites both occupied by water molecules[8]. The coordination polyhedron about the Ca^{2+} ion is square antiprismatic. It was originally predicted that the large Ca^{2+} cation would form a nine-coordinate complex with a stereochemistry similar to that of the lanthanide-edta complexes[9], (see part 1.6) but this would appear to be incorrect. The greater stability of the edta chelate of Ca^{2+} over the Mg^{2+} chelate is due to the fact that the larger Ca^{2+} ion fits better with the geometrical constraints imposed by the edta ring system. On the other hand the still larger Sr^{2+} ion is again slightly too big to accommodate itself to the geometry of the system without any strain. Thus in the Group IIA elements, it would seem that the Ca^{2+} ion has the optimum requirements for forming stable edta complexes.

1.3 COMPLEXES OF THE ALKALI METALS

The edta ligand, as a rule, does not tend to form complexes with metals carrying a unit positive charge[1], eg. the alkali metals. However, the compound, $[Co(NH_3)_6][Na(edta\text{-}4H)].3\frac{1}{2}H_2O$ was synthesised by Schlemper[10]. The compound contains two crystallographically independent octahedral $[Co(NH_3)_6]^{3+}$ ions, and a seven-coordinate Na^+ ion coordinated to the hexadentate edta ligand and a water molecule which bridges to another Na^+ ion. The coordination sphere of the Na^+ ion is similar to that of the Mg^{2+} ion (as in part 1.2). The smaller lithium ion, Li^+, forms thermodynamically more stable complexes but no structural data have been reported. Complexes of K^+ and still larger alkali cations are almost too weak to measure.

1.4 COMPLEXES OF THE TRANSITION METAL IONS

Many edta complexes of the first-row transition metal ions have been reported in the literature, while only a few of the second and third row series have been studied. It would appear that most of these transition metal ion complex anions are of the type $[M(H_2O)Y]^{n-4}$, while complex anions of the type $[M(H_2O)_2Y]^{n-4}$ and $[MY]^{n-4}$ are also reported to exist.

The transition metal-edta complex anions of the type $[M(H_2O)Y]^{n-4}$ that have been crystallographically determined to date are those for which $M = Cr^{3+}$, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ga^{3+}, Cd^{2+}, Sn^{4+} and Os^{4+}. All of these structures are either six- or seven-coordinate with one coordinated water molecule. The Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Ga^{3+} ions form six-coordinate complexes since in these cases edta acts as a pentadentate ligand with one carboxylic acid group uncoordinated[11,12,13,14,15]. The Mn^{2+}, Cd^{2+}, Sn^{4+} and Os^{4+} ions form seven-coordinate complexes where edta acts as a hexadentate ligand[16,17,18,19,26]. The Fe^{3+} ion, on the other hand, forms both six- and seven-coordinate complexes[15,20,21,22].

Of the six six-coordinate edta complexes, the complexes of Cr^{3+}, Fe^{3+} and Ga^{3+} have been characterised as being isomorphous. All three crystallize in the space group $P2_1/c$ with $Z=4$[11]. The coordination sphere around the metal ions can best be described in terms of a slightly distorted octahedral arrangement comprised of one water molecule and five of the six edta links. The sixth link, a carboxylic acid, remains free and is protonated[15]. The stabilities of these complexes versus the ionic radii are as follows:

	Cr^{3+}	Fe^{3+}	Ga^{3+}
log $\underline{K}_{MY}$:	23.4	25.1	20.3
r(Å) :	0.69	0.64	0.62

The reason for the surprisingly low stability for the Ga^{3+} complex is probably due to the fact that the small size of the Ga^{3+} ion causes the octahedral arrangement about the metal ion to be more distorted than in the other two complexes. In fact Kennard[15] reports that one of the M-O bonds of one of the rings in the Ga^{3+} structure is significantly longer than the corresponding bond in the Fe^{3+} structure (the other M-L distances are all shorter, as expected). This suggests that the closing of one of the edta links in the Ga^{3+} complex is geometrically more difficult, thus decreasing the stability of the structure.

The other three six-coordinate complexes that have been characterized are Co^{2+}, Ni^{2+} and Cu^{2+}. The complex stabilities versus the ionic radii are as follows:

		Co^{2+}	Ni^{2+}	Cu^{2+}
log $\underline{K}_{MY}$	:	16.31	18.62	18.80
r(Å)	:	0.74	0.72	0.69

In this case the order of the stabilities of the complexes versus the ionic radii is as expected. The Cu^{2+} and Ni^{2+} complexes are seen to be isomorphous[14]. The coordination spheres around these two metal ions can be described as quasi-tetragonally distorted octahedra, again comprising the one water molecule and five of the six edta links, with the sixth link remaining free and protonated. This distortion of the bonds in the Cu^{2+} complex is much greater than in the Ni^{2+} complex, however, and in fact tends towards a square-base pyramidal structure rather than a strictly tetragonal one. This is due to Jahn-Teller distortion in the case of Cu^{2+}.

In the case of the Co^{2+} complex, the free carboxylic acid group is not protonated and the ring actually remains quasi-closed[12], thereby supplementing the coordination of the Co^{2+} atom up to 7. If this seventh attenuated bond is ignored, the coordination polyhedron of the metal is an irregular octahedron, while if it is taken into account the coordination polyhedron is closer to that of a pentagonal byramid and is similar in structure to the hepta-coordinated complexes of Mn^{2+} and Fe^{3+} (see below). Figure 1.5 shows a drawing of an idealised model of the six-coordinate $[M(H_2O)Y]^{n-4}$ complex.

The five seven-coordinate complexes that have been studied, Mn^{2+}, Cd^{2+}, Fe^{3+}, Sn^{4+} and Os^{4+} are all qualitatively similar and are in fact similar to the Mg^{2+} complex (as described in part 1.2). i.e. These five complexes are also geometric hybrids between a pentagonal bipyramid and a monocapped trigonal prism. The Fe^{3+} complex exists predominantly as a pentagonal bipyramid and this geometry accounts for the high stability of the complex[20]. The Mn^{2+} and Cd^{2+} complexes, on the other hand, exist predominantly as

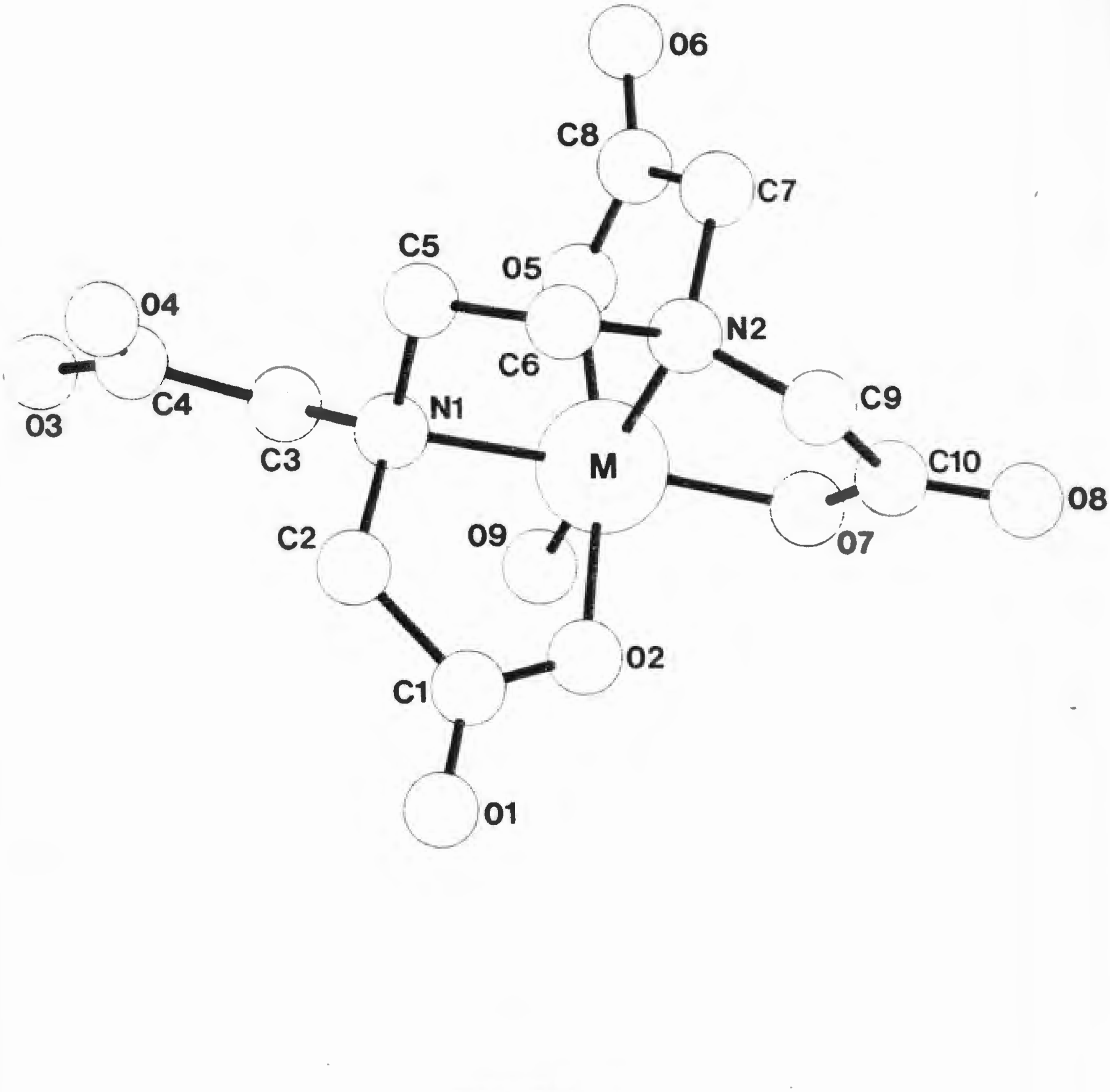


FIGURE 1·5

monocapped trigonal bipyramids[17,18,26]. This is consistent with the fact that pentagonal bipyramidal coordination is associated with smaller metal ionic radii (ionic radius of Fe^{3+} is 0.64Å), while monocapped trigonal prism coordination is associated with larger ionic radii (r of Mn^{2+} = 0.80Å and r of Cd^{2+} = 0.97Å).

The reason why the Mn^{2+} and Cd^{2+} ions form seven-coordinate complexes instead of the six-coordinate complexes described above is because of the large size of the ionic radii of these metal ions and this overcomes the increase in steric interaction between the ligands as well as the loss of the energetical advantage of octahedral coordination[18]. i.e.

		Mn^{2+}	Fe^{3+}	Cd^{2+}	Sn^{4+}	Os^{4+}
log $\underline{K}_{MY}$	:	13.87	25.1	16.46	?	?
r(Å)	:	0.80	0.64	0.97	0.71	0.69

On the other hand, it would appear surprising that the Os^{4+} complex is seven-coordinate. This was in fact the first example of seven-coordination of Os^{4+} in the literature[26]. Kennard[15] has shown that the Fe^{3+} complex exists in the six-coordinate form at low pH. When the pH is raised the proton on the free carboxylic acid arm is removed and the carboxyl group is forced into the coordination sphere producing the seven-coordinate pentagonal bipyramidal structure. Figure 1.6 shows a drawing of a idealised model of the seven-coordinate $[M(H_2O)Y]^{n-4}$ complex.

A complex anion of the type $[MY(H_2O)_2]^{n-4}$ that has been crystallographically determined is that for which M = Zr^{4+}.

This complex is an eight-coordinate structure with edta acting as a hexadentate ligand and two water molecules included in the inner coordination

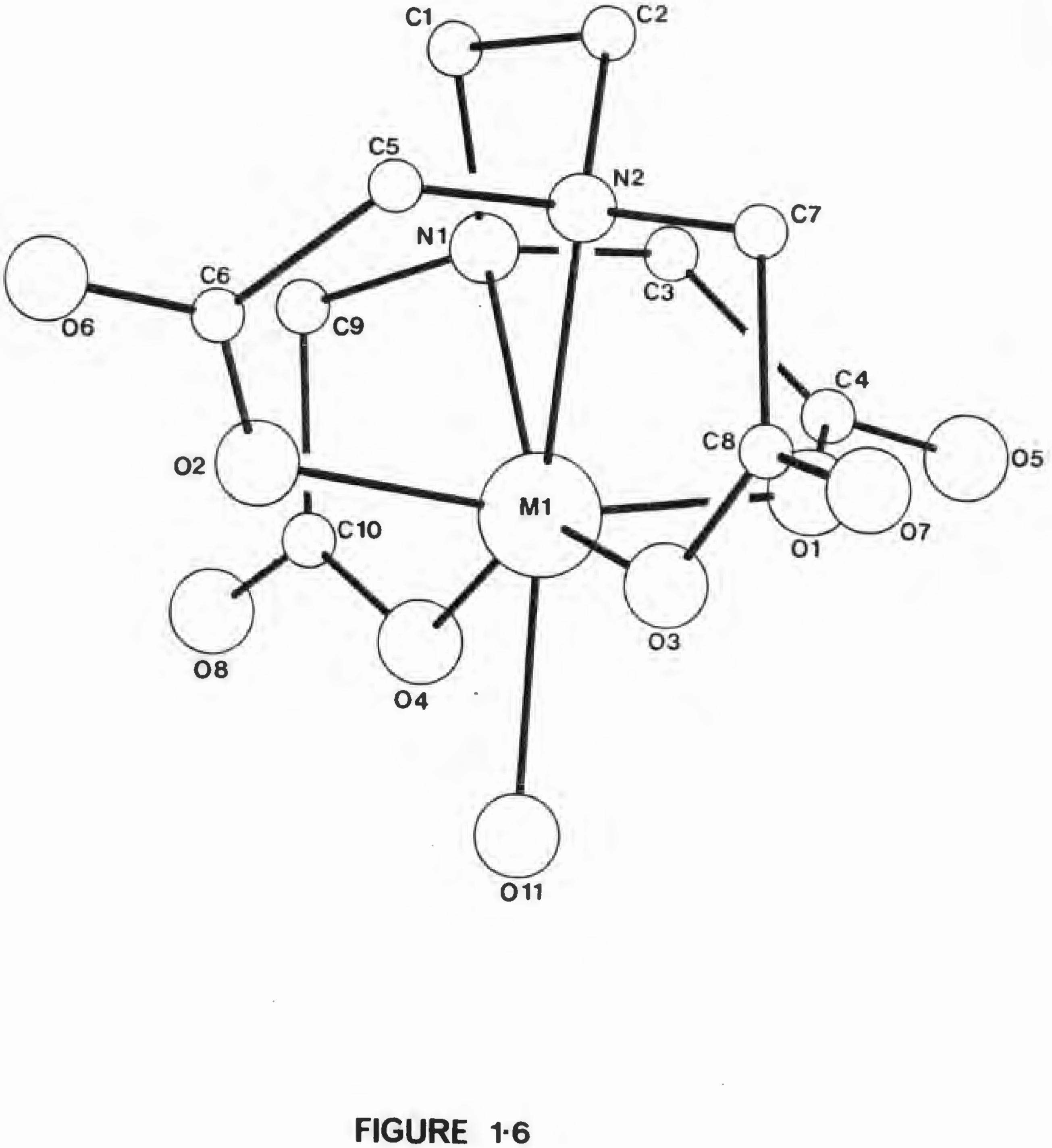


FIGURE 1·6

sphere[23]. The coordination polyhedron of the Zr^{4+} complex is intermediate between dodecahedral and antiprismatic.

A number of complex anions of the type $[MY]^{n-4}$ has been reported, i.e. for M = Al^{3+}, Mn^{3+}, Co^{3+}, Zn^{2+} and Sb^{3+}. In these complexes the metal ions are all coordinated by the hexadentate edta ligand producing distorted octahedra. There are no water molecules included in the inner coordination sphere and any water molecules are present as water of crystallization[28,29,30,31,24,25,27].

Figure 1.7 shows a drawing of an idealised model of these six-coordinate complexes.

It was always commonly assumed that the edta ligand can also act as a tetradentate donor in combination with metal ions having a coordination number of 4. This was, as previously stated, initially assumed to be so in the Mg^{2+} complex, but was later found to be incorrect. However the crystal structure of the Sn^{2+} complex has since been determined and in this case edta chelates as a tetradentate ligand[32]. The coordination sphere around the Sn^{2+} ion is that of a distorted pentagonal bipyramid. The two nitrogen atoms and two of the carboxyl groups from different nitrogen atoms are involved in the bonding. There are weak but definite links between the Sn^{2+} ion and the other two carboxyl groups.

Busch and Bailar[33] have also identified tetradentate edta complexes of Pt^{2+} and Pd^{2+} using infrared spectroscopy and potentiometric techniques. The same results were also obtained by Ezerskaya, Filimonova and Solovykh[34]. This has not been confirmed using crystallographic techniques, however.

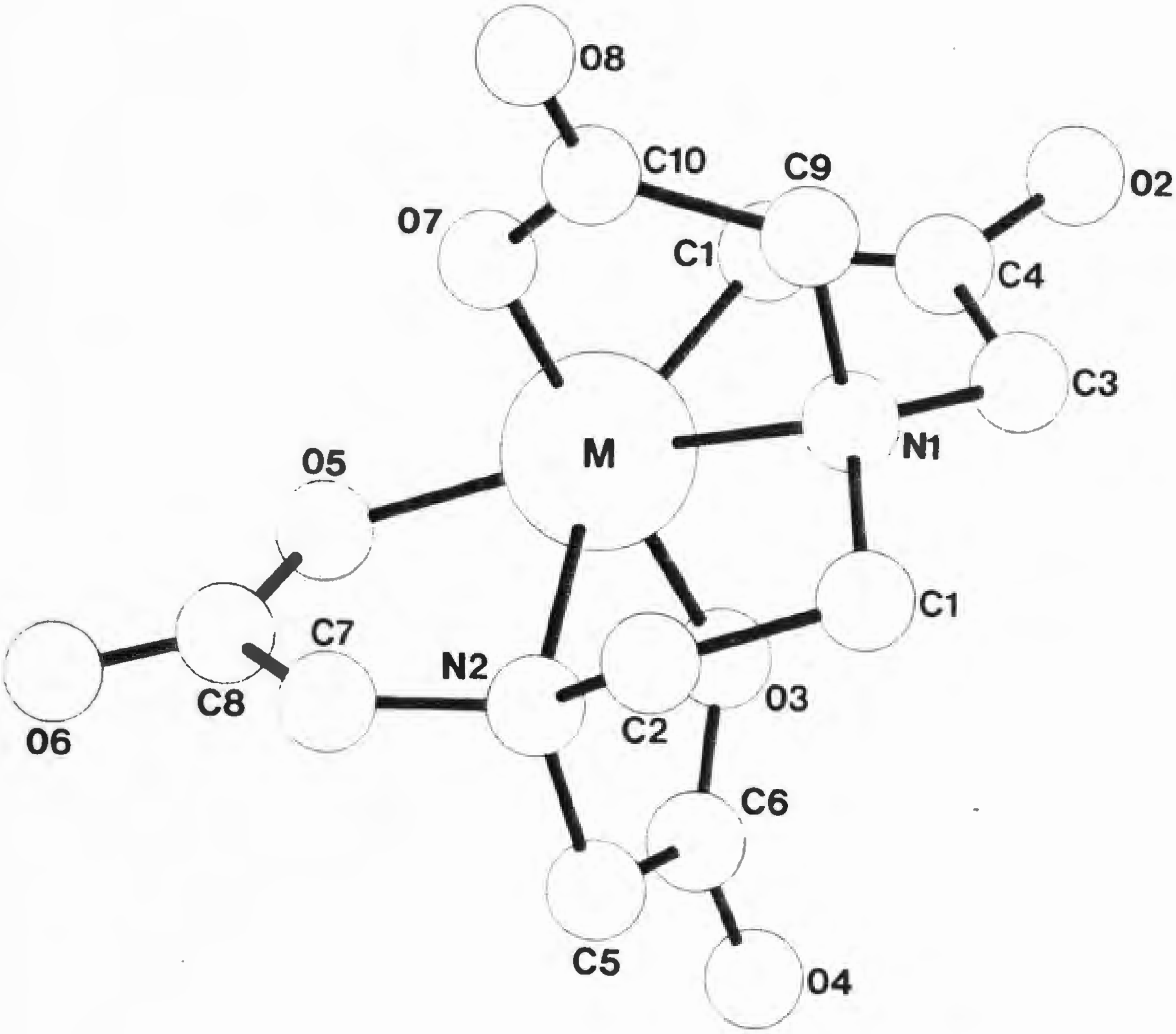


FIGURE 1·7

1.5 BINUCLEAR METAL-EDTA COMPLEXES

A number of binuclear metal-edta complexes has also been characterized. For example: The complex $[Cu_2Y.(H_2O)_2].2H_2O$ has been identified[35]. In this structure the two Cu^{2+} ions are bridged through an edta ligand. The edta ligand is shared between the two equivalent Cu^{2+} ions forming two glycine-like chelate rings about each Cu^{2+} ion. The ethylenediamine part of the ligand does not form a ring, but has a trans structure. Therefore the coordination of each Cu^{2+} ion consists of two acetate oxygen atoms, a nitrogen atom from the ethylenediamine moiety and a water molecule. The coordination sphere is expanded to a square pyramid by an acetate oxygen from a neighbouring complex.

Another type of binuclear complex that has been identified is that of $Sn_2Y.2H_2O$[36]. In this case the environments of the two Sn^{2+} ions are different. One of these two unique Sn^{2+} ions is coordinated by the hexadentate edta ligand, Y, in a distorted pentagonal-bipyramidal geometry i.e. the coordination sites about the Sn^{2+} ion are occupied by the two nitrogens and four carboxylate oxygens of the edta ligand and the seventh site is occupied by the tin lone pair electrons. This SnY unit is then bonded to four Sn^{2+} ions of the second type via carboxylate oxygens. i.e. These Sn^{2+} ions act as bridges between the SnY units. These Sn^{2+} ions are octacoordinated and this is achieved via weaker bonds with three additional oxygen atoms of the carboxylate groups. The electron lone pair of the tin then occupies the eighth coordination site.

1.6 THE LANTHANIDE-EDTA COMPLEXES

Complexing of the Ln^{3+} ions by an edta ligand in aqueous solution can be represented by[38]:

$$[\mathrm{Ln(H_2O)_h}]^{3+} + \mathrm{Y^{4-}} \quad = \quad [\mathrm{Ln(H_2O)_qY}]^- + (h-q)\mathrm{H_2O} \qquad \ldots. (1)$$

It is reasonable to assume that $q \geqslant 2$ in the bulky $[\mathrm{Ln(H_2O)_qY}]^-$ complexes since the size of the $\mathrm{Ln^{3+}}$ ions prohibits the hexadentate edta chelate from assuming standard octahedral coordination enclosing the cation (as in the case of $\mathrm{Mn^{3+}}$, for example). In fact, the edta chelation framework does not even reach as far as half-way around the central metal ion thus relegating the entire chelating ligand to one hemisphere, and leaving ample space in the other hemisphere for the coordinated water molecules.

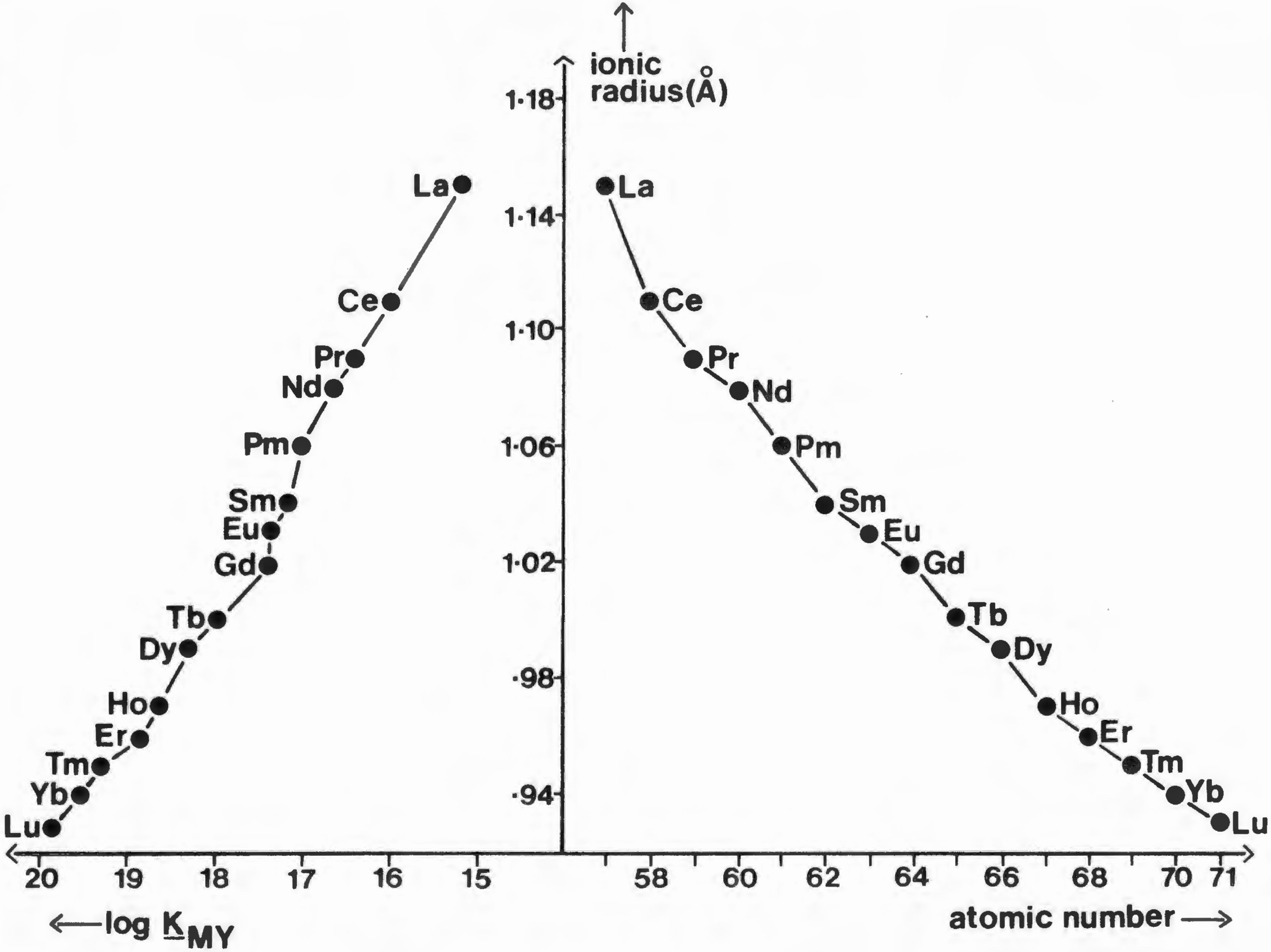
It has therefore been suggested by a number of authors that it is the cation size which plays the predominant part in determining the configuration and the coordination of the complex[38,39,40,42]. Consideration of the relative ionic sizes of the $\mathrm{Ln^{3+}}$ ions suggests that, in the sequence $\mathrm{La^{3+}}$ to $\mathrm{Lu^{3+}}$ there should be a transition from a nine-coordinate $[\mathrm{Ln(H_2O)_3Y}]^-$ complex to an eight-coordinate $[\mathrm{Ln(H_2O)_2Y}]^-$ complex as the successively smaller $\mathrm{Ln^{3+}}$ ions produce a general shrinkage of the anion finally resulting in the expulsion of one water molecule.

The lanthanide-edta complexes exhibit the same inverse relationship between the stabilities of the complexes and the radii of the ions, as described previously. i.e.

	$\mathrm{La^{3+}}$	$\mathrm{Ce^{3+}}$	$\mathrm{Pr^{3+}}$	$\mathrm{Nd^{3+}}$	$\mathrm{Pm^{3+}}$	$\mathrm{Sm^{3+}}$	$\mathrm{Eu^{3+}}$	$\mathrm{Gd^{3+}}$
log $\underline{K}_{MY}$:	15.50	15.98	16.40	16.61	17.00	17.14	17.35	17.37
r(Å) :	1.15	1.11	1.09	1.08	1.06	1.04	1.03	1.02

	$\mathrm{Tb^{3+}}$	$\mathrm{Dy^{3+}}$	$\mathrm{Ho^{3+}}$	$\mathrm{Er^{3+}}$	$\mathrm{Tm^{3+}}$	$\mathrm{Yb^{3+}}$	$\mathrm{Lu^{3+}}$
log $\underline{K}_{MY}$:	17.93	18.30	18.62	18.85	19.32	19.51	19.83
r(Å) :	1.00	0.99	0.97	0.96	0.95	0.94	0.93

FIGURE 1·8


ionic radius(Å)
1·18
1·14
1·10
1·06
1·02
·98
·94
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
20
19
18
17
16
15
58
60
62
64
66
68
70
71
← log $\underline{K}_{MY}$
atomic number →

A plot of this relationship is shown in Figure 1.8.

As can be seen, this relationship does not vary smoothly, but takes the form of a double-humped curve whith a dip occurring at Gadolinium. There is also a slight irregularity in the curve occurring at Erbium[40]. This break in the curve at Gd^{3+} would seem to imply that a change in the coordination occurs at this point. i.e. It would seem that going along the series from Lanthanum to Lutetium, there is a growing steric hindrance between the bulky ligand groups about the successively smaller metal ions and this prevents a large increase in the stabilities of the complexes. Then at the point of Gadolinium, if one water molecule were expelled, this would reduce the steric hindrance so that from this point onward, the stabilities would increase again steadily as the ionic radii became smaller. The small dip in the curve at Erbium could also possibly be explained by a further change in coordination number occurring at this point.

The stabilities of these Lanthanide-edta complexes can again be more quantitatively understood by consideration of the thermodynamic data, since:

$$\begin{aligned}\log \underline{K}_{ML} &= -\Delta G/2.303RT \\ &= (T\Delta S - \Delta H)/2.303RT\end{aligned}$$

A plot of the thermodynamic data for these complexes from Table 1.3 appears in Figure 1.9.

As can be seen, it is the large entropy effect that is the main driving force for the formation of these Lanthanide-edta complexes in aqueous solution. This is a common feature in the formation of any complex molecules involving multidentate chelates[41]. The values of ΔS^o increase across the series with decreasing radii.

TABLE 1.3

Thermodynamic data for the lanthanide-edta complexes[3].

	ΔS^o (cal.mol^{-1}.deg^{-1})[a]	$-T\Delta S^o$ (kcal.mol^{-1})	ΔH^o (kcal.mol^{-1})[b]	ΔG^o (kcal.mol^{-1})
La^{3+}	61	-18.2	-2.9	-21.1
Ce^{3+}	63	-18.8	-2.9	-21.7
Pr^{3+}	64	-19.1	-3.2	-22.3
Nd^{3+}	64	-19.1	-3.6	-22.7
(Pm^{3+})	-	-	-	-
Sm^{3+}	67	-20.0	-3.4	-23.4
Eu^{3+}	71	-21.2	-2.6	-23.8
Gd^{3+}	74	-22.1	-1.7	-23.8
Tb^{3+}	78	-23.2	-1.1	-24.3
Dy^{3+}	80	-23.8	-1.2	-25.0
Ho^{3+}	80	-23.8	-1.4	-25.2
Er^{3+}	80	-23.8	-1.7	-25.5
Tm^{3+}	82	-24.4	-1.9	-26.3
Yb^{3+}	81	-24.1	-2.3	-26.4
Lu^{3+}	82	-24.4	-2.5	-26.9

[a] 25°C and $\underline{I}$ = 0.1$\underline{M}$

[b] 20°C and $\underline{I}$ = 0.1$\underline{M}$

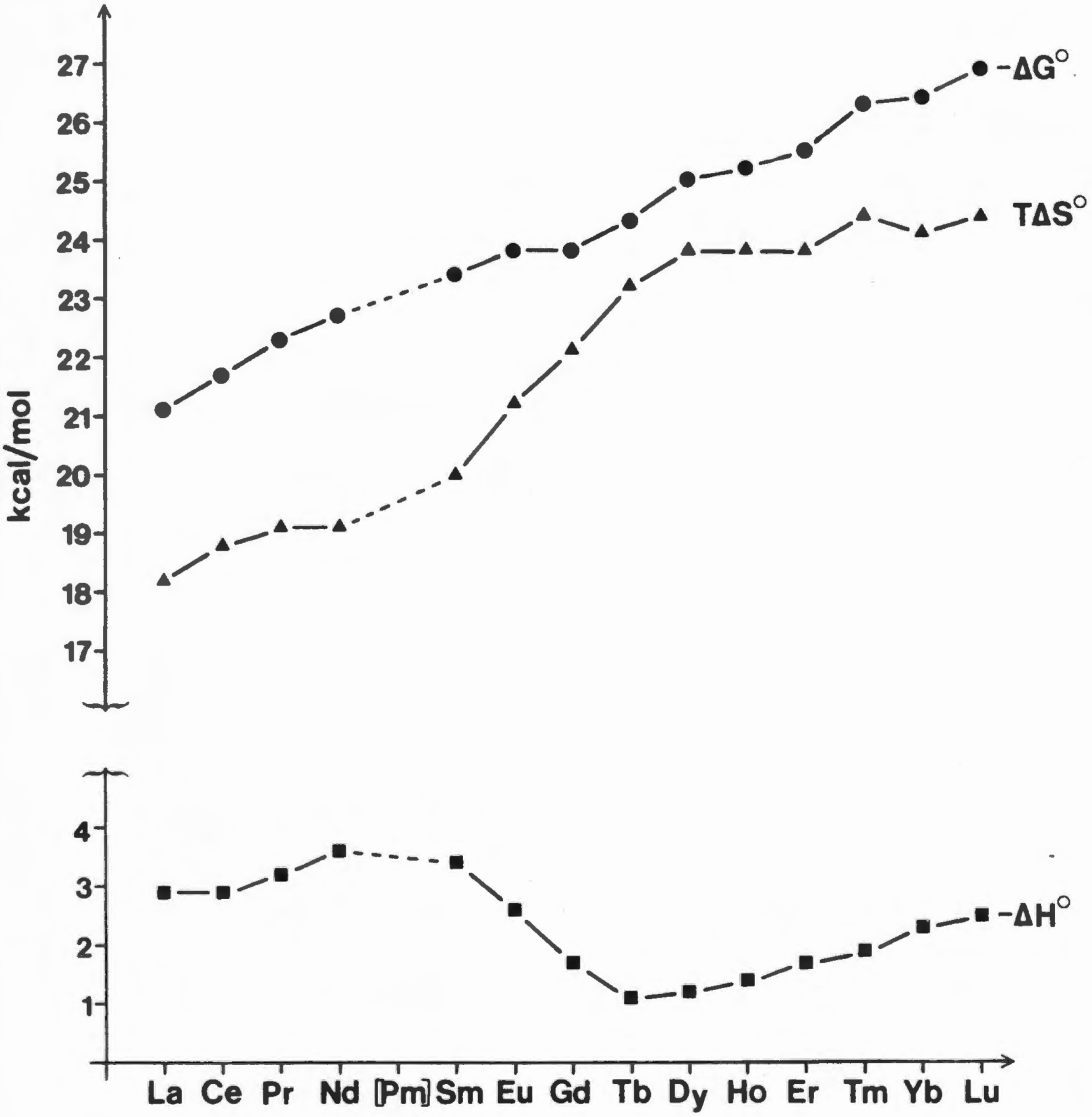

kcal/mol
27
26
25
24
23
22
21
20
19
18
17
4
3
2
1
-ΔG°
TΔS°
-ΔH°
La
Ce
Pr
Nd
[Pm]
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

FIGURE 1·9

The ΔH^o values appear to fall into two series, one for the light and one for the heavy lanthanides, with a gradual transition between the two series around Gadolinium[41]. In the region of Samarium to Terbium, there is a large increase in the standard enthalpy of formation, ΔH^o, and a large increase in the standard entropy of formation, ΔS^o. This seems to indicate that a change in coordination occurs within this region[42]. From equation (1) above, a change from a nine- to an eight-coordinate complex would increase (h-q) by unity with a corresponding increase in the standard entropy, and would decrease q by unity resulting in a less favourable enthalpy. This is in direct agreement with the thermodynamic data.

Therefore, from the stability constants and the thermodynamic data it would appear that the transition from a nine-coordinate $[Ln(H_2O)_3Y]^-$ complex to an eight-coordinate $[Ln(H_2O)_2Y]^-$ complex occurs in the region around Gadolinium.

However, this has been shown to be incorrect. The complex $H[LaY].7H_2O$ is a ten-coordinate structure crystallizing in the space group $P2_1/a$[39]. The complexes $K[LaY].8H_2O$[38], $Na[SmY].8H_2O$[44], $Na[TbY].8H_2O$[42] and $Na[DyY].8H_2O$[45] have been shown to be isomorphous since they all crystallize in the space group *Fdd2* and have a coordination number of 9. It has also since been shown that the complex $Cs[YbY].5H_2O$ is in fact an eight-coordinate structure crystallizing in the space group $P2_1/n$[45]. It would thus appear that the transition in coordination occurs within the sequence Dy^{3+} to Yb^{3+}. This could possibly account for the second dip occurring at Er^{3+} in the plot of stability constants versus ionic radii (Figure 1.8). Table 1.4 gives a summary of all the structural information known about the Lanthanide-edta complexes including the work done for this Thesis.

Alsaadi , Rossotti and Williams[55] have studied the ^1H nmr spectra of all the

TABLE 1.4

Ln^{3+}	M^+	Space group	Coordination Number	Reference
La	H^+	$P2_1/a$	10	39
	K^+	$Fdd2$	9	38
Ce	-	-	-	-
Pr	K^+	$Fdd2$	9	Hoc opus
Nd	$Guad^+$	$Pn2_1/a$	9	43
(Pm)	-	-	-	-
Sm	Na^+	$Fdd2$	9	44
Eu	K^+	$Fdd2$	9	Hoc opus
Gd	K^+	$Fdd2$	9	Hoc opus
Tb	Na^+	$Fdd2$	9	42
Dy	Na^+	$Fdd2$	9	45
Ho	K^+	$Fdd2$	9	Hoc opus
Er	NH_4^+	$P\bar{1}$	≠	46
	K^+	$C2/c$	8	Hoc opus
Tm	K^+	$C2/c$	-	Hoc opus (incomplete)
Yb	Cs^+	$P2_1/n$	8	45
	K^+	$C2/c$	8	Hoc opus
Lu	-	-	-	-

≠ Inconsistencies in the atomic coordinates.

Lanthanide-edta complexes in aqueous solution and concluded that all these complexes, from Lanthanum to Lutetium, are 9-coordinate in solution.

On balance therefore, it seems possible that for all the Lanthanide-edta complexes, the dominant species in solution is 9-coordinate, with the 8-coordinate species becoming increasingly important in the later part of the series.

In that case, the thermodynamic data could be interpreted in terms of their being a change from a 9- to an 8-coordinate complex, in solution only, in the region of Samarium to Erbium. Then the 9-coordinate complexes of Samarium to Holmium in the solid state could owe their existence to superior packing.

However, a number of other authors have stated that other factors, apart from the cation size, must also play a part in determining the coordination of these structures[41,47,51,52,53,54]. They state that it is unlikely that when a critical size of cation is reached there is an abrupt change in the coordination number. The trend of stability constants could then be interpreted as being due to varying degrees of stabilization from the interaction of the 4f orbitals with the ligand field[47].

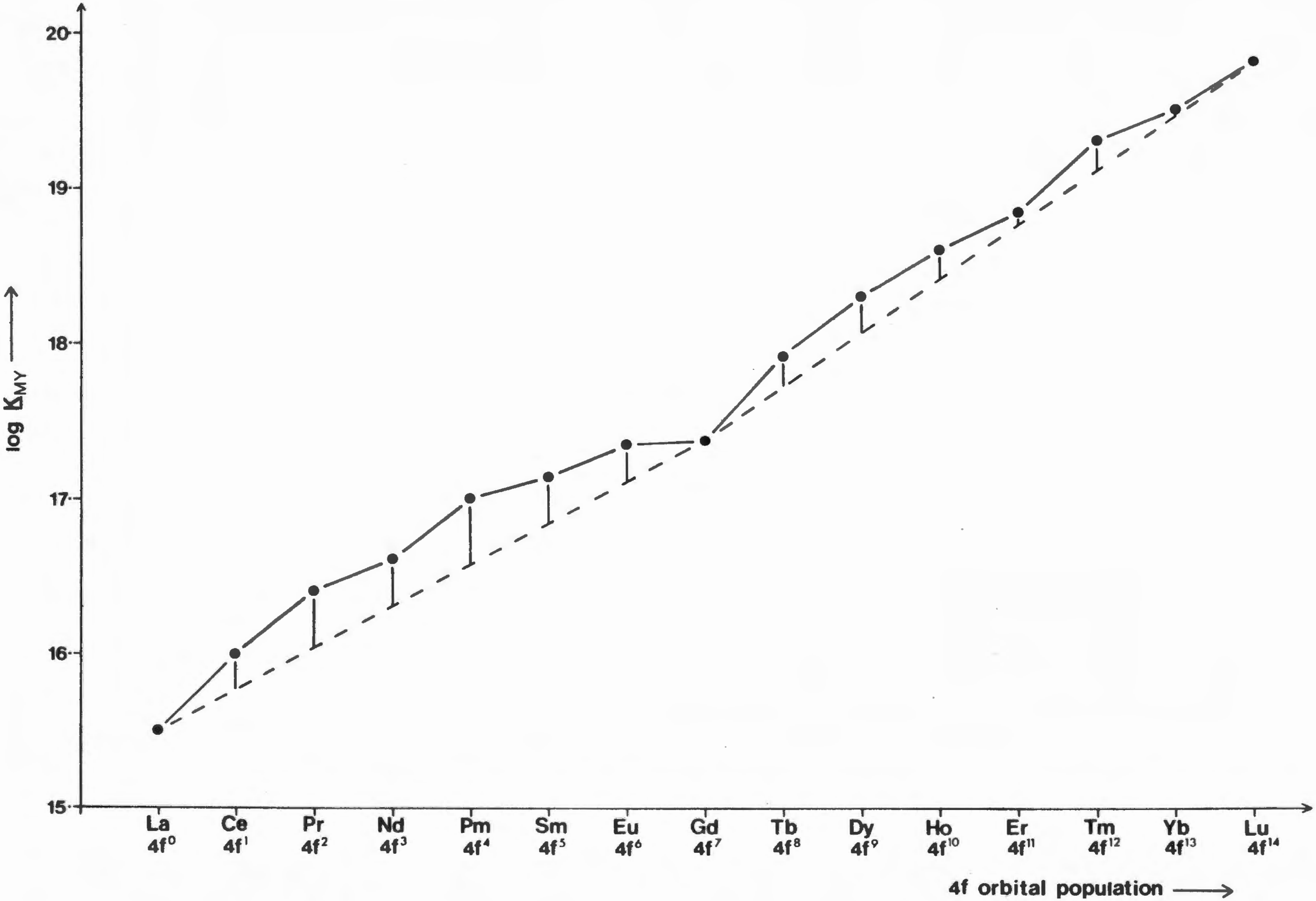
The lanthanides are characterized by the gradual filling of the 4f subshell[48]. Although the electron configurations of the neutral lanthanide atoms show some irregularities, there is strict regularity in the electron configurations of the +3 cations since they all have $4f^n5d^o6s^o$ configurations. Furthermore, the 4f electrons are buried so deeply within the atom that they seem to be largely unaffected by the environment. It was these factors that caused a number of authors to state that the f-electrons of the lanthanides have little influence over the primary bonding scheme in the complexes.

However, Holleck and Liebold[49] state that the decrease in the magnetic susceptibility of the Neodynium ion on coordination with edta is evidence that the 4f orbitals are affected by complex formation. Another indication that ligand field effects may be significant is the fact that the stability constant for the Yttrium-edta complex (log $\underline{K}_{MY}$ = 18.09) is less than that for the Holmium-edta complex (log $\underline{K}_{MY}$ = 18.62)[47]. The Y^{3+} ion has a radius almost identical to that of the Ho^{3+} ion, but Y^{3+} has no 4f electrons while Ho^{3+} has ten 4f electrons. It therefore would appear that the Ho^{3+} complex is stabilized to some extent by the ligand field. Furthermore, the thermo= dynamic properties of the complexes appear to be influenced by the ligand field splitting of the 4f orbitals[55]. From Table 1.3, it can be seen that although Nd^{3+} (with three 4f electrons) is a smaller ion than Ce^{3+} (with one 4f electron), Nd^{3+} forms its edta complex with a greater evolution of heat[47].

The relationship between log $\underline{K}_{MY}$ and the 4f-orbital population is depicted in Figure 1.10. The relationship is a double-humped curve superimposed on an interpolation line of positive slope. Using the method proposed by George and McClure[50], the interpolation line connecting the points for the $4f^o$, $4f^7$ and $4f^{14}$ complexes would represent the stabilities which arise from lanthanide-ion contraction. The difference between these values and the actual observed stabilities then represent the contribution to log $\underline{K}_{MY}$ provided by crystal field stabilization[51] (represented by the vertical lines in Figure 1.10).

Estimates[47] of the crystal field splitting for the 4f levels are of the order of $100cm^{-1}$. Since there are no f-electrons in the La^{3+} ion, and the f-electrons are distributed regularly throughout all the orbitals of the Gd^{3+} and Lu^{3+} ions, there should be no crystal field effect for these elements[52]. Relative to the complexes of La and Gd, the remaining lanthanides are stable by amounts of the order of a few hundred calories[53].

FIGURE 1·10


20
19
18
17
16
15
log K_{MY} →
La $4f^0$
Ce $4f^1$
Pr $4f^2$
Nd $4f^3$
Pm $4f^4$
Sm $4f^5$
Eu $4f^6$
Gd $4f^7$
Tb $4f^8$
Dy $4f^9$
Ho $4f^{10}$
Er $4f^{11}$
Tm $4f^{12}$
Yb $4f^{13}$
Lu $4f^{14}$
4f orbital population →

It therefore would appear to be an over-simplification to assume that an abrupt change in coordination number occurs in the lanthanide-edta complexes corresponding to the irregularities in the thermodynamic data and stability constants, since these effects could arise from the weak, but not negligible, effect of the ligand field on the 4f electrons.

However, it was considered worthwhile to determine the structures of a number of the Lanthanide-edta complexes and, with the structural information reported by other authors (see Table 1.4), to investigate the trend followed by these complexes. The structures that we determined crystallographically in this work were: $K^+[Ln(edta)].8H_2O$ for Ln = Praseodymium, Europium, Gadolinium and Holmium, and $K^+[Ln(edta)].6H_2O$ for Ln = Erbium and Ytterbium.

The complexes of Ho^{3+}, Er^{3+} and Yb^{3+} were investigated to identify exactly at which point the change in coordination from 9 to 8 does occur. The structures of Eu^{3+} and Gd^{3+} were studied to ascertain whether there are, after all, any structural differences which could account for the breaks in the stability constants series and the thermodynamic data. The effect of the counter-ion on the structures of these complexes was also investigated.

CHAPTER 2

CHAPTER 2

GENERAL EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

This chapter comprises a general summary of the synthesis and characterization of the compounds as well as of the X-ray crystallographic methods used in the structural determination of the compounds, and will not be repeated in later chapters.

2.1 CRYSTAL PREPARATION

The seven lanthanide-edta complexes that were studied in this work were all of the form $K^+[Ln(edta)].nH_2O$, for which Ln = Praseodymium (Pr), Europium (Eu), Gadolinium (Gd), Holmium (Ho), Erbium (Er), Thulium (Tm) and Ytterbium (Yb).

All these complexes were prepared in the following way:
10mmol of the solid lanthanide oxide (Ln_2O_3) were added to 50cm^3 of distilled water containing 25mmol of ethylenediaminetetraacetic acid (edta) and 20mmol of potassium hydroxide (KOH). The suspension was heated under reflux until a clear solution was obtained. The cool solution was filtered, the pH of the filtrate adjusted to ca. 6.5 and excess water slowly evaporated until crystallization occurred. The salts were recrystallized from water[56].

The Pr, Eu, Gd and Ho crystals obtained were all diamond-shaped, the Pr crystals being bright green in colour, the Eu and Gd colourless and the Ho pale pink in colour. The Er, Tm and Yb crystals were all rhomboidal in shape, the Er crystals being pale pink in colour while the Tm and Yb crystals were colourless.

2.2 THE CHARACTERIZATION OF THE COMPOUNDS

The stoicheiometric compositions of the compounds were determined by microanalysis as shown in Table 2.1.

TABLE 2.1 Microanalysis Results

$K^+[Ln(edta)].nH_2O$		Experimental			Calculated		
Ln	n	%C	%H	%N	%C	%H	%N
Pr	8	19.6	4.5	4.6	19.61	4.58	4.58
Eu	8	19.3	4.5	4.5	19.25	4.49	4.49
Gd	8	19.2	4.3	4.5	19.10	4.46	4.46
Ho	8	19.1	4.3	4.5	18.87	4.40	4.40
Er	6	19.9	4.0	4.6	19.92	3.98	4.65
Yb	6	19.6	4.0	4.9	19.73	3.95	4.60

The Thulium crystals obtained were of very poor quality, so the study of the Thulium compound was not pursued after the initial photography.

The crystal densities were determined by flotation in a mixture of methyliodide and tetrachloromethane.

Thermogravimetric analysis was employed to assist in the determination of the number of water molecules present.

2.3 PRELIMINARY X-RAY ANALYSIS[57,58,59]

In all seven cases, single crystals with uniform extinction under plane polarised light were selected and mounted on glass fibres. A two-circle optical goniometer was used for alignment. Oscillation, Weissenberg (zero layer and upper layer) and precession photographs were taken using a non-integrating Stoë (Heidelberg) goniometer using nickel filtered CuK_α radiation (λ=1.5418Å) and a camera of radius 28.65mm. The X-ray generators that were used were the Philips PW1120 and PW1008 and were operated at 20mA and 40kV. The X-ray films (3M Medical) were processed using Kodak X-ray developer and fixer solutions.

Approximate unit cell parameters and space group symmetries were determined for all the compounds based on layer-line spacings and systematic absences of reflections in the photographs.

2.4 DIFFRACTOMETER DATA COLLECTION

Suitable crystals were selected and mounted on glass fibres and sent to Mr J. Albain at the National Physical Research Laboratory, C.S.I.R. (Pretoria), for diffractometer data collections. Small crystals were chosen so as to minimise absorption problems. The data collection was obtained (i.e. the relative intensities of the reflections were measured) using a Philips PW1100 computer-controlled four-circle diffractometer. A Philips PW1130 X-ray generator operating at 20mA and 50kV provided the source of radiation, it being monochromated MoK_α radiation (λ=0.7107Å).

Accurate lattice constants were obtained at room temperature by a least squares analysis of the χ, ϕ and 2θ angles of 25 standard reflections accurately centred on the diffractometer. The intensities of three reference reflections were monitored periodically throughout the data collection to check the stability of the crystal and the instrument. The standard error $\sigma I_{(rel)}$ in the relative integrated intensity $I_{(rel)}$ was calculated from:

$$\sigma I_{(rel)} = [(0.02N_o)^2 + K^2N_b + N_o]^{\frac{1}{2}}$$

where: N_o = the gross peak count for a particular reflection.

N_b = the background count, measured on each side of the peak.

K = the ratio of scan to background times.

The criterion for a reflection being considered 'observed' was $I_{(rel)} > 2\sigma I_{(rel)}$. Lorentz polarisation corrections were applied automatically to all the reflection data at the C.S.I.R.

2.5 COMPUTATION

All computations were performed on a Univac 1106 computer at the University of Cape Town.

The program SHELX76[60] was used for crystallographic data reduction, structure determination and refinement. Solutions were effected by Patterson and Fourier techniques.

In all cases, the agreement between observed (F_o) and calculated (F_c) structure factors is expressed by the conventional residual factors defined by:

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = \frac{\Sigma|\Delta|}{\Sigma|F_o|}$$

and $$R\omega = \frac{\Sigma\omega^{\frac{1}{2}}||F_o| - |F_c||}{\Sigma\omega^{\frac{1}{2}}|F_o|} = \frac{\Sigma\omega^{\frac{1}{2}}|\Delta|}{\Sigma\omega^{\frac{1}{2}}|F_o|}$$

where $$\omega = \frac{k}{[\sigma^2(F) + gF^2]}$$

k was redetermined after each structure factor calculation. The value of g was chosen to give the smallest variation of $\omega\Delta^2$ with the magnitude of F_c.

Thermal parameters are of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

where : U_{ij} are the anisotropic temperature factors referred to in the text.

The accuracy of the structures was expressed using the following criteria:

(i) A low value for the residual factor R. (i.e. $R<10\%$)

(ii) A low shift/esd of each parameter in the final cycle. (i.e. <0.1)

(iii) A satisfactory analysis of variance calculated after the final refinement.

(iv) Chemically feasible molecular geometry. (i.e. acceptable coordination, bond lengths and angles)

The complex scattering factors for the non-hydrogen atoms were taken from Cromer and Mann[61]. Anomalous dispersion corrections were taken from Cromer and Liberman[62]. Atomic radii used were those of Pauling[63].

The program PLUTO[64] was used for molecular illustrations and projections.

The program XANADU[65] was used to calculate geometric parameters.

CHAPTER 3

CHAPTER 3

THERMOGRAVIMETRIC ANALYSIS

3.1 GENERAL THEORY[66]

Thermogravimetric analysis is a technique that measures the change in the weight of a sample as a function of increasing temperature. A plot of the weight as a function of the temperature is called a thermogram and can provide both qualitative and quantitative information. TGA can provide information relating to certain physical and chemical phenomena that are accompanied by a change in weight.

A thermogram may have the following features:

(i) A plateau which indicates constant weight.

(ii) A curved portion, the steepness of which indicates the rate of weight loss.

(iii) An inflection at which dw/dt is a minimum. This may imply the formation of an intermediate compound.

To obtain quantitative results, it is best to use the complementary technique of differential thermal analysis (DTA). DTA measures changes in heat content as a function of increasing temperature. This technique was not used, however. Due to technical problems with the apparatus used, only qualitative results could be obtained.

Useful applications of TGA are in the study of decomposition reactions, the loss of constituent volatile ligands and the loss of constituent water molecules. It was the latter application that was applicable to the study of the water molecules of crystallization of the edta complexes.

This study was made in an attempt to obtain more information regarding the water molecules present in the structures, particularly the water molecules of crystallization, so that the results obtained could be used in conjunction with the microanalysis data and the structure determinations.

3.2 EXPERIMENTAL

A thermogram was recorded of the compound $K^+[Gd(edta)].8H_2O$. It was assumed that the information obtained regarding this compound could be applied to the isomorphous compounds $K^+[Pr(edta)].8H_2O$, $K^+[Eu(edta)].8H_2O$ and $K^+[Ho(edta)].8H_2O$ since the four compounds are isomorphous (see Chapter 4). Similarly, a thermogram was recorded of the compound $K^+[Er(edta)].6H_2O$ assuming the results obtained could be applied to the isomorphous compound $K^+[Yb(edta)].6H_2O$ (see Chapter 5).

The TGA measurements were recorded on a Stanton-Redcroft model TR thermobalance. The thermobalance was checked for reproducibility using a $CuSO_4.5H_2O$ sample and the result obtained agreed well with the literature. Quartz sample tubes were used which hold 100 to 200mg samples. A 'blank' TGA curve was recorded on an empty quartz tube in order to take into account the effect of the apparent mass change of the empty tube. The TGA curves were recorded on the Stanton twin pen recorder which gives continuous records of sample weight and furnace temperature against time. The left-hand chart record is scaled in mass, on a 20mg full scale. The right-hand chart record is scaled in degree centigrade. The chart speed was 300mm/hour. The heating rate was 6^oC/minute. Atmosphere control was not used, so the environmental conditions were static air, which, as the reaction proceeds, consists of air and evolved volatiles (i.e. H_2O) from the sample[67].

The TGA curve of the compound $K^+[Gd(edta)].8H_2O$ was recorded using 140.9mg of sample in the quartz tube. The sample was heated to a temperature of 700°C. The TGA curve of $K^+[Er(edta)].6H_2O$ was recorded using 162.8mg of sample and it was heated to a temperature of 550°C.

3.3 DISCUSSION OF THE $K^+[Gd(edta)].8H_2O$ CURVE

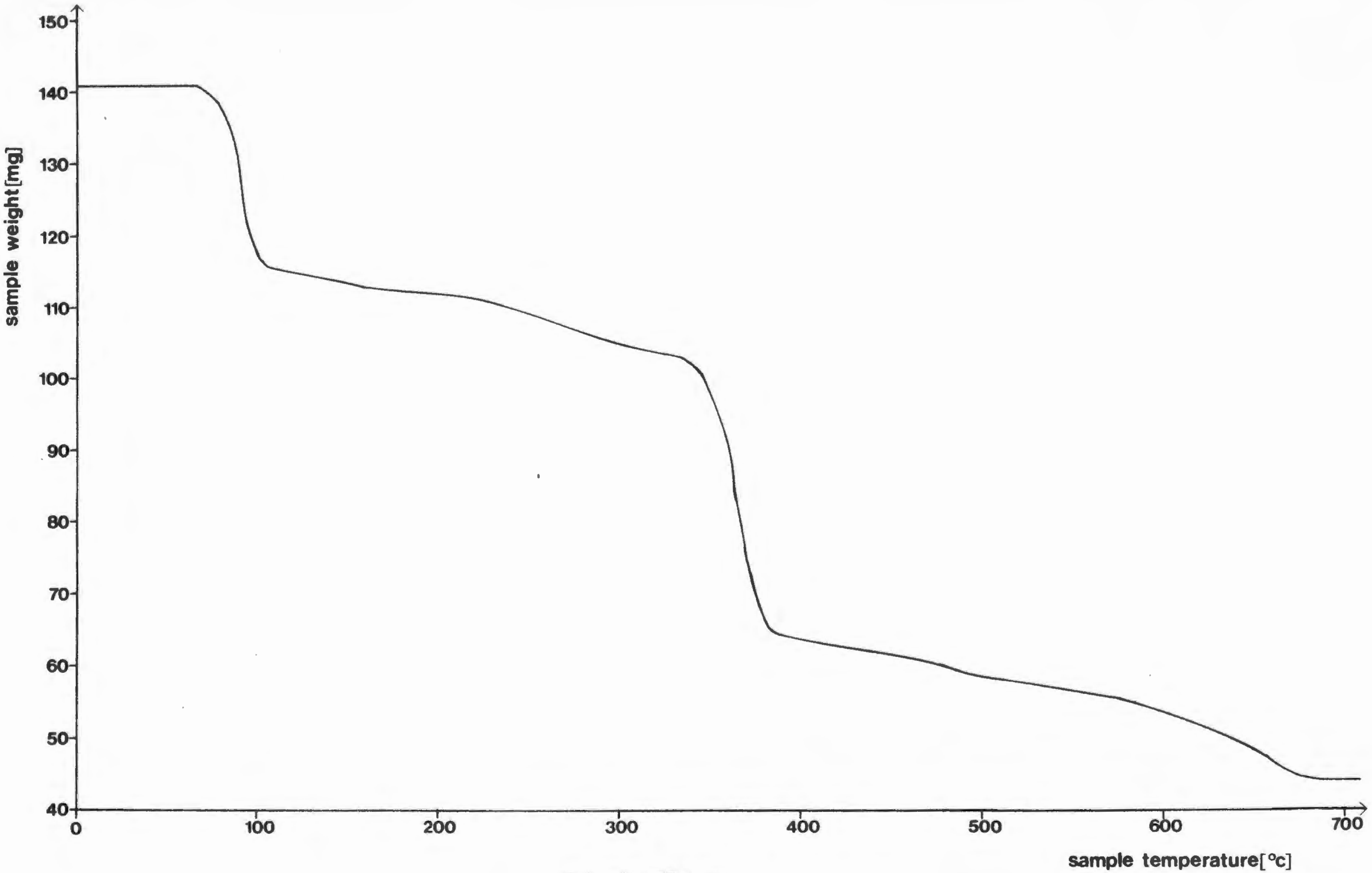
A graphical representation of the TGA data obtained from the curve is shown in Figure 3.1.

From the TGA curve, it can be seen that there is a plateau between 0°C and 67°C indicating zero weight loss. Then between 67°C and 110°C there is a large, sudden weight loss. This is followed by a gradual weight loss to 346°C. An extremely large and sudden weight loss then follows between 346°C and 384°C. Then follows another gradual weight loss to 662°C. Thereafter, constant weight is maintained.

From these results we surmised that a loss of five water molecules has occurred, each separate weight loss corresponding to the loss of one water molecule with the third large weight loss corresponding to the sudden loss of two water molecules. This would imply that these five water molecules are water mole= cules of crystallization and thus are held only loosely in the structure. The other three water molecules therefore must be coordinated to the central metal ion, and would not be lost from the extremely stable and rigid metal-edta complex at such low temperatures and atmospheric pressure.

The most probable order in which these five water molecules are lost is discussed in Chapter 4, part 4.8.

FIGURE 3-1



Gd-edta TGA curve

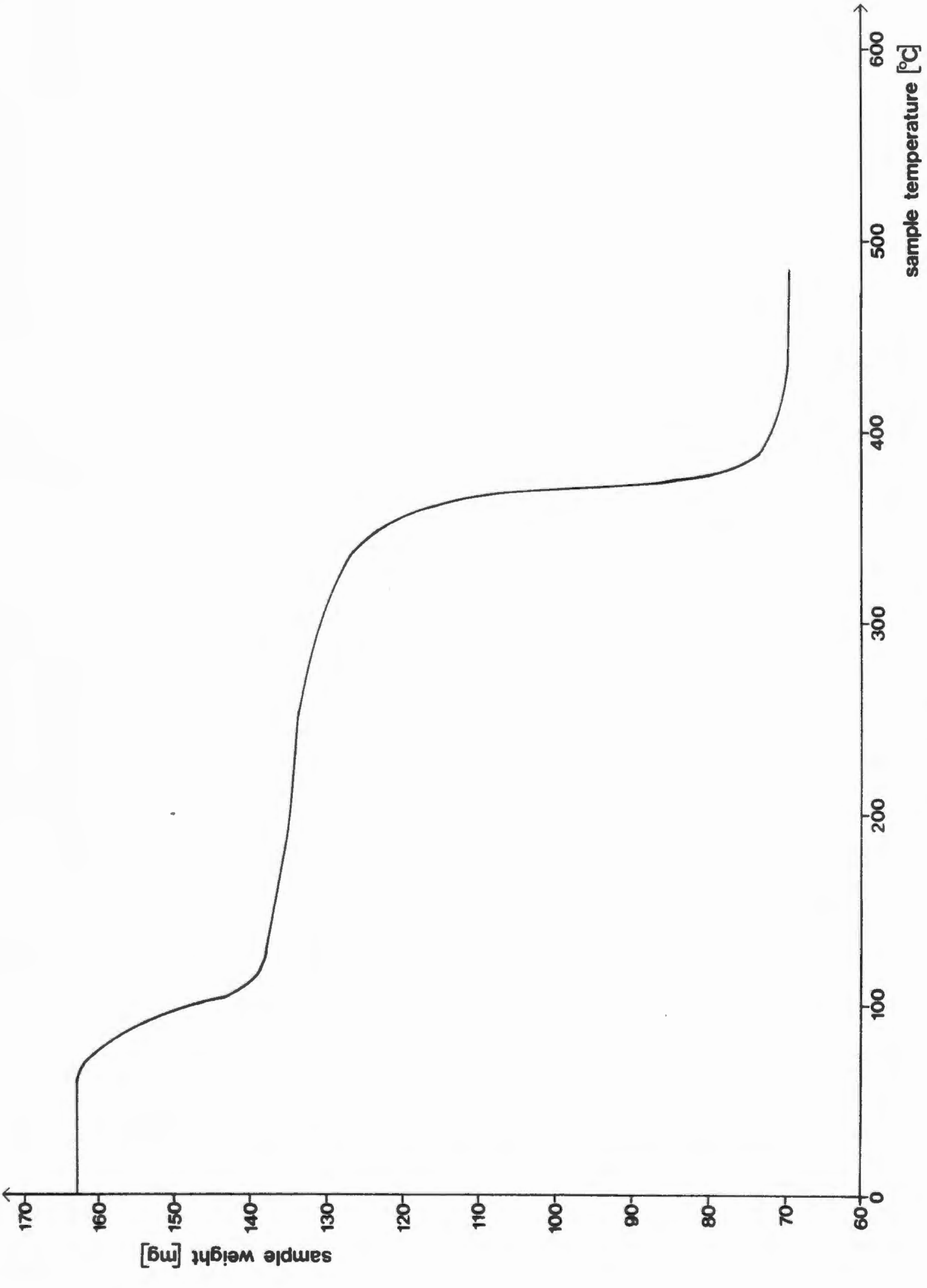
3.4 DISCUSSION OF THE $K^+[Er(edta)].6H_2O$ CURVE

The TGA data obtained from the curve is represented graphically in Figure 3.2.

From the TGA curve, it can be seen that there is a plateau between $0^{\circ}C$ and $62^{\circ}C$ indicating zero weight loss. Then between $62^{\circ}C$ and $106^{\circ}C$ there is a large, sudden weight loss. This is followed by a gradual weight loss to $350^{\circ}C$. Then follows an extremely large and sudden weight loss between $350^{\circ}C$ and $386^{\circ}C$, after which constant weight is maintained.

It therefore can be surmised that a loss of four water molecules has occurred. The loss of the first water molecule corresponds to the initial sudden weight loss, the second molecule to the following gradual weight loss and then the loss of two water molecules corresponding to the final large weight loss. This indicates that the compound contains four water molecules of crystallization, also loosely held in the structure. The other two water molecules can be deduced to be coordinated to the central metal ion.

It must be stressed that although these results are only qualitative, they agree well with the microanalyses as well as with the results obtained from the X-ray studies.



Er–edta TGA curve

FIGURE 3·2

CHAPTER 4

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPOUNDS $K^+[Ln(edta)].8H_2O$ FOR Ln = Pr, Eu, Gd AND Ho.

4.1 PRELIMINARY X-RAY ANALYSIS

Oscillation, Weissenberg and precession photographs were taken of crystals of all four compounds. The photographs obtained indicated that the four structures were in fact isomorphous, since:

(i) In all cases the photographs indicated an orthorhombic space group

(ii) The approximate unit cell parameters that were obtained from the photographs were similar for all four structures.

i.e. for Ln = Pr; a = 20.0Å, b = 36.1Å, c = 12.3Å
Ln = Eu; a = 19.9Å, b = 35.8Å, c = 12.3Å
Ln = Gd; a = 19.8Å, b = 35.6Å c = 12.2Å
Ln = Ho; a = 19.7Å, b = 35.5Å c = 12.2Å

(iii) Z was calculated to be 16.

(iv) The Weissenberg and precession photographs showed that the conditions for non-extinction of reflections were:

hkl : $h + k,\ k + l,\ (l + h) = 2n$
$0kl$: $k + l = 4n;\ \ (k,\ l = 2n)$
$h0l$: $l + h = 4n;\ \ (l,\ h = 2n)$
$hk0$: $(h,\ k = 2n)$
$h00$: $(h = 4n)$
$0k0$: $(k = 4n)$
$00l$: $(l = 4n)$

These systematic absences indicate the space group $Fdd2$[68]. These conditions were later confirmed by inspection of the diffractometer data.

For this reason the structure of $K^+[Eu(edta)].8H_2O$ was determined by the usual crystallographic techniques while the other three structures were determined by the technique of isomorphous replacement. However for all four structures, the positions of all the water molecules of crystallization were determined uniquely.

4.2 INTENSITY DATA COLLECTIONS

Diffractometer data collections were obtained for all four compounds at the C.S.I.R. in Pretoria. Inspection of the data collections confirmed the space group *Fdd*2 for all four compounds and accurate unit cell parameters were determined by least squares analyses as described in Chapter 2. All the relevant crystal data plus information pertaining to the data collections are listed in Tables 4.1 and 4.2.

4.3 SOLUTION AND REFINEMENT OF THE $K^+[Eu(edta)].8H_2O$ STRUCTURE

A three-dimensional Patterson vector map was computed in order to find the position of the Europium ion. A vector grid for the space group *Fdd*2 was constructed and appears in Table 4.3.

i.e. This gave rise to 12 non-origin vectors.

Vector position	Multiplicity
$0,0,0$	4
$\frac{1}{4}+2x,\frac{1}{4},\frac{1}{4}$	2
$\frac{1}{4}-2x,\frac{1}{4},\frac{1}{4}$	2
$\frac{1}{4},\frac{1}{4}+2y,\frac{1}{4}$	2
$\frac{1}{4},\frac{1}{4}-2y,\frac{1}{4}$	2
$2x,2y,0$	1
$-2x,-2y,0$	1

$2x,-2y,0$	1
$-2x,2y,0$	1

The Eu-Eu peaks corresponding to the above vectors were readily recognised by virtue of their magnitudes and the Eu ion was located at position x = 0.086, y = 0.155, z = 0. The two-fold axis parallel to the z-axis allows the z-coordinate to be arbitrarily placed at 0 and it was kept fixed at zero thereafter.

A weighted electron density difference map, calculated from the structure factors derived from the position of the Eu^{3+} ion, gave an R value of 0.20 and revealed the positions of the Potassium ion and ten other non-hydrogen atoms. The positions of all these atoms were inserted and subsequent weighted electron density calculations revealed the positions of the remaining coordinated non-hydrogen atoms. The final full-matrix least-squares refinement was carried out with the Europium and Potassium ions anisotropic and the remaining atoms isotropic. At this point, the R-value was lowered to 0.048 (without corrections due to anomalous dispersion). At no stage of the refinement could hydrogen atoms be located in the difference maps and they therefore were omitted.

4.4 SOLUTION AND REFINEMENT OF THE STRUCTURES K$^+$[Ln(edta)].8H$_2$O FOR Ln = Pr, Gd AND Ho.

The structures K$^+$[Pr(edta)].8H$_2$O, K$^+$[Gd(edta)].8H$_2$O and K$^+$[Ho(edta)].8H$_2$O were all solved by the technique of isomorphous replacement. The positions of all the coordinated atoms were located in this way. The R values obtained at this point were 0.062, 0.054 and 0.057 respectively (again prior to anomalous dispersion corrections).

TABLE 4.1 CRYSTAL DATA AND DATA COLLECTION

Molecular formula:	$K^+[Pr(edta)(H_2O)_3].5H_2O$	$K^+[Eu(edta)(H_2O)_3].5H_2O$
Molecular weight:	612.01	623.06
Space group:	*Fdd*2	*Fdd*2
Z:	16	16
a:	19.97(1)Å	19.86(1)Å
b:	36.11(2)Å	35.77(2)Å
c:	12.274(6)Å	12.249(6)Å
D_m:	$1.82 g.cm^{-3}$	$1.89 g.cm^{-3}$
D_c:	$1.84 g.cm^{-3}$	$1.90 g.cm^{-3}$
Volume:	$8853.05 Å^3$	$8699.11 Å^3$
$F(000)$:	4864	4928
$\mu(MoK_\alpha)$:	$23.21 cm^{-1}$	$29.67 cm^{-1}$
Cyystal Dimensions:	0.38x0.38x0.38mm	0.20x0.30x0.20mm
Scan mode:	$\omega/2\theta$	ω
Scan width:	$1.2^\circ\theta$	$0.7^\circ\theta$
Scan speed:	$0.04\theta s^{-1}$	$0.023\theta s^{-1}$
Range scanned (2θ):	4 - 46	6 - 46
Stability of standard reflections:	0.99%	1.4%
Number of reflections collected:	1670	1678
Number of observed reflections:	1535 with $I_{(rel)}>2\sigma I_{(rel)}$	1515 with $I_{(rel)}>2\sigma I_{(rel)}$
Number of variables:	130	130

TABLE 4.2 CRYSTAL DATA AND DATA COLLECTION

Molecular formula:	$K^+[Gd(edta)(H_2O)_3].5H_2O$	$K^+[Ho(edta)(H_2O)_3].5H_2O$
Molecular weight:	628.37	636.03
Space group:	*Fdd2*	*Fdd2*
Z:	16	16
a:	19.84(1)Å	19.70(1)Å
b:	35.77(2)Å	35.51(2)Å
c:	12.246(6)Å	12.217(6)Å
D_m:	1.93g.cm^{-3}	1.96g.cm^{-3}
D_c:	1.92g.cm^{-3}	1.98g.cm^{-3}
Volume:	8688.17Å^3	8546.85Å^3
F(000):	4944	4992
$\mu(MoK_\alpha)$:	34.16cm^{-1}	37.77cm^{-1}
Crystal Dimensions:	0.25x0.25x0.25mm	0.25x0.38x0.38mm
Scan mode:	$\omega/2\theta$	$\omega/2\theta$
Scan width:	1.2$^\circ\theta$	1.2$^\circ\theta$
Scan speed:	0.04θs^{-1}	0.04θs^{-1}
Range scanned (2θ):	6 - 52	6 - 52
Stability of standard reflections:	2.2%	1.6%
Number of reflections collected:	2277	1786
Number of observed reflections:	1959 with $I_{(rel)}>2\sigma I_{(rel)}$	1563 with $I_{(rel)}>2\sigma I_{(rel)}$
Number of variables:	130	130

TABLE 4.3

	x,y,z	$-x,-y,z$	$\frac{1}{4}-x,\frac{1}{4}+y,\frac{1}{4}+z$	$\frac{1}{4}+x,\frac{1}{4}-y,\frac{1}{4}+z$
x,y,z	$0,0,0$	$-2x,-2y,0$	$\frac{1}{4}-2x,\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4}-2y,\frac{1}{4}$
$-x,-y,z$	$2x,2y,0$	$0,0,0$	$\frac{1}{4},\frac{1}{4}+2y,\frac{1}{4}$	$\frac{1}{4}+2x,\frac{1}{4},\frac{1}{4}$
$\frac{1}{4}-x,\frac{1}{4}+y,\frac{1}{4}+z$	$\frac{1}{4}+2x,\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4}-2y,\frac{1}{4}$	$0,0,0$	$2x,-2y,0$
$\frac{1}{4}+x,\frac{1}{4}-y,\frac{1}{4}+z$	$\frac{1}{4},\frac{1}{4}+2y,\frac{1}{4}$	$\frac{1}{4}-2x,\frac{1}{4},\frac{1}{4}$	$-2x,2y,0$	$0,0,0$

4.5 LOCATION OF THE WATER MOLECULES

From these structure determinations, it could be seen that the metal ions in all four structures were bonded, in fact, to the hexadentate edta ligand plus three water molecules (see the description of the structures, part 4.7).

Therefore, according to the microanalyses and thermogravimetric analyses, all four structures should contain five uncoordinated water molecules of crystallization. However, considerable difficulty was encountered in locating the positions of these water molecules.

For each structure, a final difference map was performed based on the structure factors derived from the positions of all the atoms that had been located. All the peaks that arose in these final maps were considered as possible positions for the oxygen atoms of the five water molecules. Some of the positions were impossible and were thus discarded, the reasons being that they either lay too close to the positions of other known atoms, or the heights of the peaks were deemed much too low thus indicating that they probably arose from hydrogen atoms.

For each structure, there remained seven peaks each having a peak height of about 2 electrons/Å^3. These could still be assigned to oxygen atoms, however, when one takes into account the fact that it is only when the scattering of the X-rays by the electron cloud occurs at very low angles, that the total scattering is the algebraic sum of the scattering by the individual atoms[59] i.e. only when the scattering angle $\sin\theta/\lambda$ equals 0 is the scattering factor of the oxygen atom equal to 8. The value of the scattering factor is markedly reduced at higher angles.

Therefore, for this reason, for all four structures the positions of all seven peaks were inserted into the program runstreams as oxygen atoms and, in each case, a further difference map was computed phased on all the atoms.

For each structure, the five atoms with the lowest thermal parameters were chosen as the molecules of water of crystallization. In each case, the thermal parameters of four of these water molecules were fairly high, much higher than the values for the coordinated water molecules. This is to be expected because the molecules of water of crystallization are only held in the structure by weak hydrogen-bonds (see part 4.8). It is probable that some fraction of these water molecules diffused out of the crystal during the period of the data collection and this would result in increased thermal motion of the remaining water molecules since they occupy a relatively empty region of the crystal. There is direct evidence of this diffusion in that, in a dry atmosphere, the translucent crystals become opaque with time, and their resultant diffraction patterns therefore weaken. This is attributed to loss of structure occurring with effusion of the water molecules of crystallization. It is thus difficult to ascertain the positions of the water molecules accurately and unambiguously.

In all four of these structures, identical positions were chosen for the five water molecules of crystallization. However, Lee[42], in the structure determination of the complexes $K^+[La(edta)(H_2O)_3].5H_2O$ and $Na^+[Tb(edta)(H_2O)_3].5H_2O$, identified different positions for two of the water molecules. It is probable that these molecules of water of crystallization are, in fact, disordered and their positions therefore cannot be said to have been determined unequivocally.

For each structure, the final cycle of refinement, which included the five chosen water molecules, was seen to converge successfully by the average shift to error ratios being less than 0.1.

Each structure was in fact refined twice, first with positive values for the imaginary components of the anomalous dispersion, $\Delta f''$, of the Ln^{3+} and K^+ ions, and then with negative values for these terms (see part 4.6 for detailed discussion).

The final R factors obtained for each of the refinements for each structure are as follows (the weighting scheme of $\omega = (\sigma^2 F + 0.002F^2)^{-1}$ was used in all cases):

i.e. $K^+[Ln(edta)(H_2O)_3].5H_2O$

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
+ve $\Delta f''$ terms for Ln^{3+} and K^+	$R = 0.049$ $R_\omega = 0.053$	$R = 0.043$ $R_\omega = 0.046$	$R = 0.046$ $R_\omega = 0.051$	$R = 0.047$ $R_\omega = 0.050$
-ve $\Delta f''$ terms for Ln^{3+} and K^+	$R = 0.047$ $R_\omega = 0.051$	$R = 0.041$ $R_\omega = 0.044$	$R = 0.044$ $R_\omega = 0.049$	$R = 0.045$ $R_\omega = 0.047$

For each structure, the refinement using the negative $\Delta f''$ terms was concluded to be correct (see part 4.6 for the explanation), and therefore all the reported tables refer to the results from this refinement. The analysis of variance for each structure computed after the final cycle of refinement showed that the weighting scheme was satisfactory. These analyses of variance appear in Tables 4.4 to 4.7.

The final atomic coordinates with corresponding thermal motion parameters are listed in Tables 4.8 to 4.11. Lists of observed and calculated structure factors appear in Appendices A to D.

TABLE 4.4 ANALYSIS OF VARIANCE FOR THE PR-EDTA STRUCTURE

(a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	778	0	0	0	0	0	0	757	1535
V	1221	0	0	0	0	0	0	1132	1178

(b) As a function of $\sin\theta$

$\sin\theta$	0.00-0.18	0.18-0.23	0.23-0.26	0.26-0.29	0.29-0.31	0.31-0.33	0.33-0.35	0.35-0.37	0.37-0.38	0.38-0.40
N	160	178	142	177	145	152	184	186	100	111
V	1624	1307	1245	1165	1045	1124	988	935	1169	1016

(c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00-0.31	0.31-0.38	0.38-0.43	0.43-0.46	0.46-0.50	0.50-0.54	0.54-0.59	0.59-0.63	0.63-0.70	0.70-1.00
N	162	170	159	123	153	173	170	126	150	149
V	1488	1519	1306	1119	958	953	1068	970	973	1165

(d) As a function of |Miller Index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	55	101	107	102	104	100	94	93	94	85	87	79	79	66	289
V	1479	1250	1288	1256	1131	1077	1236	824	1211	955	1128	1081	1028	1091	1285

TABLE 4.4 CONT/....

TABLE 4.4 CONTINUED

$\|k\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	33	57	58	57	58	57	58	57	57	56	56	52	56	49	774
V	1576	1268	1347	1564	1559	1179	1265	1064	1529	1359	1202	1257	1086	1033	1027

$\|l\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	148	163	150	164	148	146	124	123	101	93	76	55	31	13	0
V	1600	1434	1299	1159	996	1035	1085	897	1124	937	996	1052	1000	1148	0

N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2/N\Sigma\omega]$

M = total no. of reflections

TABLE 4.5 ANALYSIS OF VARIANCE FOR THE EU-EDTA STRUCTURE

(a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	766	0	0	0	0	0	0	749	1515
V	1122	0	0	0	0	0	0	1065	1094

(b) As a function of sinθ

sinθ	0.00-0.18	0.18-0.23	0.23-0.26	0.26-0.29	0.29-0.31	0.31-0.33	0.33-0.35	0.35-0.37	0.37-0.38	0.38-0.40
N	157	172	139	172	143	155	172	196	93	116
V	1631	1201	1168	1023	1018	885	968	898	952	950

(c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00-0.30	0.30-0.37	0.37-0.41	0.41-0.45	0.45-0.48	0.48-0.52	0.52-0.56	0.56-0.61	0.61-0.68	0.68-1.00
N	153	176	133	171	128	168	140	167	141	138
V	1417	1213	1112	993	968	1014	942	1050	1000	1117

(d) As a function of |Miller Index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	55	103	105	101	105	98	88	91	94	83	86	78	77	66	285
V	1286	1274	1104	1190	1228	1150	1034	952	1136	900	1017	1063	1045	938	1046

TABLE 4.5 CONT/....

TABLE 4.5 CONTINUED

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	32	57	58	55	59	56	57	56	55	55	55	53	54	48	765
V	1327	1310	1288	1266	1178	1113	1249	1020	1471	1217	1179	1263	1013	867	973
$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	142	166	151	160	145	144	121	123	103	93	76	53	28	10	0
V	1402	1190	1083	1254	1143	1008	1099	865	920	899	881	863	958	1026	0

N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections

TABLE 4.6 ANALYSIS OF VARIANCE FOR THE GD-EDTA STRUCTURE

(a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	965	0	0	0	0	0	0	994	1959
V	1505	0	0	0	0	0	0	1109	1319

(b) As a function of sinθ

sinθ	0.00-0.20	0.20-0.25	0.25-0.29	0.29-0.32	0.32-0.34	0.34-0.36	0.36-0.38	0.38-0.41	0.41-0.42	0.42-0.44
N	218	194	220	210	152	181	198	298	95	193
V	1518	978	1394	984	1280	1004	1129	1163	1043	2158

(c) As a function of $\surd(F/F_{max})$

$\surd(F/F_{max})$	0.00-0.31	0.31-0.37	0.37-0.41	0.41-0.44	0.44-0.47	0.47-0.51	0.51-0.55	0.55-0.60	0.60-0.67	0.67-1.00
N	198	234	214	178	196	211	171	181	186	190
V	2388	1605	1274	1093	1076	972	914	985	976	1010

(d) As a function of |Miller Index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	63	124	113	110	119	117	99	115	107	98	102	98	86	90	518
V	1320	1436	1589	1307	1413	1202	1383	912	2717	1007	1106	1054	1127	840	1060

TABLE 4.6 CONT/....

TABLE 4.6 CONTINUED

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	37	69	69	70	76	65	67	67	61	65	65	62	64	57	1065
V	1346	1143	993	1173	1304	1402	1435	1004	3418	1307	1514	1137	1147	805	1167

$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	174	201	182	197	168	184	153	166	136	131	95	79	38	34	21
V	1560	1184	1361	1097	1108	948	1054	1018	1256	1179	1007	1273	1507	1230	5590

N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections

TABLE 4.7 ANALYSIS OF VARIANCE FOR THE HO-EDTA STRUCTURE

(a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	786	0	0	0	0	0	0	777	1563
V	1310	0	0	0	0	0	0	1219	1266

(b) As a function of sinθ

sinθ 0.00-0.19-0.23-0.27-0.29-0.32-0.34-0.36-0.38-0.39-0.44

N	184	141	190	111	194	161	173	193	94	122
V	1704	1272	1314	1243	1080	1212	1193	1166	1257	996

(c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$ 0.00-0.30-0.36-0.40-0.43-0.46-0.50-0.54-0.59-0.66-1.00

N	158	160	163	144	160	180	136	175	135	152
V	1627	1420	1088	1190	1113	1198	1317	1133	1180	1309

(d) As a function of |Miller Index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	60	109	111	101	111	107	87	104	100	89	90	82	68	65	279
V	1317	1341	1335	1304	1271	1282	1322	1243	1170	1175	1241	1119	1350	1025	1301

TABLE 4.7 CONT/....

TABLE 4.7 CONTINUED

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	34	60	62	56	64	59	65	60	50	60	58	54	61	48	772
V	1577	1461	1448	1421	1547	1219	1277	1340	1560	1011	1481	1180	1220	1134	1169

$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	142	157	145	152	138	142	118	117	96	89	67	70	57	50	23
V	1703	1484	1194	1315	1295	1088	1283	1117	1155	1063	1204	1051	984	1042	1025

N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections

TABLE 4.8 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$K^+[Pr(edta)(H_2O)_3].5H_2O$

Atom	*x*	*y*	*z*	*U*
Pr^{3+}	874(0)	1541(0)	0000(0)	*
K^+	1339(2)	1322(1)	3323(4)	*
O(1)	1027(5)	1837(3)	1803(9)	32(2)
O(2)	-216(5)	1715(3)	706(8)	31(2)
O(3)	2087(5)	1675(3)	256(8)	31(2)
O(4)	222(5)	1654(3)	-1627(9)	27(2)
O(5)	1067(8)	2315(5)	2910(14)	66(4)
O(6)	-916(6)	2130(4)	1470(13)	59(3)
O(7)	3113(5)	1745(3)	-392(9)	41(3)
O(8)	108(5)	1757(3)	-3428(9)	36(3)
O(9)	89(5)	976(2)	-180(9)	29(2)
O(10)	1396(6)	1081(3)	-1337(9)	34(3)
O(11)	1379(6)	1026(3)	1161(9)	32(3)
N(1)	636(5)	2293(3)	69(12)	28(3)
N(2)	1500(6)	1925(4)	-1626(11)	27(3)
C(1)	841(7)	2467(4)	-957(14)	28(4)
C(2)	1529(8)	2331(5)	-1333(14)	33(4)
C(3)	1006(9)	2432(5)	1016(16)	40(4)
C(4)	1048(8)	2169(4)	1981(14)	31(3)
C(5)	-103(9)	2346(5)	238(14)	43(4)
C(6)	-418(7)	2041(4)	848(14)	34(4)

TABLE 4.8 CONT/....

TABLE 4.8 CONTINUED

Atom	x	y	z	U
C(7)	2216(8)	1797(4)	-1635(13)	34(3)
C(8)	2500(7)	1733(4)	-524(12)	24(3)
C(9)	1180(7)	1865(4)	-2679(13)	32(3)
C(10)	428(6)	1752(3)	-2571(14)	28(3)
W(1)	659(6)	397(4)	5990(11)	52(3)
W(2)	1434(9)	953(4)	5410(15)	72(5)
W(3)	723(20)	1783(15)	4462(49)	265(21)
W(4)	-19(15)	1070(8)	2938(25)	155(10)
W(5)	2813(13)	2164(6)	5667(22)	131(8)

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[*] Anisotropic parameters as defined in Chapter 2, page 33.

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr^{3+}	22(0)	20(0)	15(0)	0(0)	-2(0)	0(0)
K^+	75(3)	69(3)	35(2)	14(2)	12(2)	31(2)

TABLE 4.9 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$K^+[Eu(edta)(H_2O)_3].5H_2O$

Atom	*x*	*y*	*z*	*U*
Eu^{3+}	865(0)	1546(0)	0000(0)	*
K^+	1329(3)	1330(1)	3361(4)	*
O(1)	1011(5)	1820(3)	1788(8)	32(2)
O(2)	-212(5)	1702(3)	730(8)	34(2)
O(3)	2060(5)	1669(2)	270(7)	31(2)
O(4)	203(5)	1645(3)	-1584(8)	26(2)
O(5)	1096(8)	2293(5)	2908(13)	77(4)
O(6)	-930(6)	2098(4)	1477(13)	63(4)
O(7)	3096(5)	1738(3)	-362(8)	42(3)
O(8)	60(5)	1754(3)	-3371(9)	38(3)
O(9)	84(4)	986(2)	-171(8)	28(2)
O(10)	1373(5)	1090(3)	-1283(8)	31(2)
O(11)	1334(5)	1041(3)	1160(8)	30(2)
N(1)	623(5)	2282(3)	91(11)	29(2)
N(2)	1490(5)	1927(3)	-1602(10)	27(3)
C(1)	822(7)	2473(4)	-956(14)	32(4)
C(2)	1517(7)	2330(4)	-1311(12)	33(3)
C(3)	995(9)	2436(5)	1024(15)	41(4)
C(4)	1044(8)	2168(5)	1969(15)	40(4)
C(5)	-132(8)	2331(4)	252(12)	42(4)
C(6)	-431(7)	2026(4)	865(14)	40(4)

TABLE 4.9 CONT/....

TABLE 4.9 CONTINUED

Atom	*x*	*y*	*z*	*U*
C(7)	2211(7)	1794(4)	-1624(13)	34(3)
C(8)	2482(6)	1731(3)	-501(11)	26(3)
C(9)	1156(7)	1855(4)	-2659(13)	35(3)
C(10)	410(6)	1748(3)	-2528(14)	31(3)
W(1)	661(6)	389(4)	5984(10)	55(3)
W(2)	1456(9)	966(4)	5486(16)	83(5)
W(3)	356(23)	1698(12)	4311(39)	249(18)
W(4)	-18(16)	1055(8)	2912(28)	175(12)
W(5)	2799(15)	2137(8)	5686(26)	178(11)

*Anisotropic parameters:

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Eu^{3+}	21(0)	18(0)	20(0)	0(0)	-2(0)	0(0)
K^+	81(3)	83(3)	52(2)	21(2)	19(2)	41(3)

TABLE 4.10 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$K^+[Gd(edta)(H_2O)_3].5H_2O$

Atom	*x*	*y*	*z*	*U*
Gd^{3+}	863(0)	1545(0)	0000(0)	*
K^+	1319(3)	1331(2)	3381(5)	*
O(1)	1018(5)	1812(3)	1775(9)	34(2)
O(2)	-212(6)	1699(3)	742(10)	42(3)
O(3)	2057(5)	1660(3)	265(8)	31(2)
O(4)	200(5)	1647(3)	-1560(9)	29(2)
O(5)	1106(10)	2294(5)	2905(16)	76(5)
O(6)	-933(8)	2100(5)	1492(15)	68(4)
O(7)	3102(6)	1741(3)	-355(10)	41(3)
O(8)	52(6)	1754(3)	-3363(10)	39(3)
O(9)	88(5)	989(2)	-184(9)	28(2)
O(10)	1353(6)	1097(3)	-1298(10)	38(3)
O(11)	1331(5)	1044(3)	1140(9)	29(2)
N(1)	619(6)	2277(3)	65(13)	32(3)
N(2)	1492(6)	1929(3)	-1601(11)	26(3)
C(1)	819(9)	2463(5)	-940(16)	38(4)
C(2)	1503(9)	2332(5)	-1305(15)	38(4)
C(3)	981(11)	2442(6)	988(19)	47(5)
C(4)	1046(9)	2153(5)	2004(15)	37(4)
C(5)	-141(9)	2336(5)	253(14)	42(4)
C(6)	-422(9)	2025(5)	855(15)	40(4)

TABLE 4.10 CONT/....

TABLE 4.10 CONTINUED

Atom	*x*	*y*	*z*	*U*
C(7)	2212(9)	1803(5)	-1617(15)	37(4)
C(8)	2481(7)	1733(4)	-478(13)	30(3)
C(9)	1155(7)	1855(4)	-2653(15)	35(3)
C(10)	393(7)	1750(4)	-2527(16)	31(3)
W(1)	650(8)	389(4)	5970(13)	62(4)
W(2)	1452(10)	972(5)	5499(18)	80(5)
W(3)	346(2)	1692(13)	4346(40)	213(17)
W(4)	8(21)	1027(10)	2866(34)	181(15)
W(5)	2816(19)	2167(10)	5718(34)	188(14)

*Anisotropic parameters:

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd^{3+}	17(0)	24(0)	25(0)	0(0)	-2(0)	0(0)
K^+	78(4)	98(4)	57(3)	34(3)	26(3)	49(3)

TABLE 4.11 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$K^+[Ho(edta)(H_2O)_3].5H_2O$

Atom	*x*	*y*	*z*	*U*
Ho^{3+}	849(0)	1548(0)	0000(0)	*
K^+	1330(4)	1352(2)	3421(6)	*
O(1)	1000(5)	1803(3)	1764(9)	33(3)
O(2)	-220(6)	1687(4)	741(11)	44(3)
O(3)	2035(5)	1668(3)	278(8)	29(2)
O(4)	181(6)	1643(3)	-1536(9)	29(2)
O(5)	1112(9)	2284(5)	2915(15)	75(5)
O(6)	-962(8)	2082(5)	1467(15)	67(4)
O(7)	3074(6)	1739(3)	-326(10)	44(3)
O(8)	16(6)	1755(3)	-3311(10)	42(3)
O(9)	68(6)	991(3)	-164(9)	33(2)
O(10)	1330(6)	1099(3)	-1270(10)	37(3)
O(11)	1296(6)	1046(3)	1146(9)	31(3)
N(1)	604(6)	2279(4)	107(12)	34(3)
N(2)	1476(7)	1928(4)	-1595(11)	30(3)
C(1)	796(9)	2470(6)	-931(17)	42(5)
C(2)	1489(9)	2330(5)	-1302(14)	38(4)
C(3)	959(10)	2433(6)	1027(16)	39(5)
C(4)	1054(10)	2149(6)	1963(18)	47(5)
C(5)	-157(9)	2330(5)	257(15)	47(5)
C(6)	-445(9)	2013(5)	889(15)	41(4)

TABLE 4.11 CONT/....

TABLE 4.11 CONTINUED

Atom	*x*	*y*	*z*	*U*
C(7)	2198(10)	1795(5)	-1625(16)	43(4)
C(8)	2465(8)	1728(5)	-462(13)	32(3)
C(9)	1134(7)	1852(4)	-2632(15)	34(4)
C(10)	374(7)	1746(4)	-2506(16)	31(3)
W(1)	633(8)	380(4)	5980(12)	59(4)
W(2)	1470(11)	969(5)	5569(20)	91(6)
W(3)	258(25)	1634(13)	4363(43)	246(20)
W(4)	-29(24)	1027(11)	2864(39)	219(19)
W(5)	2788(26)	2169(14)	5758(46)	272(23)

*Anisotropic parameters:

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ho^{3+}	22(0)	21(0)	25(0)	1(0)	-2(0)	0(0)
K^+	102(5)	144(7)	84(4)	60(5)	42(4)	75(5)

4.6 ANOMALOUS DISPERSION CORRECTIONS

4.6.1 THEORY

X-rays are scattered by the electron cloud surrounding an atom. The X-ray scattering power of a specific atom for a specific reflection is known as its scattering factor, f_0, and is expressed in terms of the scattering power of the electrons of the atoms.

If the atoms are assumed to be spherical, then the scattering power is a function of the atom type and the scattering angle (i.e. $(\sin\theta)/\lambda$), but is independent of the position of the atom in the cell. At very low scattering angles, the value of the scattering factor of an atom is the algebraic sum of the scattering by the individual electrons, i.e. for a carbon atom, the value of the scattering factor equals 6 at $(\sin\theta)/\lambda = 0$. However, as $(\sin\theta)/\lambda$ increases, the scattering factor decreases, since X-rays scattered from an electron in one part of the atom are increasingly out of phase with those scattered in another part of the atom. Temperature also has an effect on the X-ray intensities. The higher the temperature, the greater the vibration of the atoms in the crystal. The effect of this thermal motion is to spread the electron cloud over a larger volume causing the scattering power of the atom to decrease[57].

At first it would seem that the relative scattering powers of different kinds of atoms are the same regardless of the radiation used. This is not so, however, as anomalous dispersion effects arise when the wavelength of the X-rays used is near an absorption edge in the scattering element. This effect is found particularly in the case of heavy atoms.

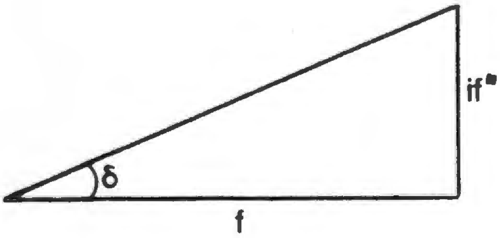
Anomalous dispersion corrections involve the introduction of two scattering-factor corrections, $\Delta f'$ and $\Delta f''$, for each type of atom which displays this effect. Then the total atomic scattering factor, f, is a complex function and is represented as[69,70]:

$$f = f_o + \Delta f' + i\Delta f''$$
$$= f_{re} + if''$$

where:

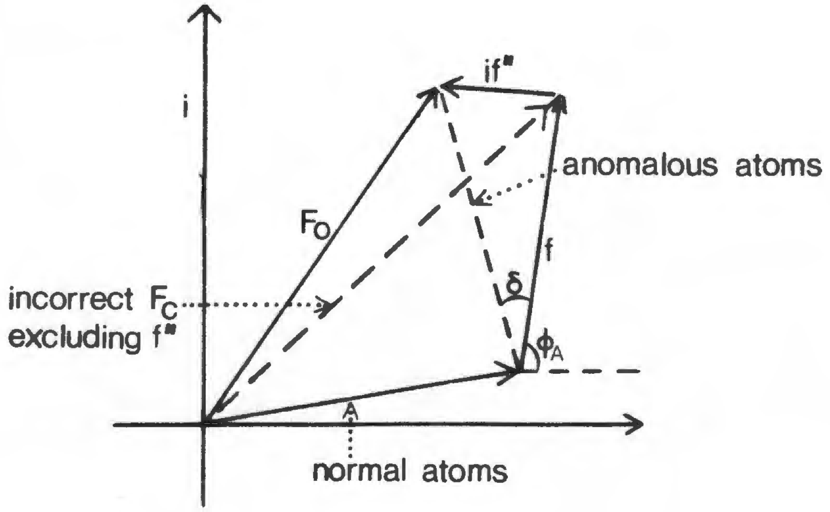
$\Delta f'$ and $\Delta f''$ are the real and imaginary components of the anomalous dispersion and are functions of λ but are nearly independent of θ because the tightly bound electrons responsible for these effects are concentrated in a small volume near the atomic nucleus[71]. f_o is the atomic scattering factor for radiation with frequency much higher than any absorption edge. i.e. f_o is the value of the scattering factor at very low wavelengths when f' and $f'' \longrightarrow 0$, δ is the phase shift (relative to a free electron) where $\delta = f''/f_{re}$. (see Figure 4.1)

FIGURE 4.1



The structure factor F for a certain reflection hkl is made up of contributions from the normal atoms and the anomalous atoms as shown in Figure 4.2. The contribution of the anomalous atom, A, with complex scattering factor f_A is $f_A e^{i\phi_A}$ where ϕ_A is the phase factor for the anomalous atom due to its position in the unit cell[72].

FIGURE 4.2



If the imaginary part of the scattering factor, $\Delta f''$, is not included in the structure refinement, or if $\Delta f''$ is included but in the wrong sense[76], then certain errors occur in the structural parameters (both positional and temperature parameters can be affected). An attempt is then made to compensate in the refinement process for this omission and the structure factors are brought into more or less agreement with the observed ones by adjustment of the normalization factor and by use of incorrect temperature factors[70].

That is, if the term $i\Delta f''$ is not included in the calculation of F and if the atoms are placed in their correct positions, then the calculated structure factor F_c will not agree with the observed structure factor F_o[72]. In order to obtain better agreement between F_c and F_o, the contribution of the anomalous atom A must be rotated by the phase angle δ (see Figure 4.3). This can be done by moving the atom normal to the reflecting plane by an amount δl (see Figure 4.4).

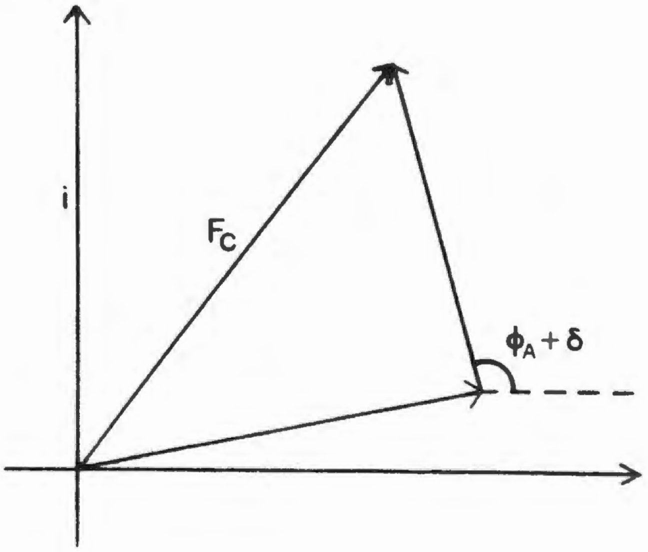


FIGURE 4·3

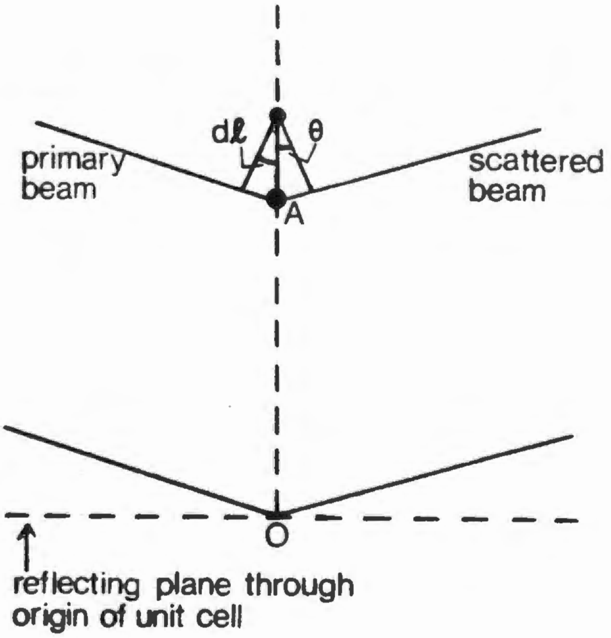


FIGURE 4·4

Then;

$$\text{the phase difference}, \delta = \frac{2\pi}{\lambda} \,.\, \text{path difference}$$

$$= \frac{2\pi}{\lambda} \,.\, 2dl \sin\theta$$

$$= 4\pi(\sin\theta/\lambda)dl$$

$$\text{Hence, } dl = \delta/4\pi(\sin\theta/\lambda)$$

where: dl = the shift of the anomalous atom.

δ = the phase difference achieved.

θ = the Bragg scattering angle.

Thus better agreement between F_c and F_o is achieved but the position of the atom is incorrect as the refinement has compensated for the omission of $\Delta f''$.

Each set of reflection planes has a different normal direction so that the effect on the refinement as a whole is a shift of the anomalous atom towards the general direction in which the measurements have been made[72]. If the reflections $\pm h$, $\pm k$, $+l$ have been measured, then the shift is in the direction z.

However, it is not sufficient to simply shift one anomalous atom, all the atoms that are related by symmetry must be shifted. Often if one atom A_1 is shifted in the $+z$ direction, a related one A_2 must be moved in the $-z$ direction, resulting in a cancellation of the two effects so that the shift does not improve agreement between F_o and F_c. Only in the case of polar space groups can all the atoms be shifted in the same direction without breaking the crystal symmetry. In polar space groups, the position of the origin in one or more dimensions is not fixed by reference to symmetry elements. *Fdd2* is a polar space group, the two-fold rotation axis being the polar axis. The origin of this space group is not fixed along the twofold axis along z so that all the anomalous atoms can be moved along z in the same direction.

The formula for the shift along a polar axis due to the omission of f'' is reported by Cruickshank and McDonald[74] as:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{\max}$$

where: $\bar{\delta}$ = an average δ over the range of $\sin\theta/\lambda$ values used.

$\lambda = 0.7107\text{Å}$ (when the reflections are measured with MoK_α radiation).

f_o and f'' values are obtained from "International Tables for X-ray Crystallography";

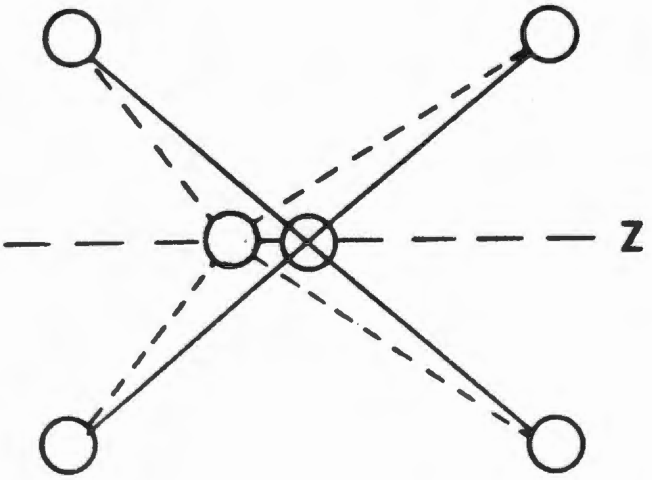
f' is neglected in the calculation.

This value was calculated for each of the four *Fdd2* structures refined in this Thesis.

Now if the term $\Delta f''$ is not omitted from the structure refinement but is in fact included, but in the wrong sense, then more serious errors arise in the positional parameters[74]. This means that the incorrect orientation of the polar axis is chosen and a set of atomic coordinates are obtained which correspond to a crystal whose polar axis is pointing in the incorrect (opposite) direction[72]. Therefore, care must be exercised in determining the correct crystal orientation. This is done by repeating the structure refinement, initially with a positive $\Delta f''$ term and then with a negative $\Delta f''$ term and then comparing R factors for the two orientations. Then provided one of the crystal orientations has a significantly lower R factor, it can be stated categorically which orientation is correct.

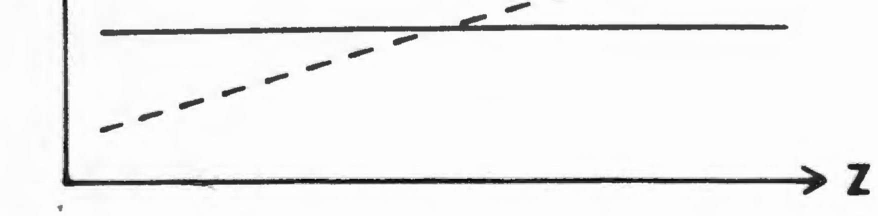
Another method is available that gives a good indication as to which crystal orientation is correct. If the lanthanide ion is centrally positioned in its "cage", the bond lengths are roughly equal. However, if the ion is shifted in the *z*-direction, then a systematic trend is observed with the bond lengths being larger on one side than on the other (see Figure 4.5).

FIGURE 4.5



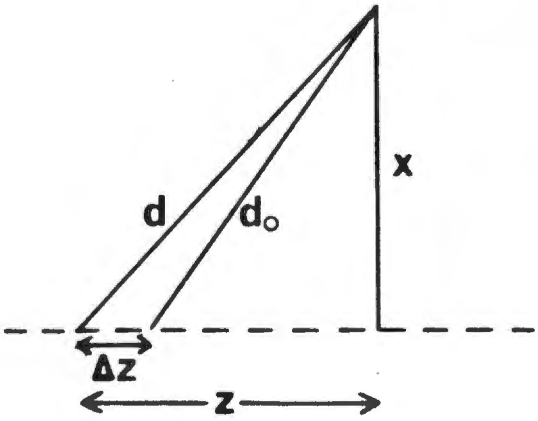
The differences between the two structures of inverse orientation (refined using opposite $\Delta f''$ values) can be shown by plotting their bond lengths as a function of *z*, the fractional *z*-coordinate of the ligand atoms relative to the central ion (see Figure 4.6).

FIGURE 4.6



Then the plot that has the steeper slope has the lanthanide ion incorrectly shifted in the *z*-direction and follows the systematic trend whereby the bond lengths are larger on the one side than on the other. This is then the plot of the structure with the incorrect orientation. The plot that has zero slope has all the bond lengths roughly equal and this is then the plot of the structure with the correct orientation.

Now from FIGURE 4.7;



where: d = the correct bond length.

d_o = the observed bond length.

Hence:
$$d^2 = x^2 + z^2$$
$$d_o^2 = x^2 + (z - \Delta z)^2$$
$$d_o \approx d - z\Delta z/d \qquad (z \text{ and } \Delta z \text{ in Å})$$
$$d_o \approx d - zc\Delta z/d \qquad (z \text{ is fractional coordinate}).$$

Therefore, d_o vs z is a straight line with slope of $m = -c\Delta z/d$. Then the spurious shift of the lanthanide ion is $z = -md/c$ (in Å).

The computing technique that was used involved fixing the z-coordinate of the Ln^{3+} ion to zero in each structure refinement, that is, for the refinement with $\Delta f''$ positive and the refinement with $\Delta f''$ negative. The relative shift was therefore manifested in the changing coordinates of the light atoms (i.e.

C, O and N). The K^+ ion was in each case given the same sign for its $\Delta f''$ term as was the Ln^{3+} ion.

Therefore, the equation, $z = -md/c$, can be used to calculate the amount by which all the light atoms of the incorrect structure appear to be shifted along the z-axis (although it is actually the Ln^{3+} ion that is shifted). This amount should be twice that obtained using the equation of Cruickshank and McDonald (which calculates the shift due to omission of the $\Delta f''$ term altogether).

For all the *Fdd2* structures refined in this work, the structure refinement was repeated, first with positive $\Delta f''$ values, then with negative $\Delta f''$ values for the Ln^{3+} and K^+ ions. Plots were drawn of the Ln - O bond lengths as a function of z for each structure obtained, as seen in Figures 4.8 to 4.12. (In each graph the squares indicate the values obtained from the refinement using positive $\Delta f''$ values with the solid line representing the least-squares equation through these points. The circles indicate the values obtained from the refinement using negative $\Delta f''$ values with the dashed line representing the least-squares equation through these points).

Although in these structures the lanthanide coordination is four edta oxygens (O(1), O(2), O(3) and O(4)), three water oxygens (O(9), O(10) and O(11)) and two edta nitrogens, giving ninefold coordination, only the Ln - O distances have been plotted against the z-coordinates.

In each case, the plot of the crystal orientation that showed no marked trend was concluded to be the correct orientation. This was then confirmed by comparing the *R* values of the two orientations.

4.6.2 CALCULATIONS

The Praseodymium structure

The shift along the *z*-axis of the Pr^{3+} ion that would result from omission of the $\Delta f''$ term can be calculated from the equation of Cruickshank and McDonald:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{max}$$

For this structure, the reflections were measured between 4° and 46° 2θ.

That is:

$2\theta(^\circ)$	$\theta(^\circ)$	$\sin\theta/\lambda$	f''	f_o	$\delta = f''/f_o$	$\bar{\delta}$
4	2	0.049	2.8	58	0.048	∿ 0.07
46	23	0.550	2.8	31	0.090	

Therefore,

$$dz = 0.07/(2\text{x}\pi\text{x}0.550)$$
$$= 0.020\text{Å}$$

Thus, if $\Delta f''$ is omitted altogether in the structure refinement, an error of approximately 0.02Å will occur in the position of the Pr^{3+} ion along the *z*-axis.

Therefore, if $\Delta f''$ is incorrectly assigned, the error in *z* of the Pr^{3+} ion will be 0.04Å.

From Figure 4.8, it can be seen that the structure orientation obtained using the negative values for $\Delta f''$ shows no marked trend and the slope of the graph is approximately zero. However, the structure orientation obtained using the positive values for $\Delta f''$ does show a marked trend and the slope of this graph is:

$$\text{slope, } m = (l_2 - l_1)/(z_2 - z_1)$$
$$= (2.54 - 2.50)/(0.20 - 0.0)$$
$$= 0.2\text{Å}$$

Therefore, the spurious shift in the z-direction can be calculated.

i.e. $z = -md/c$

where $d = 2.50\text{Å}$

$c = 12.27\text{Å}$

Hence, $z = (-0.2 \times 2.50)/12.27$

$= -0.04\text{Å}$

This is in good agreement with the value predicted by the Cruickshank and McDonald equation.

Therefore, if the Pr^{3+} ion in the structure of incorrect orientation were shifted 0.04Å along the z-direction and the distances recalculated, the structure of correct orientation would be obtained.

From Table 4.12, it can be seen that for the structure of incorrect orientation, the apparent incorrect shift of all the light atoms in the z-direction is an average value of 0.046Å. (This applies to all the atoms of the structure, although only the coordinated oxygen atoms are recorded here).

TABLE 4.12

Atom	(I) z-coordinate (+$\Delta f''$ refinement)	(II) z-coordinate (-$\Delta f''$ refinement)	Shift [=(I-II)x12.27]
O(1)	0.1840	0.1803	0.045
O(2)	0.0747	0.0706	0.050
O(3)	0.0295	0.0256	0.048
O(4)	-0.1595	-0.1627	0.039
O(9)	-0.0137	-0.0180	0.053
O(10)	-0.1298	-0.1337	0.048
O(11)	0.1198	0.1161	0.045

The R-factor $\mathcal{R}$ ratio test was employed to decide whether there is a significant difference in the correctness of the two structures of different orientation[79]. Each refinement was carried out with 130 parameters and 1535 reflections. The orientation refined with the positive $\Delta f''$ values had a final R_ω of 0.053, while the orientation refined with the negative $\Delta f''$ values had a final R_ω of 0.051. A null hypothesis, H_0, proposed that the former orientation is correct. This statement is a one-dimensional hypothesis. The value of the R-factor ratio is:

$$\mathcal{R} = 0.053/0.051 = 1.039$$

From Tables,

$$\mathcal{R}_{1,1405,0.01} = 1.002$$

Hence, we may reject at the 0.01 level the hypothesis that the orientation refined with the positive $\Delta f''$ values is correct.

Therefore, it can be concluded finally that the structure orientation refined with negative $\Delta f''$ values for the Pr^{3+} and K^+ ions is correct.

The Europium structure

The shift along the z-axis of the Eu^{3+} ion that would result from omission of the $\Delta f''$ term can be calculated from:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{max}$$

That is:

$2\theta(^{o})$	$\theta(^{o})$	$\sin\theta/\lambda$	f''	f_o	$\delta = f''/f_o$	$\bar{\delta}$
6	3	0.074	3.7	61	0.061	~ 0.09
46	23	0.550	3.7	33	0.112	

Hence,

$$\begin{aligned} dz &= 0.09/(2\times\pi\times0.550) \\ &= 0.026\text{Å} \end{aligned}$$

Therefore, if $\Delta f''$ is omitted altogether in the structure refinement, an error of approximately 0.026Å will occur in the position of the Eu^{3+} ion along the z-axis.

Thus if $\Delta f''$ is incorrectly assigned, the error in z of the Eu^{3+} ion will be 0.052Å.

From Figure 4.9, the structure orientation obtained using the negative value for $\Delta f''$ again shows no marked trend and the slope of the graph is approximately zero. The structure orientation obtained using the positive value for $\Delta f''$ shows a marked trend and the slope of the graph is:

$$m = (2.50 - 2.44)/(0.20 - 0.0)$$
$$= 0.3\text{Å}$$

Hence, the spurious shift in the z-direction is:

$$z = -md/c$$

where $d = 2.44\text{Å}$

$c = 12.25\text{Å}$

Therefore, $z = -(0.3 \times 2.44)/12.25$

$$= -0.06\text{Å}$$

This is in fairly good agreement with the value predicted by the Cruickshank and McDonald equation.

Therefore, if the Eu^{3+} ion in the structure of incorrect orientation were shifted approximately 0.06Å along the z-direction and the distances recalculated, the structure of the correct orientation would be obtained.

From Table 4.13, it can be seen that for the structure of incorrect orientation, the apparent incorrect shift in the z-direction of all the light atoms is on average 0.056Å.

TABLE 4.13

Atom	(I) z-coordinate ($+\Delta f''$ refinement)	(II) z-coordinate ($-\Delta f''$ refinement)	Shift [=(I-II)x12.25]
O(1)	0.1833	0.1788	0.055
O(2)	0.0780	0.0730	0.061
O(3)	0.0316	0.0270	0.056
O(4)	-0.1538	-0.1584	0.056

TABLE 4.13 CONT/....

TABLE 4.13 CONTINUED

O(9)	-0.0122	-0.0171	0.060
O(10)	-0.1240	-0.1283	0.053
O(11)	0.1202	0.1160	0.051

The R-factor ratio test was again employed to decide whether there is a significant difference in the correctness of the two different orientations. Each refinement was carried out with 130 parameters and 1515 reflections. The orientation refined with the positive $\Delta f''$ values had a final R_ω of 0.046 and the orientation refined with the negative $\Delta f''$ values had a final R_ω of 0.044. H_o proposed that the former orientation is correct. This statement is a one-dimensional hypothesis. The value of the R-factor ratio is:

$$\mathcal{R} = 0.046/0.044 = 1.045$$

From Tables, $\mathcal{R}_{1,1385,0.01} = 1.002$

Hence, we may reject at the 0.01 level the hypothesis that the orientation refined with the positive $\Delta f''$ values is correct.

Therefore, it can be concluded finally that the structure orientation refined with negative $\Delta f''$ terms for the Eu^{3+} and K^+ ions is correct.

The Gadolinium structure

The shift along the z-axis of the Gd^{3+} ion that would result from omission of the $\Delta f''$ term can be calculated from:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{max}$$

That is:

$2\theta(^\circ)$	$\theta(^\circ)$	$\sin\theta/\lambda$	f''	f_0	$\delta = f''/f_0$	$\bar{\delta}$
6	3	0.074	3.9	62	0.063	~ 0.09
52	26	0.617	3.9	32	0.122	

Hence,

$$dz = 0.09/(2\text{x}\pi\text{x}0.617)$$
$$= 0.024\text{Å}$$

Therefore, if $\Delta f''$ is omitted altogether in the structure refinement, an error of approximately 0.024Å will occur in the position of the Gd^{3+} ion along the z-axis.

Thus, if $\Delta f''$ is incorrectly assigned, the error in z of the Gd^{3+} ion will be 0.048Å.

From Figure 4.10, the structure orientation obtained using the negative value for $\Delta f''$ again shows no marked trend and the slope of the graph is approximately zero. The structure orientation obtained using the positive value for $\Delta f''$ does show a marked trend and the slope of the graph is:

$$m = (2.49 - 2.43)/(0.2 - 0.0)$$
$$= 0.3\text{Å}$$

Hence, the spurious shift in the z-direction is:

$$z = -md/c$$

where $d = 2.43\text{Å}$

$c = 12.25\text{Å}$

Therefore, $z = -(0.3 \text{ x } 2.43)/12.25$

$= -0.06\text{Å}$

This is in fairly good agreement with the value predicted by the equation of Cruickshank and McDonald.

Hence, if the Gd^{3+} ion in the structure of incorrect orientation were shifted approximatedly 0.06Å along the *z*-direction and the distances recalculated, the structure of correct orientation would be obtained.

From Table 4.14, it can be seen that for the structure of incorrect orientation, the apparent incorrect shift in the *z*-direction of all the light atoms is on average 0.059Å.

TABLE 4.14

Atom	(I) *z*-coordinate ($+\Delta f''$ refinement)	(II) *z*-coordinate ($-\Delta f''$ refinement)	Shift [=(I-II)x12.25]
O(1)	0.1819	0.1775	0.054
O(2)	0.0794	0.0742	0.064
O(3)	0.0313	0.0265	0.059
O(4)	-0.1512	-0.1560	0.059
O(9)	-0.0133	-0.0184	0.062
O(10)	-0.1250	-0.1298	0.059
O(11)	0.1185	0.1140	0.055

The *R*-factor ratio test was again used to decide whether there is a significant difference in the correctness of the two different orientations. Each refinement was carried out with 130 parameters and 1959 reflections. The orientation refined with the positive $\Delta f''$ values had a final R_ω of 0.051 and the orientation refined with the negative $\Delta f''$ values had a final R_ω of 0.049. H_o proposed that the former orientation is correct. This statement is a one-dimensional hypothesis. The value of the *R*-factor ratio is:

$$\mathcal{R} = 0.051/0.049 = 1.041$$

From Tables, $$\mathcal{R}_{1,1829,0.01} = 1.002$$

Hence, we may reject at the 0.01 level the hypothesis that the orientation refined with the positive $\Delta f''$ values is correct.

Hence it can be concluded finally that the structure orientation refined with negative $\Delta f''$ terms for the Gd^{3+} and K^+ ions is correct.

The Holmium structure

The shift along the z-axis of the Ho^{3+} ion that would result from omission of the $\Delta f''$ term can be calculated from:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{max}$$

Then;

$2\theta(^{o})$	$\theta(^{o})$	$\sin\theta/\lambda$	f''	f_o	$\delta = f''/f_o$	$\bar{\delta}$
6	3	0.074	4.7	65	0.072	∿ 0.11
52	26	0.617	4.7	33	0.142	

Hence,

$$dz = 0.11/(2\times\pi\times0.617)$$
$$= 0.028\text{Å}$$

Therefore, if $\Delta f''$ is omitted altogether in the structure refinement, an error of approximately 0.028Å will occur in the position of the Ho^{3+} ion along the z-axis.

Thus, if $\Delta f''$ is incorrectly assigned, the error in z of the Ho^{3+} ion will be

0.056Å.

From Figure 4.11, the structure orientation obtained using the negative value for $\Delta f''$ again shows no marked trend and the slope of the graph is approximately zero. The structure orientation obtained using the positive value for $\Delta f''$ does show a marked trend and the slope of the graph is:

$$m = 0.07/0.2$$
$$= 0.35\text{Å}$$

Hence, the spurious shift in the z-direction is:

$$z = -md/c$$

where $d = 2.40\text{Å}$

$c = 12.22\text{Å}$

Therefore, $z = -(0.35 \times 2.40)/12.22$

$$= -0.07\text{Å}$$

This is in fairly good agreement with the value predicted by the Cruickshank and McDonald equation.

Hence, if the Ho^{3+} ion in the structure of incorrect orientation were shifted approximately 0.07Å along the z-direction and the distances recalculated, the structure of correct orientation would be obtained.

From Table 4.15, it can be seen that for the structure of incorrect orientation, the apparent incorrect shift in the z-direction of all the light atoms is on average 0.067Å.

TABLE 4.15

Atom	(I) *z*-coordinate (+$\Delta f''$ refinement)	(II) *z*-coordinate (-$\Delta f''$ refinement)	Shift [=(I-II)x12.22]
O(1)	0.1815	0.1764	0.062
O(2)	0.0800	0.0741	0.072
O(3)	0.0330	0.0278	0.064
O(4)	-0.1481	-0.1536	0.067
O(9)	-0.0109	-0.0164	0.067
O(10)	-0.1215	-0.1270	0.067
O(11)	0.1201	0.1146	0.067

The *R*-factor test again was used to decide whether there is a significant difference in the correctness of the two different orientations. Each refinement was carried out with 130 parameters and 1563 reflections. The orientation refined with the positive $\Delta f''$ values had a final R_ω of 0.050 and the orientation refined with the negative $\Delta f''$ values had a final R_ω of 0.047. H_o proposed that the former orientation is correct. This statement is a one-dimensional hypothesis. The value of the *R*-factor ratio is:

$$\mathcal{R} = 0.050/0.047 = 1.064$$

From Tables, $$\mathcal{R}_{1,1433,0.01} = 1.002$$

Hence, we may reject at the 0.01 level the hypothesis that the orientation refined with the positive $\Delta f''$ values is correct.

Hence it can be concluded finally that the structure orientation refined with negative $\Delta f''$ terms for the Ho^{3+} and K^+ ions is correct.

The Dysprosium structure

The structure Na[Dy(edta)$(H_2O)_3$].$5H_2O$, which is isomorphous with the four *Fdd2* structures refined in this Thesis, was refined by Nassimbeni, Wright, van Niekerk and McCallum[45] using positive $\Delta f''$ values only for the Dy^{3+} and Na^+ ions. We have now repeated the refinement of this structure using negative $\Delta f''$ values for the Dy^{3+} and Na^+ ions so as to ascertain which structure is correct.

Now the shift along the *z*-axis of the Dy^{3+} ion that would result from omission of the $\Delta f''$ term is calculated from:

$$dz = \bar{\delta}/2\pi(\sin\theta/\lambda)_{max}$$

Then;

$2\theta(^o)$	$\theta(^o)$	$\sin\theta/\lambda$	f''	f_o	$\delta = f''/f_o$	$\bar{\delta}$
6	3	0.074	4.4	63	0.070	∿ 0.10
44	22	0.527	4.4	33	0.133	

Therefore,

$$dz = 0.10/(2x\pi x0.527)$$
$$= 0.030Å$$

Thus, if $\Delta f''$ were omitted altogether in the structure refinement, an error of approximately 0.03Å would occur in the position of the Dy^{3+} ion along the *z*-axis.

Therefore, if $\Delta f''$ is incorrectly assigned, the error in *z* of the Dy^{3+} ion will be 0.06Å.

From Figure 4.12, it can be seen that the structure orientation obtained using the negative values for $\Delta f''$ shows no marked trend and the slope of the graph is approximately zero. The structure orientation obtained using the positive values for $\Delta f''$ (refined by Nassimbeni *et al.*) does show a marked trend and the slope of this graph is:

$$m = 0.075/0.2$$
$$= 0.38\text{Å}$$

Hence, the spurious shift in the z-direction can be calculated.

i.e. $z = -md/c$

where $d = 2.40\text{Å}$

$c = 12.16\text{Å}$

Hence, $z = -(0.38 \times 2.40)/12.16$

$= -0.075\text{Å}$

This is in good agreement with the value predicted by the Cruickshank and McDonald equation.

Therefore, if the Dy^{3+} ion in the structure of incorrect orientation were shifted 0.075Å along the z-direction and the distances recalculated, the structure of correct orientation would be obtained.

From Table 4.16, it can be seen that for the structure of incorrect orientation, the apparent incorrect shift of all the light atoms in the z-direction is an average value of 0.071Å.

TABLE 4.16

Atom	(I) z-coordinate ($+\Delta f''$ refinement)	(II) z-coordinate ($-\Delta f''$ refinement)	Shift [=(I-II)x12.16]
O(1)	0.1854	0.1800	0.066
O(2)	0.0782	0.0721	0.074
O(3)	0.0389	0.0329	0.073
O(4)	-0.1559	-0.1612	0.064
O(9)	-0.0086	-0.0147	0.074
O(10)	-0.1165	-0.1226	0.074
O(11)	0.1245	0.1187	0.071

The R-factor test again was used to decide whether there is a significant difference in the correctness of the two different orientations. Each refinement was carried out with 130 parameters and 1325 reflections. The orientation refined with the positive $\Delta f''$ values had a final R_{ω} of 0.053 and the orientation refined with the negative $\Delta f''$ values had a final R_{ω} of 0.051. H_o proposed that the former orientation is correct. This statement is a one-dimensional hypothesis. The value of the R-factor ratio is:

$$\mathcal{R} = 0.053/0.051 = 1.039$$

From Tables,

$$\mathcal{R}_{1,1195,0.01} = 1.003$$

Hence, we may reject at the 0.01 level the hypothesis that the orientation refined with the positive $\Delta f''$ values is correct.

Hence it can be concluded finally that the structure orientation refined with negative $\Delta f''$ terms for the Dy^{3+} and K^{+} ions is correct.

The Lanthanum and Terbium structures

These two lanthanide-edta structures reported by Lee[42] are isomorphous with the *Fdd2* structures refined in this Thesis (see Introduction, Table 1.4). For each of these two structures, plots were drawn of the Ln - O bond lengths as a function of z (see Figures 4.13 and 4.14). In each case, no marked trend can be seen and the slope of the graph is approximately zero. It can therefore be concluded that the correct orientation of each of these structures has been reported.

Although the Samarium structure has been refined, no atomic coordinates have been reported[77].

Templeton, Templeton, Zalkin and Ruben[78] refined the structures of $Na[Pr(edta)(H_2O)_3].5H_2O$ and $Na[Gd(edta)(H_2O)_3].5H_2O$ to obtain experimental values of f'' for Pr and Gd for MoK_α radiation. Their results are in good agreement with the theoretical values. (The Pr and Gd structures refined in this Thesis had K^+ as the counter-ion. The refinement of our structures was performed prior to the article being published by Templeton *et al.* The atomic coordinates, bond lengths and bond angles obtained in this work for the two structures with the K^+ counter-ion are in close agreement with the values obtained by Templeton *et al.*)

FIGURE 4·8

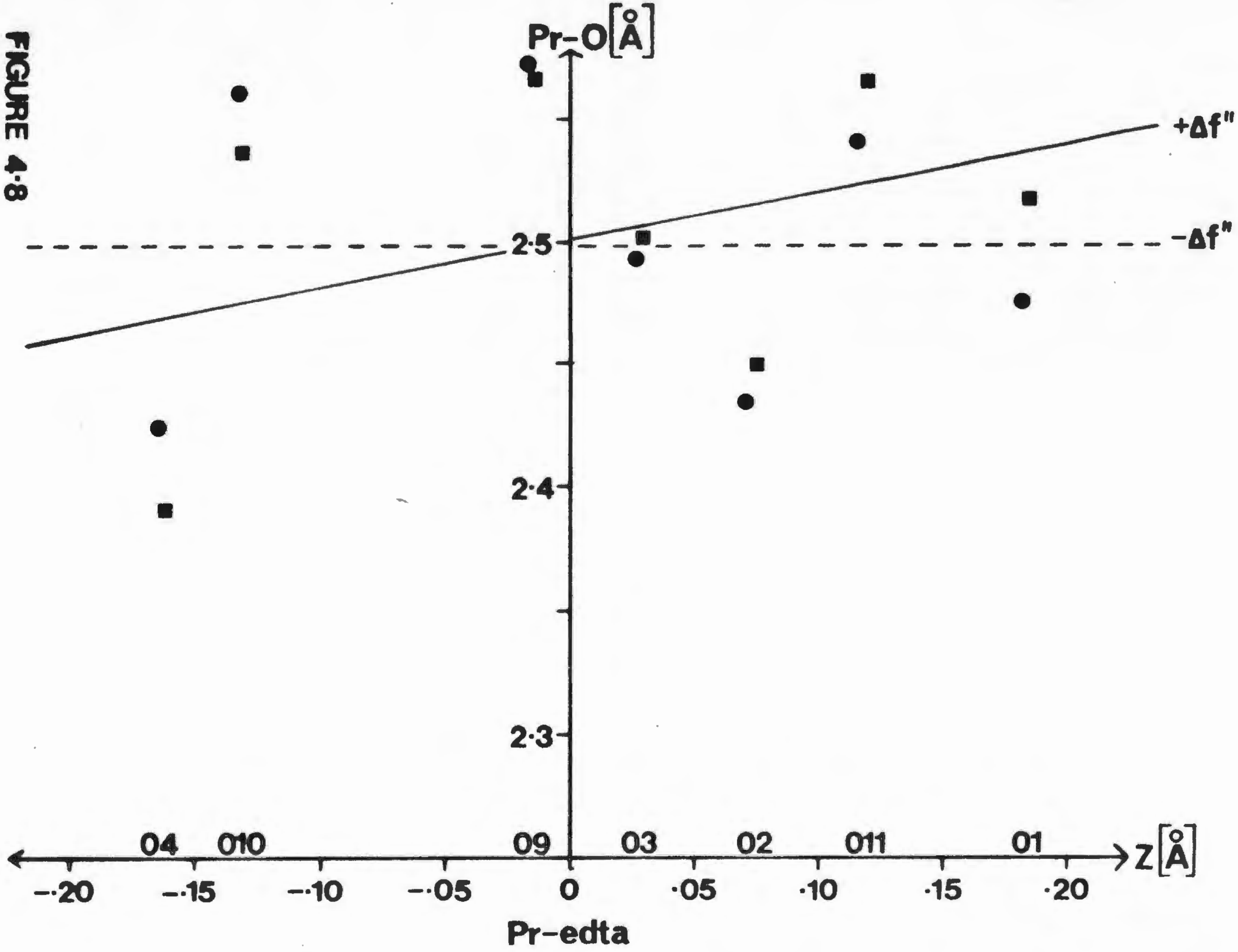

Pr-O [Å]
+Δf"
−Δf"
2·5
2·4
2·3
04
010
09
03
02
011
01
Z [Å]
−·20
−·15
−·10
−·05
0
·05
·10
·15
·20
Pr-edta

FIGURE 4·9

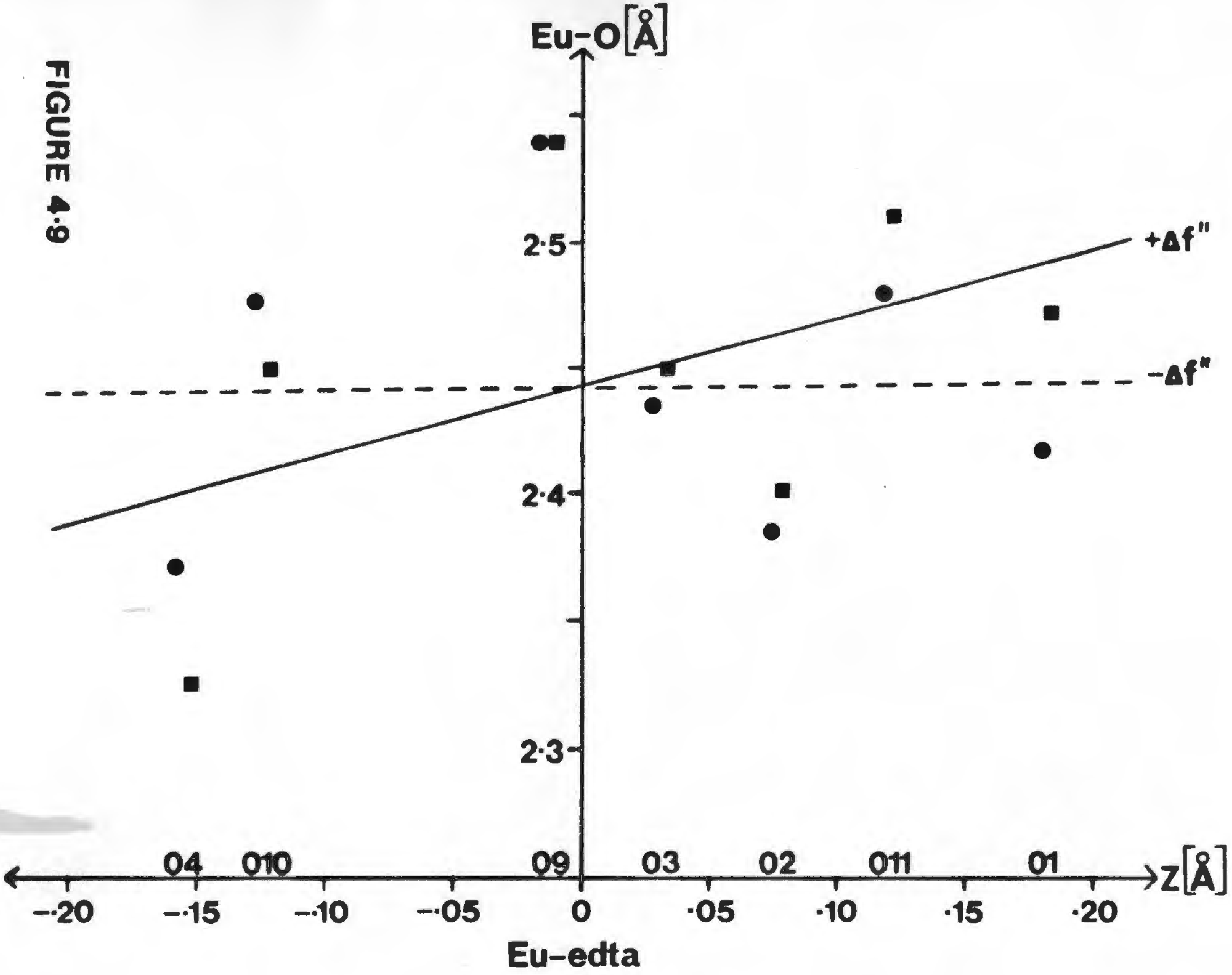
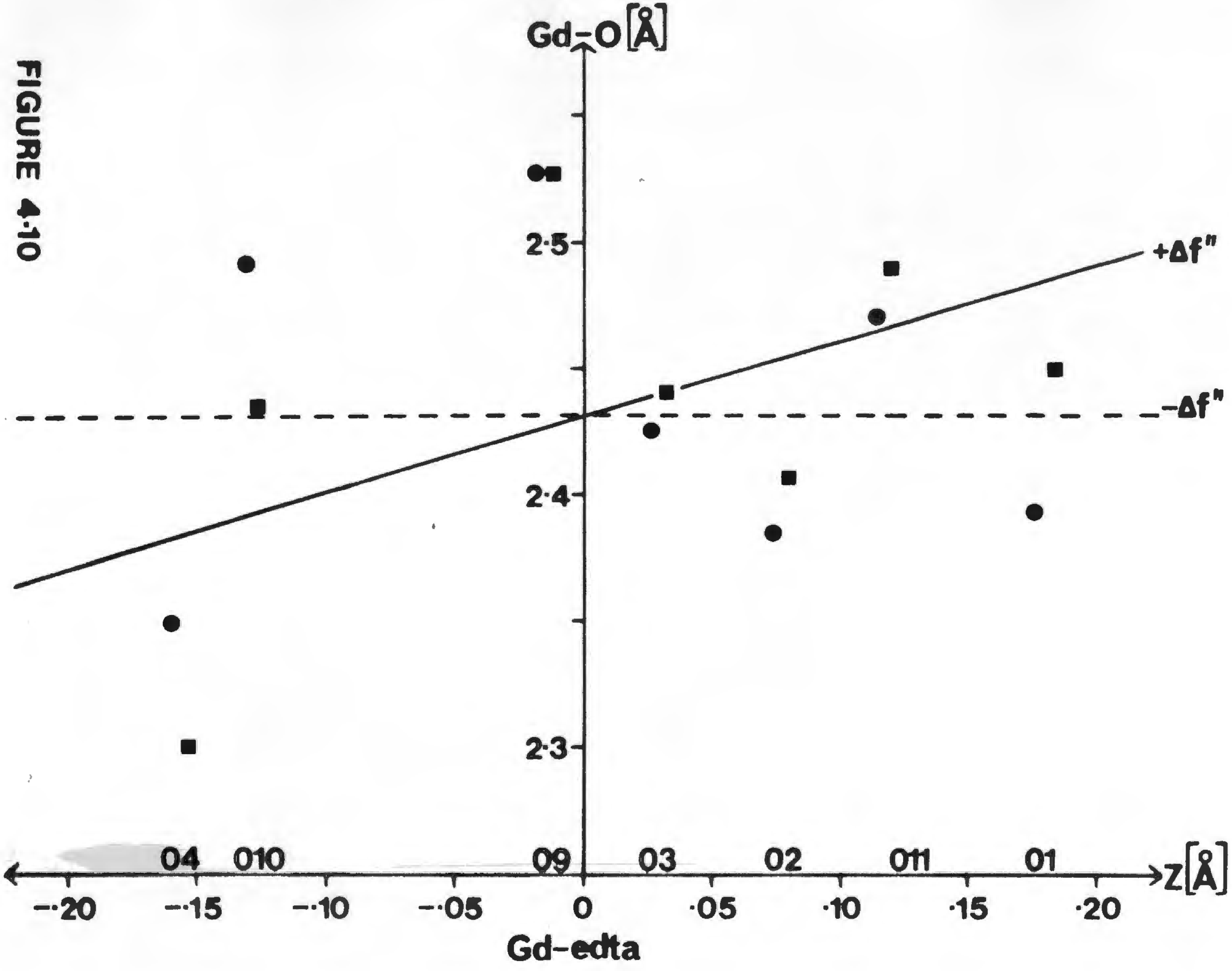

Eu-O[Å]
2·5
2·4
2·3
+Δf"
−Δf"
04
010
09
03
02
011
01
Z[Å]
−·20
−·15
−·10
−·05
0
·05
·10
·15
·20
Eu−edta

FIGURE 4·10


Gd–O [Å]
2·5
2·4
2·3
+Δf"
−Δf"
04
010
09
03
02
011
01
Z [Å]
−·20
−·15
−·10
−·05
0
·05
·10
·15
·20
Gd-edta

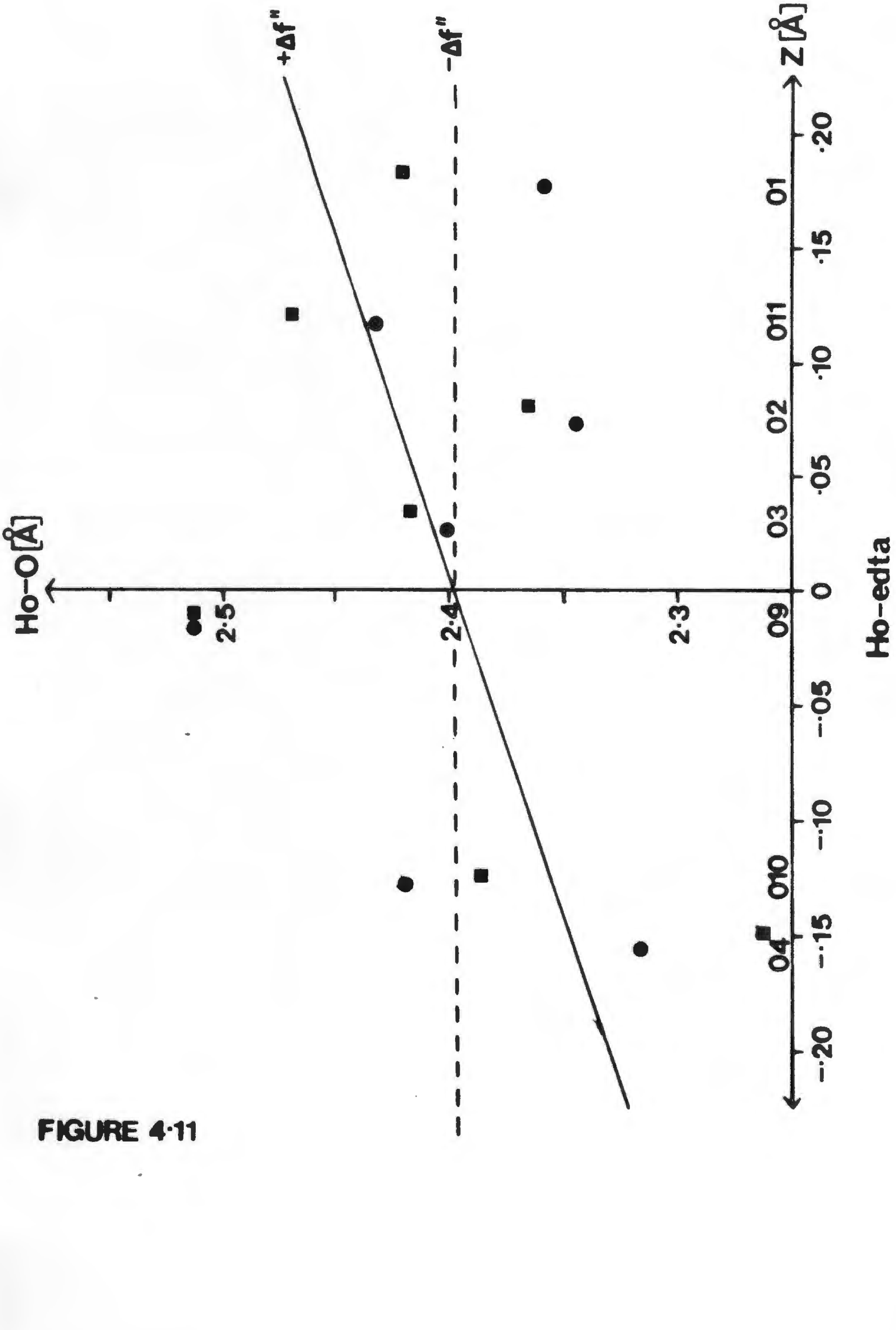

Ho-O[Å]
2·5
2·4
2·3
Z[Å]
·20
·15
·10
·05
0
-·05
-·10
-·15
-·20
O1
O11
O2
O3
O9
O10
O4
+Δf"
-Δf"
Ho-edta

FIGURE 4·11

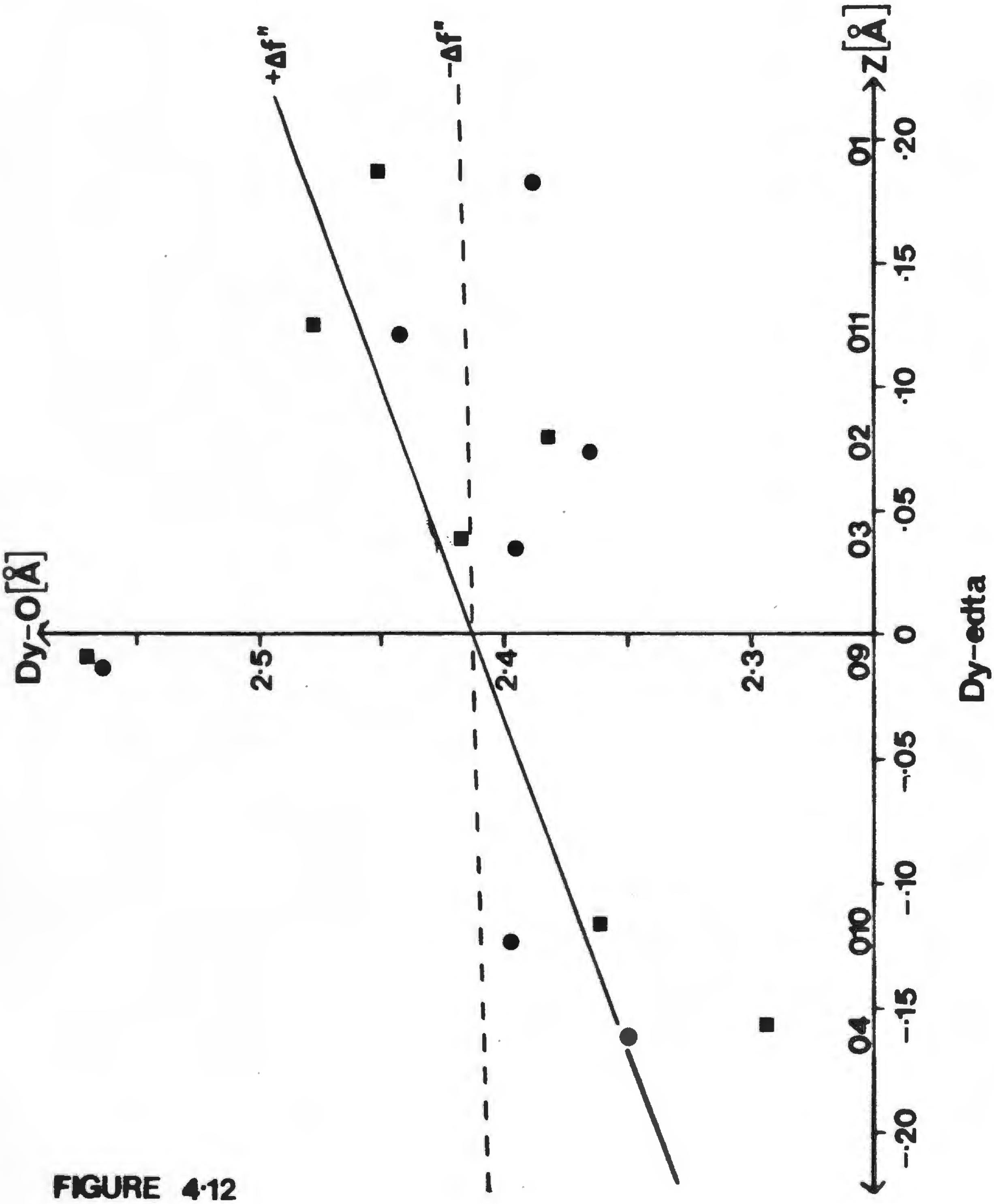

Dy–O[Å]
2·5
2·4
2·3
+Δf"
−Δf"
Z[Å]
·20
·15
·10
·05
0
−·05
−·10
−·15
−·20
O1
O11
O2
O3
O9
O10
O4
Dy–edta

FIGURE 4·12

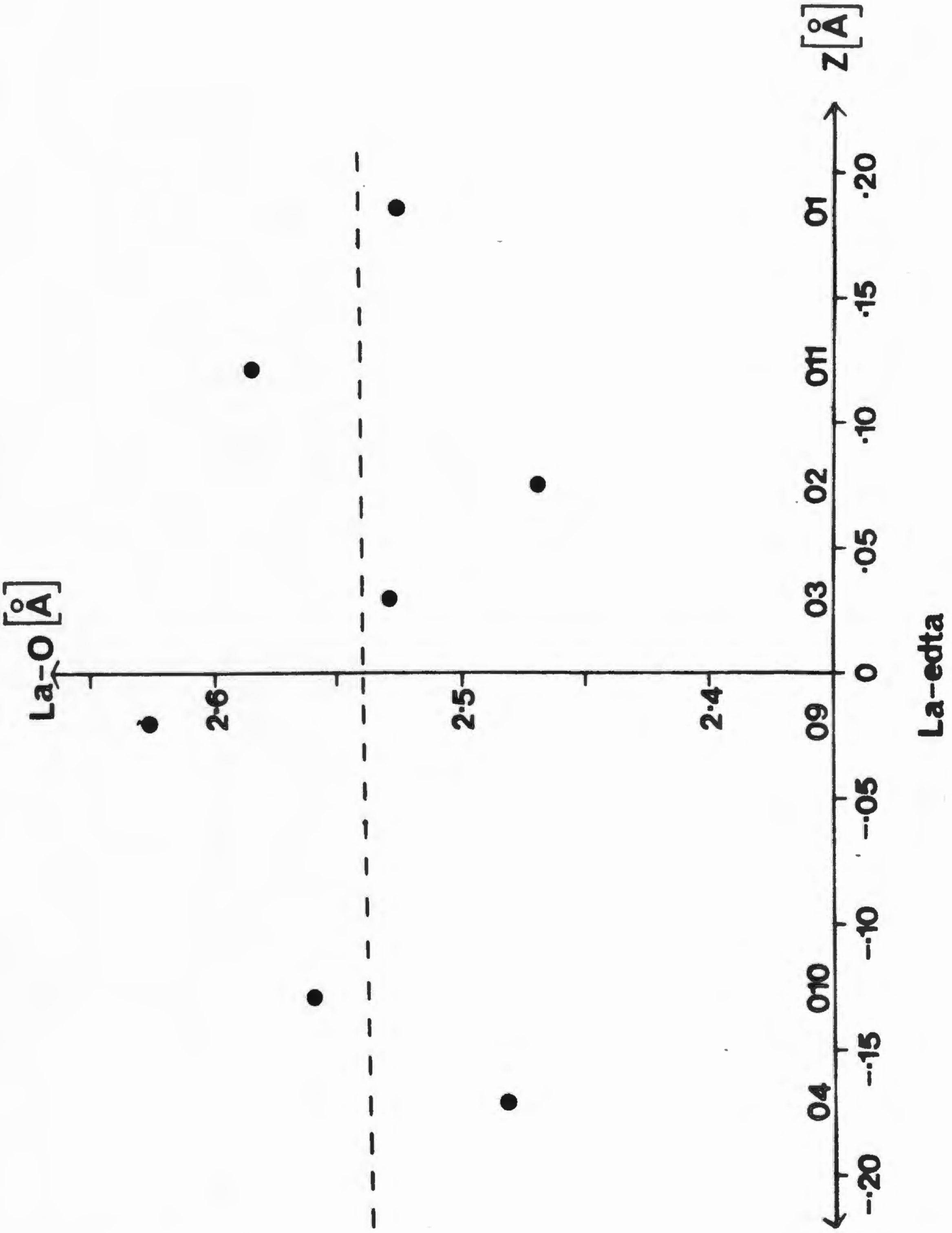
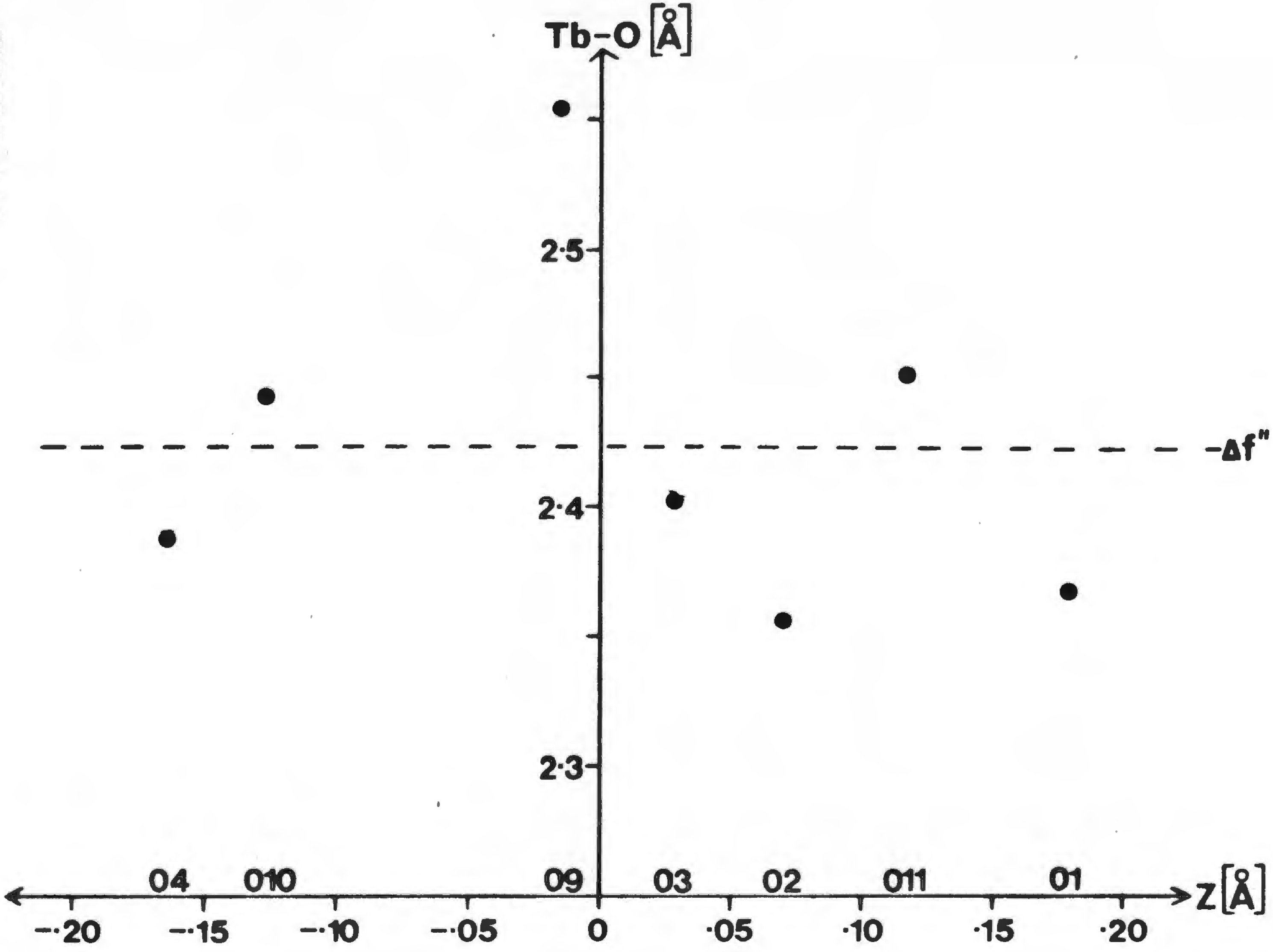

La-O [Å]
2·6
2·5
2·4
Z [Å]
·20
·15
·10
·05
0
-·05
-·10
-·15
-·20
O1
O11
O2
O3
O9
O10
O4
La-edta

FIGURE 4·13

FIGURE 4·14



Tb–edta

4.7 DESCRIPTION OF THE STRUCTURES

The compounds $K^+[Ln(edta)(H_2O)_3].5H_2O$ for Ln = Pr, Eu, Gd and Ho are therefore all isomorphous. They crystallize in the space group *Fdd2* with sixteen mole= cules per unit cell. In each structure, the metal ion is seen to have a coordination number of nine. In each case, edta acts as a hexadentate ligand i.e. the structure around the central metal ion consists of a girdle of four oxygen atoms, one from each of the four acetate groups, and the two nitrogen atoms. In all four structures, this chelation framework only reaches about half-way around the central metal ion, thus leaving ample space for the three water molecules which are also bonded to the central metal ion.

A perspective view of these four isomorphous structures is shown in Figure 4.15. The coordination geometry can best be described by a quasi-mirror passing through the metal ion and the two nitrogen atoms, ignoring C(1) and C(2) of the puckered ethylenediamine ring. Figure 4.16 shows the central metal ion surrounded by the edta chelate with the three coordinated water molecules deleted.

Intramolecular bond lengths and angles for all four structures are listed in Tables 4.17 and 4.18 respectively.

In all four structures, the mean values of the C - C and C - N bond lengths are close to the accepted standard values of 1.54Å and 1.47Å respectively[63]. The metal-ligand bond lengths are unusually long. For the Ln - $O_{coord.}$ bonds, this is due to the fact that these bonds are primarily ionic[42]. In fact, the mean values of the Ln - $O_{coord.}$ bond lengths in the four structures approach the sum of the crystal radii for Ln^{3+} and O^{2-}, which are 2.49Å for the Pr^{3+} structure, 2.43Å for the Eu^{3+} structure, 2.42Å for the Gd^{3+} structure and

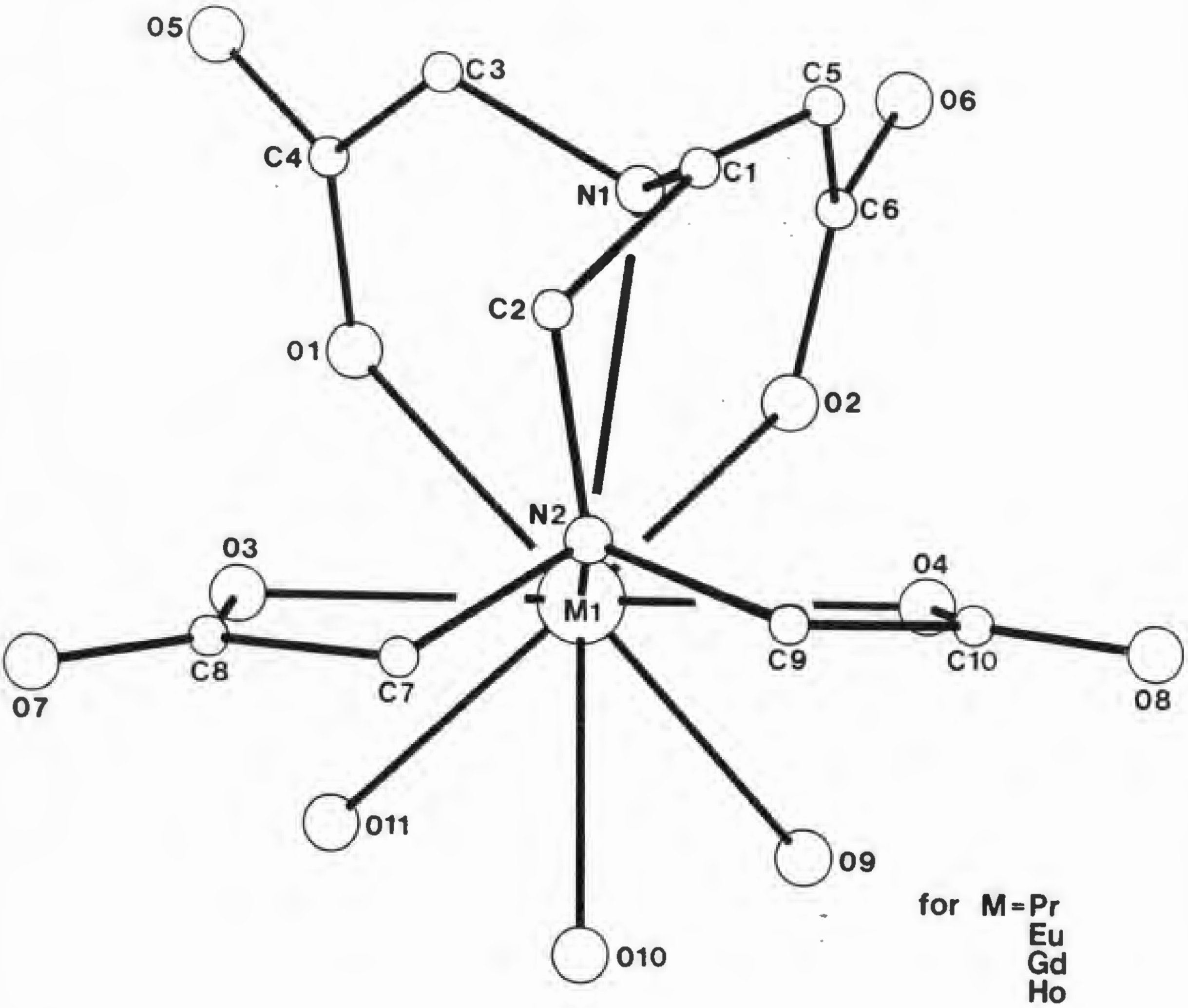

O5
C3
C5
O6
C4
N1
C1
C6
C2
O1
O2
N2
O3
O4
M1
O7
C8
C7
C9
C10
O8
O11
O9
for M=Pr
Eu
Gd
Ho
O10

FIGURE 4·15

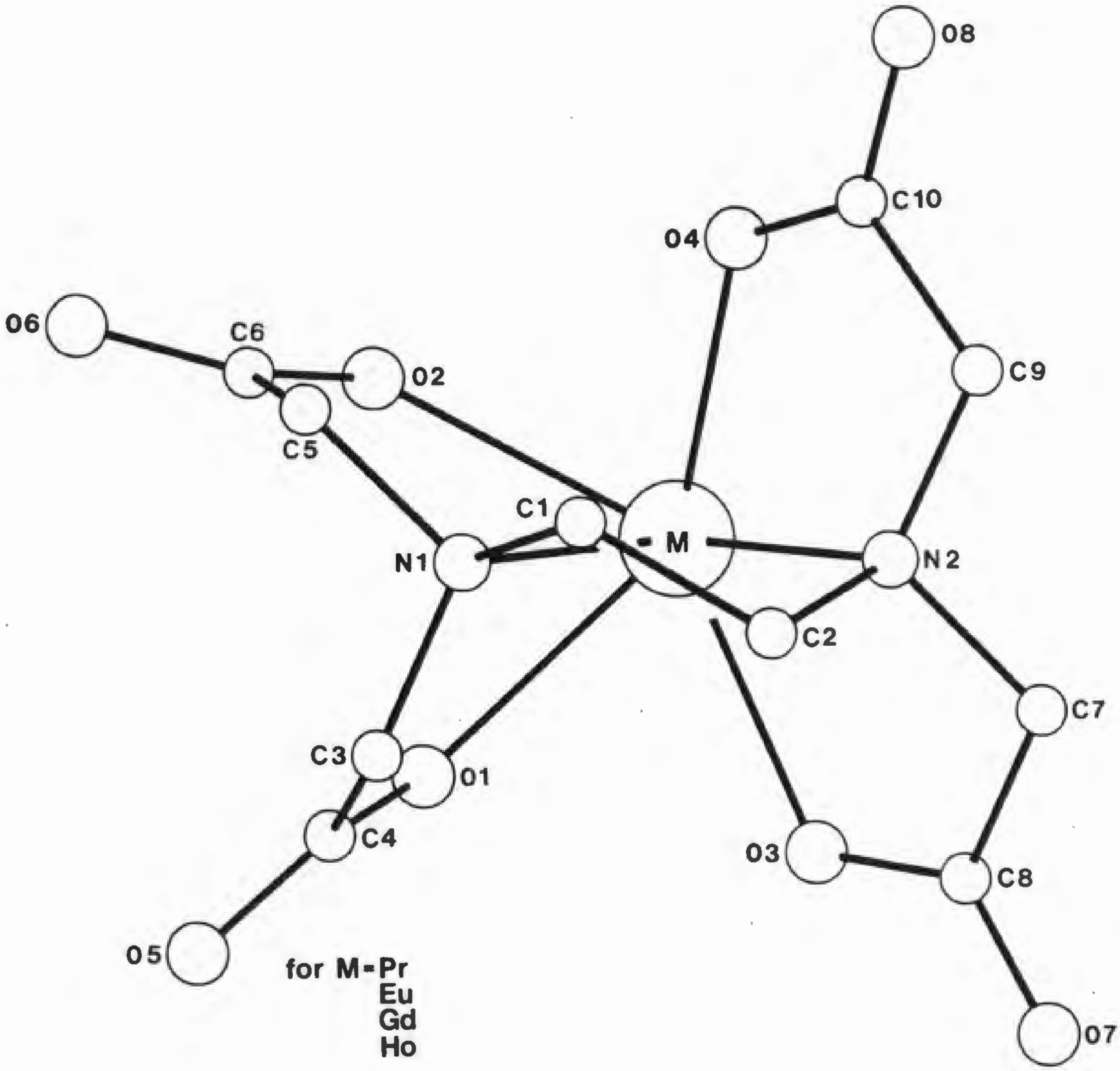

O8
C10
O4
O6
C6
O2
C9
C5
C1
M
N1
N2
C2
C7
C3
O1
C4
O3
C8
O5
for M = Pr
Eu
Gd
Ho
O7

FIGURE 4·16

TABLE 4.17 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $K^+[Ln(edta)(H_2O)_3].5H_2O$ FOR Ln = Pr, Eu, Gd AND Ho.

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
O(1) - Ln	2.48(1)	2.42(1)	2.39(1)	2.36(1)
O(2) - Ln	2.43(1)	2.39(1)	2.38(1)	2.34(1)
O(3) - Ln	2.49(1)	2.44(1)	2.43(1)	2.40(1)
O(4) - Ln	2.42(1)	2.37(1)	2.35(1)	2.32(1)
O(9) - Ln	2.58(1)	2.54(1)	2.53(1)	2.51(1)
O(10) - Ln	2.56(1)	2.48(1)	2.46(1)	2.42(1)
O(11) - Ln	2.55(1)	2.48(1)	2.46(1)	2.43(1)
N(1) - Ln	2.76(1)	2.68(1)	2.66(1)	2.64(1)
N(2) - Ln	2.73(1)	2.69(1)	2.70(1)	2.67(1)
N(1) - C(1)	1.47(2)	1.51(2)	1.45(2)	1.49(2)
N(1) - C(3)	1.47(2)	1.47(2)	1.46(3)	1.43(2)
N(1) - C(5)	1.50(2)	1.52(2)	1.54(2)	1.52(2)
N(2) - C(2)	1.51(2)	1.49(2)	1.49(2)	1.47(2)
N(2) - C(7)	1.50(2)	1.51(2)	1.50(2)	1.50(2)
N(2) - C(9)	1.46(2)	1.48(2)	1.48(2)	1.46(2)
C(1) - C(2)	1.53(2)	1.53(2)	1.50(2)	1.52(3)
C(3) - C(4)	1.52(2)	1.51(3)	1.62(3)	1.54(3)
C(5) - C(6)	1.47(2)	1.45(2)	1.44(2)	1.48(3)
C(7) - C(8)	1.50(2)	1.49(2)	1.51(2)	1.53(2)
C(9) - C(10)	1.56(2)	1.54(2)	1.56(2)	1.55(2)
C(4) - O(1)	1.22(2)	1.27(2)	1.26(2)	1.26(2)
C(4) - O(5)	1.26(2)	1.24(2)	1.22(2)	1.26(3)

TABLE 4.17 CONT/....

TABLE 4.17 CONTINUED

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
C(6) - O(2)	1.26(2)	1.25(2)	1.25(2)	1.26(2)
C(6) - O(6)	1.29(2)	1.27(2)	1.31(2)	1.26(2)
C(8) - O(3)	1.28(2)	1.28(2)	1.27(2)	1.26(2)
C(8) - O(7)	1.24(2)	1.23(2)	1.24(2)	1.21(2)
C(10) - O(4)	1.28(2)	1.28(2)	1.30(2)	1.30(2)
C(10) - O(8)	1.23(2)	1.25(2)	1.23(2)	1.21(2)

TABLE 4.18 SELECTED BOND ANGLES(^{o}) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $K^{+}[Ln(edta)(H_2O)_3].5H_2O$ FOR Ln = Pr, Eu, Gd AND Ho.

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
O(1) - Ln - O(2)	71.3(3)	70.9(3)	71.1(4)	71.3(4)
O(1) - Ln - O(3)	71.5(3)	71.7(3)	71.7(3)	71.3(3)
O(1) - Ln - O(4)	137.0(3)	138.3(3)	138.5(4)	139.2(4)
O(1) - Ln - O(11)	76.5(3)	74.4(3)	74.1(4)	73.1(4)
O(2) - Ln - O(3)	141.0(3)	141.2(3)	141.6(4)	141.5(4)
O(2) - Ln - O(4)	76.6(3)	76.9(3)	76.9(4)	76.8(4)
O(2) - Ln - O(9)	72.0(3)	70.7(3)	70.8(4)	69.3(4)
O(3) - Ln - O(4)	126.5(3)	128.6(3)	129.0(3)	129.9(4)
O(3) - Ln - O(11)	71.7(3)	71.8(3)	71.2(3)	72.3(4)
O(4) - Ln - O(9)	74.7(3)	73.3(3)	73.0(3)	72.7(4)
O(9) - Ln - O(10)	71.3(3)	71.2(3)	70.6(4)	70.7(4)
O(9) - Ln - O(11)	73.2(3)	72.7(3)	72.8(3)	72.0(4)
O(10) - Ln - O(11)	74.0(3)	74.5(3)	75.0(3)	75.2(3)
N(1) - Ln - O(9)	132.6(3)	131.9(3)	131.8(3)	131.7(4)
N(2) - Ln - O(10)	71.0(3)	71.5(3)	71.3(4)	71.6(4)
N(1) - Ln - N(2)	66.5(4)	67.4(3)	66.8(4)	67.9(4)
C(1) - N(1) - Ln	110.4(8)	111.3(8)	112.0(10)	111.1(10)
C(3) - N(1) - Ln	106.0(9)	108.2(9)	109.2(11)	109.0(11)
C(5) - N(1) - Ln	107.5(8)	107.2(8)	108.4(9)	107.5(10)
C(1) - N(1) - C(3)	113.1(9)	111.1(10)	109.7(12)	111.8(12)
C(1) - N(1) - C(5)	109.7(11)	108.4(11)	109.4(13)	107.4(13)
C(3) - N(1) - C(5)	110.0(12)	110.6(12)	108.0(14)	109.9(14)
C(2) - C(1) - N(1)	111.8(11)	109.0(12)	110.8(14)	109.5(15)

TABLE 4.18 CONT/....

TABLE 4.18 CONTINUED

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
C(4) - C(3) - N(1)	115.4(13)	113.0(13)	112.1(15)	113.1(16)
C(3) - C(4) - O(5)	116.3(14)	119.2(16)	116.1(17)	116.6(19)
C(3) - C(4) - O(1)	118.3(14)	119.2(15)	116.4(16)	119.2(18)
C(4) - O(1) - Ln	126.0(10)	124.3(10)	126.6(11)	124.3(12)
C(6) - C(5) - N(1)	113.1(13)	112.5(12)	110.5(14)	110.6(15)
C(5) - C(6) - O(6)	116.2(13)	118.2(14)	116.6(16)	117.1(17)
C(5) - C(6) - O(2)	119.5(13)	119.0(14)	122.3(16)	119.5(17)
C(6) - O(2) - Ln	125.5(8)	125.5(9)	123.8(11)	124.5(12)
C(2) - N(2) - Ln	109.6(8)	109.4(8)	108.8(9)	108.7(10)
C(7) - N(2) - Ln	106.5(8)	106.9(8)	107.3(9)	107.4(10)
C(9) - N(2) - Ln	111.8(8)	110.1(8)	109.5(8)	109.0(9)
C(2) - N(2) - C(7)	105.4(11)	106.0(11)	106.3(12)	107.1(13)
C(2) - N(2) - C(9)	111.8(11)	113.3(11)	113.2(12)	113.4(13)
C(7) - N(2) - C(9)	111.4(11)	110.8(11)	111.5(12)	111.0(13)
C(1) - C(2) - N(2)	110.4(12)	111.0(12)	111.2(14)	111.9(15)
C(8) - C(7) - N(2)	113.7(12)	111.9(12)	111.9(13)	110.6(14)
C(7) - C(8) - O(7)	119.4(12)	118.7(12)	117.3(14)	117.6(15)
C(7) - C(8) - O(3)	117.5(10)	118.0(11)	117.5(13)	117.5(13)
C(8) - O(3) - Ln	124.4(8)	124.6(8)	126.0(9)	125.8(9)
C(10) - C(9) - N(2)	112.6(12)	112.6(12)	113.2(14)	113.9(14)
C(9) - C(10) - O(8)	115.1(13)	116.6(14)	116.6(16)	118.4(15)
C(9) - C(10) - O(4)	117.3(12)	118.4(13)	116.3(14)	116.2(15)
C(10) - O(4) - Ln	128.4(8)	127.1(8)	128.3(9)	127.9(10)

2.37Å for the Ho^{3+} structure[63]. The Ln - N bond lengths are even longer and this is due to the weak interaction of the uncharged nitrogen atoms with the metal ion. In all four structures, the C - $O_{coord.}$ bond lengths are generally only slightly longer than the C - $O_{uncoord.}$ bond lengths. In fact, in each structure, one C - $O_{uncoord.}$ bond is significantly longer than the corresponding C - $O_{coord.}$ bond. This is presumably also due to the ionic nature of the Ln - $O_{coord.}$ bonds.

In fact, the bond lengths and angles of the four structures do not differ greatly from those found in other edta complexes. Any small deviations would be due to some repulsion between the ligands. There is, however, a certain amount of puckering of the five chelate rings of the edta ligand due to the long Ln - Ligand bond lengths.

From Table 4.17, it can be seen that there is a general shortening of the bond lengths in the chelation framework across the series from the Pr^{3+} structure to the Ho^{3+} structure. This is in agreement with the fact that as the size of the central metal ion decreases, there is shrinkage in the size of the corresponding anion. This fact can be further emphasised by comparison with three of the other known isomorphous Lanthanide-edta structures (see Table 1.4). i.e. The average of the four Ln^{3+} - O bond lengths in the La^{3+} structure is 2.50Å[38], 2.46Å in the Pr^{3+} structure, 2.41Å in the Eu^{3+} structure, 2.39Å in the Gd^{3+} structure, 2.38Å in the Tb^{3+} structure[42], 2.37Å in the Dy^{3+} structure and 2.36Å in the Ho^{3+} structure. The average Ln^{3+} - N bond lengths in these structures indicate similar shortening, having average values of 2.77Å[38], 2.74Å, 2.69Å, 2.68Å, 2.67Å[42], 2.67Å and 2.66Å respectively. The same applies to the average Ln^{3+} - OH_2 bond lengths, having average value of 2.59Å[38], 2.56Å, 2.50Å, 2.48Å, 2.48Å[42], 2.47Å and 2.45Å respectively. (Standard deviations range from 0.01Å to 0.02Å throughout).

This shortening of the bond lengths across the series is also due to increasing electrostatic interaction between the Ln^{3+} ion and the Ligand, thus increasing the stability of the complex as the size of the Ln^{3+} ion decreases[80] (See Figure 1.8).

In all these structures, the four coordinated oxygen atoms of the edta ligand lie approximately on the vertices of an isosceles trapezoid[42]. All the atoms of the edta ligand are confined to one side of the mean plane of these four oxygen atoms, while the Ln^{3+} ion is situated significantly off this plane on the other side. This illustrates the fact that the edta ligand does not reach even half-way around the central metal ion. Calculation of this displacement of the Ln^{3+} ion from the mean plane of the coordinated oxygen atoms for each structure can be used to illustrate the fact that, as the ionic radii of the successive cations decrease, they are enveloped to a greater extent by the edta chelate. These values were calculated using the program XANADU[65]. This distance in the La^{3+} structure is 0.62Å, 0.58Å in the Pr^{3+} structure, 0.52Å in the Eu^{3+} structure, 0.51Å in the Gd^{3+} structure, 0.49Å in the Tb^{3+} structure, 0.49Å in the Dy^{3+} structure and 0.48Å in the Ho^{3+} structure. (The equations of these least squares mean planes and the atomic deviations therefrom are listed in Table 4.19). The decrease in this displacement from the La^{3+} to the Ho^{3+} structures is almost comparable with the decrease in the successive ionic radii. (See Chapter 6 for further discussion).

In all the structures, the large space around the central metal ion on the opposite side of the edta ligand is filled with three water molecules. These water molecules, which are free of ring constraints, are subject solely to the ligand repulsions and orient themselves so as to minimise these repulsive forces.

TABLE 4.19 LEAST SQUARES PLANES

Equations of least squares planes are expressed in direct space as: $pX + qY + rZ = S$. All the least squares planes are calculated through the respective O(1), O(2), O(3) and O(4) atoms.

---

(1) Lanthanum structure:

$0.3024X + 35.8457Y - 1.6495Z = 6.1492$

(2) Praseodymium structure:

$0.4559X + 35.6891Y - 1.8468Z = 6.1224$

(3) Europium structure:

$0.3501X + 35.3947Y - 1.7565Z = 6.0229$

(4) Gadolinium structure:

$0.4453X + 35.4137Y - 1.6901Z = 6.0187$

(5) Terbium structure:

$-0.0764X + 35.1278Y - 1.6044Z = 5.9337$

(6) Dysprosium structure:

$0.2794X + 35.1054Y - 1.5525Z = 5.9193$

(7) Holmium structure:

$0.1563X + 35.2109Y - 1.5799Z = 5.9492$

TABLE 4.19 CONT/....

TABLE 4.19 CONTINUED

Atomic deviations from the planes expressed in Å ($\sigma < 0.02$Å)

	O(1)	O(2)	O(3)	O(4)	Ln^{3+}
(1) La^{3+}	0.127	-0.119	-0.083	0.075	-0.621
(2) Pr^{3+}	0.148	-0.142	-0.097	0.091	-0.583
(3) Eu^{3+}	0.140	-0.134	-0.091	0.085	-0.521
(4) Gd^{3+}	0.144	-0.137	-0.093	0.087	-0.505
(5) Tb^{3+}	0.157	-0.148	-0.103	0.094	-0.492
(6) Dy^{3+}	0.153	-0.143	-0.101	0.091	-0.490
(7) Ho^{3+}	0.136	-0.130	-0.088	0.082	-0.485

The coordination polyhedra of these structures are seen to be geometric hybrids between dodecahedral and square antiprismatic geometries.

4.8 PACKING PATTERNS AND CLOSE CONTACTS

Figure 4.17 depicts the [001] projection of all four isomorphous structures.

The molecular packing scheme in the crystals contains an infinite chain of molecules formed from one discrete unit by repeated operation of the glide planes.

The environment of the Potassium ion is such that it is closely surrounded by seven oxygen atoms. In fact, each K^+ ion is shared by two neighbouring molecules and is entrapped by O(1) and O(11) from one molecule and O(2) and O(9) from the other. The seven-coordinate arrangement around the K^+ ions is completed by three water molecules of crystallization, W(2), W(3) and W(4).

The K^+...O distances for the four compounds are reported in Table 4.20. These distances are seen to vary from 2.50Å to 2.99Å and these values agree favourably with similar results reported in the literature,[81,82,83,84,85,86] as well as with the fact that the sum of the ionic radii for potassium and oxygen is 2.73Å[63]. The K^+...O close contacts are depicted by broken lines in the right half of Figure 4.17.

To study the molecular packing pattern of the crystals, it is necessary to take into account the hydrogen bonding scheme. Unfortunately, this cannot be done accurately using the technique of X-ray diffraction, since, at best, only approximate positions for hydrogen atoms can be obtained using X-ray data at room temperature. X-rays are scattered mainly by electrons, so the scattering power of an atom is greater the higher its atomic number. The

TABLE 4.20 K^+...O CLOSE CONTACTS (Å) FOR $K^+[Ln(edta)(H_2O)_3].5H_2O$ FOR Ln = Pr, Eu, Gd AND Ho. (E.S.D.'S IN PARENTHESES)

Symmetry code

(i) ½+x, y, ½+z

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
K^+...O(1)	2.71(1)	2.68(1)	2.68(1)	2.66(1)
K^+...O(11)	2.86(1)	2.89(1)	2.93(1)	2.99(1)
K^+...O(2^i)	2.71(1)	2.70(1)	2.70(1)	2.68(1)
K^+...O(9^i)	2.88(1)	2.87(1)	2.91(1)	2.83(1)
K^+...W(2)	2.90(2)	2.92(2)	2.91(2)	2.97(2)
K^+...W(3)	2.50(5)	2.61(5)	2.61(5)	2.61(5)
K^+...W(4)	2.90(3)	2.90(3)	2.89(4)	2.99(5)

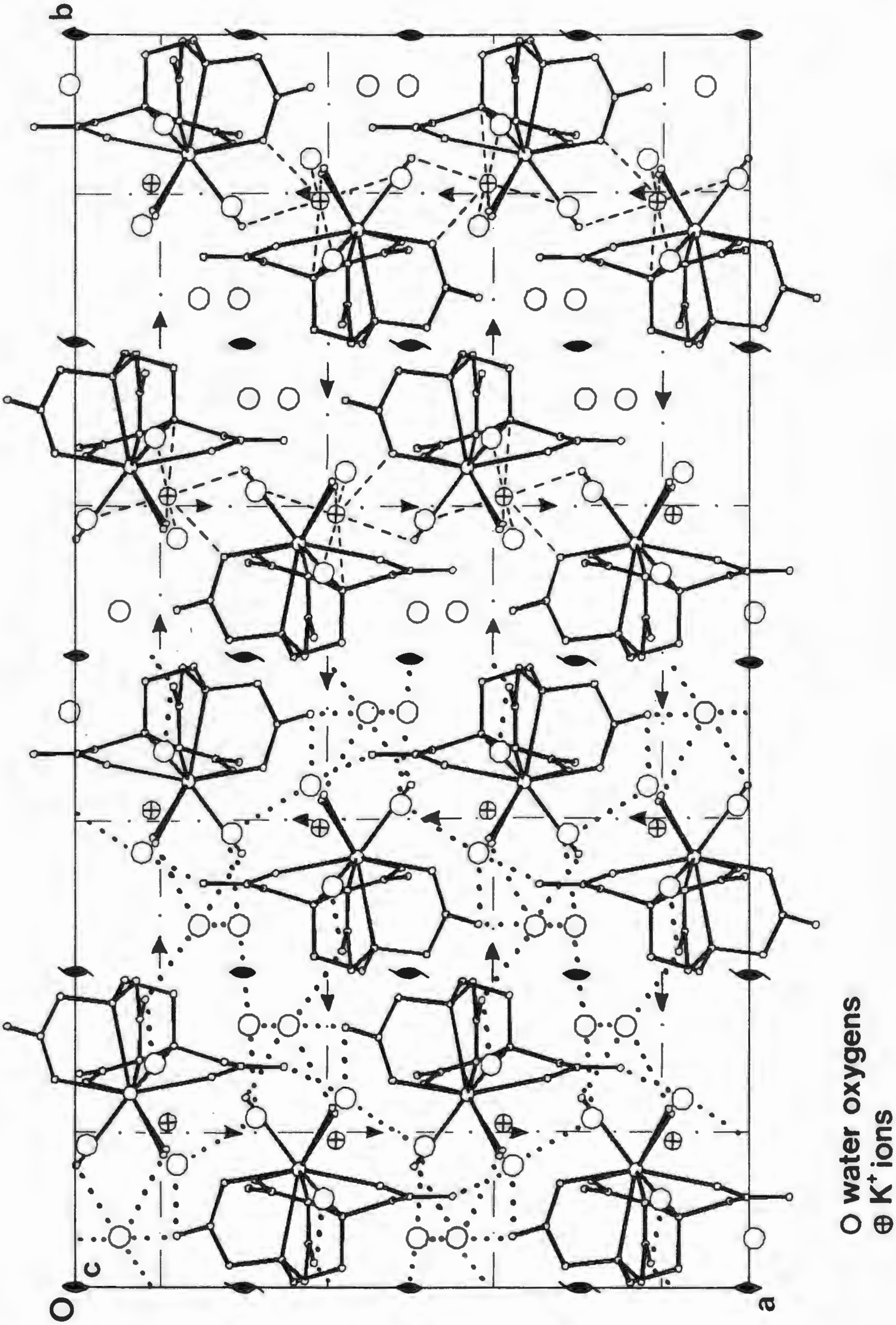


FIGURE 4·17

scattering power of the hydrogen atom is thus the smallest of any atom. The positions of hydrogen atoms can only be obtained accurately using the technique of neutron diffraction. Neutrons are scattered by the nuclei themselves and the hydrogen atom has a favourable scattering factor relative to heavier atoms[87].

Therefore, it was only possible to predict the most probable H-bonding scheme and this was done taking into account the distances between the oxygen atoms, the thermal parameters of these oxygen atoms and a certain amount of knowledge about H-bonding.

In general, it is now widely accepted that Hydrogen bonds may vary from weak bonds (O...O$\simeq$3.2Å) to very strong bonds (O...O$\simeq$2.4Å)[87,88,89,90,91].

All the water molecules can be assumed to be donors of two hydrogen bonds as well as being potential acceptors of two hydrogen bonds[92,93].

The thermal parameters of the oxygen atoms also give some indication of the hydrogen bonding scheme.

Therefore, using these criteria, the most probable hydrogen bonding scheme was predicted. The O...O close contacts in the range 2.58Å to 3.16Å representing the most probable H-bonding are recorded in Table 4.21 and are shown by dotted lines in Figure 4.18 as well as by dotted lines in the left half of the [001] projection in Figure 4.17.

As can be seen, the coordinated water molecules O(9), O(10) and O(11) in one discrete unit serve as links, by means of hydrogen bonds, to attach adjacent units together. The molecule O(10) is hydrogen bonded to O(7) of one neighbour

TABLE 4.21 INTRAMOLECULAR AND INTERMOLECULAR HYDROGEN BONDING (Å) IN $K^+[Ln(edta)(H_2O)_3].5H_2O$ FOR Ln = Pr, Eu, Gd AND Ho. (E.S.D.'S IN PARENTHESES)

Symmetry code

(i) $\frac{1}{2}+x, y, \frac{1}{2}+z$

(ii) $x, y, 1+z$

(iii) $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$

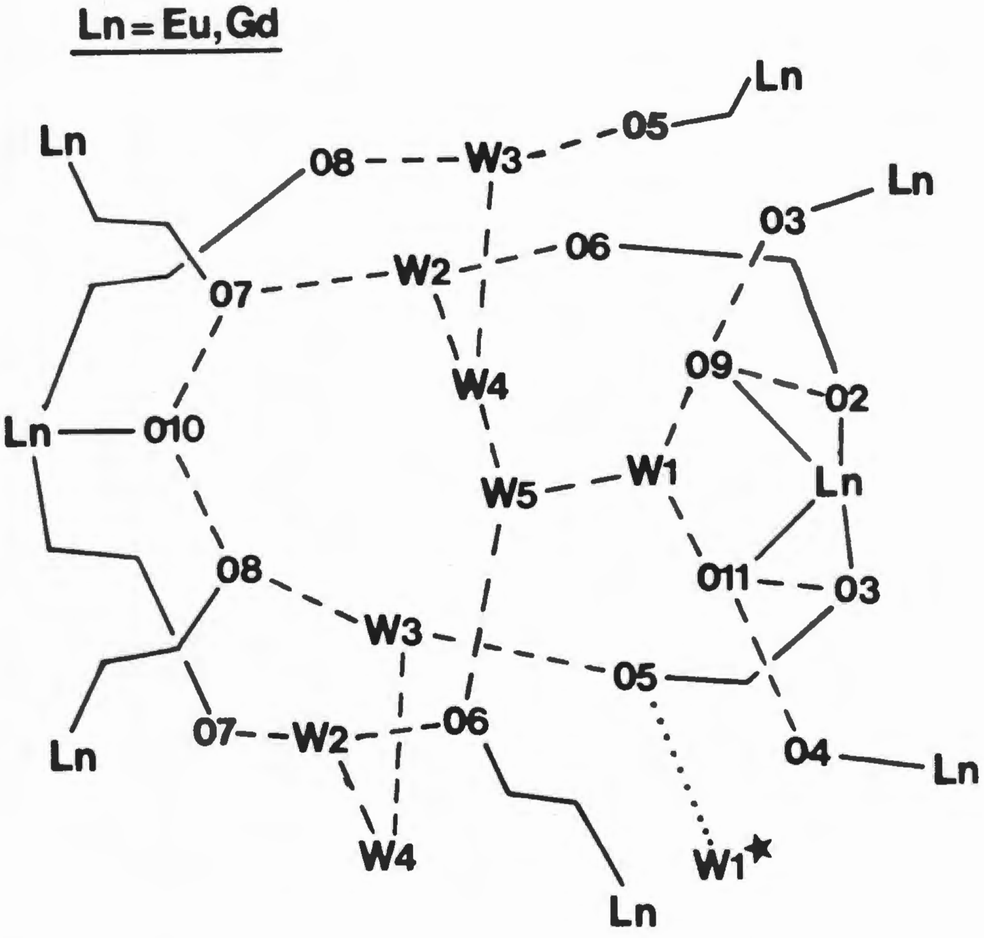
(iv) $\frac{1}{4}+x, \frac{1}{4}-y, -\frac{3}{4}+z$

(v) $-\frac{1}{4}+x, \frac{1}{4}-y, -\frac{1}{4}+z$

(vi) $\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$

(vii) $\frac{1}{2}-x, \frac{1}{2}-y, z$

	Ln = Pr	Ln = Eu	Ln = Gd	Ln = Ho
O(7)...O(10^{iii})	2.73(2)	2.74(2)	2.70(2)	2.70(2)
O(10)...O(8^{iii})	2.76(2)	2.71(2)	2.74(2)	2.71(2)
O(3)...O(9^{iii})	2.78(2)	2.79(2)	2.78(2)	2.78(2)
O(11)...O(4^{iii})	2.78(2)	2.81(2)	2.81(2)	2.82(2)
O(9)...O(2)	2.95(2)	2.85(2)	2.84(2)	2.77(2)
O(11)...O(3)	2.95(2)	2.88(2)	2.84(2)	2.85(2)
W(1)...O(9)	2.78(2)	2.81(2)	2.80(2)	2.81(2)
W(1)...O(11)	2.70(2)	2.70(2)	2.71(2)	2.71(2)
W(5)...W(1^{iii})	2.77(4)	2.79(4)	2.84(4)	2.87(4)
O(7)...W(2^{iv})	2.75(3)	2.75(3)	2.74(3)	2.74(3)
W(3)...O(8^{ii})	2.87(3)	2.91(3)	2.87(3)	2.91(3)
W(2)...O(6^{iii})	2.77(3)	2.75(3)	2.76(3)	2.77(3)
W(5)...O(6^{i})	2.73(4)	2.71(4)	2.67(4)	2.63(4)
O(5)...W(3)	2.79(3)	3.11(3)	3.16(3)	-
W(4)...W(3)	-	2.96(3)	3.07(3)	2.88(3)
W(2)...W(4^{iii})	2.71(3)	2.66(3)	2.76(3)	2.67(3)
W(4)...W(5^{v})	2.74(4)	2.58(4)	2.59(4)	2.59(4)
W(1)...O(5^{vi})	2.70(2)	2.69(2)	2.68(2)	2.68(2)
W(5)...W(5^{vii})	2.75(5)	2.86(5)	2.69(5)	2.61(5)



★adjacent layer

FIGURE 4·18

and O(8) of another. The molecule O(9) is bonded to O(3) of one adjacent unit and the molecule O(11) is bonded to O(4) of another neighbour. The water molecule of crystallization, W(1), is also hydrogen bonded to both the molecules O(9) and O(11) of the same unit.

Of the four oxygen atoms of the anion that are not coordinated to the central metal ion (i.e. O(5), O(6), O(7) and O(8)), O(5) and O(6) have higher thermal parameters than O(7) and O(8). This is because O(7) and O(8) are more strongly H-bonded in the crystal, since they are both bonded to one coordinated water molecule, O(10), as well as being bonded to one water molecule of crystallization i.e. O(7) to W(2) and O(8) to W(3). The atoms O(5) and O(6) are H-bonded to uncoordinated water molecules only. The molecule O(6) is H-bonded to W(2) and W(5). The H-bonding of O(5) is slightly different in the four structures. In the Pr^{3+}, Eu^{3+} and Gd^{3+} structures, O(5) is H-bonded to W(3) as well as to W(1) of a unit in an adjacent layer, while in the Ho^{3+} structure, O(5) is only H-bonded to W(1) of a unit in an adjacent layer. In the structures of Eu^{3+}, Gd^{3+} and Ho^{3+}, a H-bond exists between W(3) and W(4), whereas this bond is absent in the Pr^{3+} structure. (The H-bonding schemes represented in Figures 4.17 and 4.18 are therefore actually representative of the Eu^{3+} and Gd^{3+} structures). As was stated previously, a small fraction of these uncoordinated water molecules almost certainly diffuse out of the crystals during the period of the data collection, resulting in increased thermal parameters of those molecules to which they are H-bonded.

In each structure, the thermal parameter for one of the water molecules of crystallization, W(1), is fairly low and is in fact comparable with the values for O(7) and O(8). This is due to the fact that W(1) is H-bonded to the coordinated water molecules O(9) and O(11) of one unit. On the other hand, the thermal parameters of the water molecules W(3), W(4) and W(5) are particularly high, while that for W(2) is also fairly high. These molecules occupy a relatively empty region in the crystal and are only H-bonded to one another and to the uncoordinated oxygen atoms of the anion. They also appear to be disordered to some extent.

The adjacent layers are held together primarily by van der Waals interaction. There is also one hydrogen bond per molecule between the layers, occurring between O(5) of one unit and W(1) of another.

Using this hydrogen bonding scheme and the thermal parameters of the oxygen atoms of the molecules of water of crystallization, the most probable order in which the five water molecules are lost in the thermogravimetric analysis (see Chapter 3, part 3.3) can be predicted. The first sudden weight loss in the TGA curve of the $K^+[Gd(edta)(H_2O)_3].5H_2O$ complex is surmised to correspond to the loss of W(3), the second gradual weight loss to the loss of W(4), the third large weight loss to the simultaneous loss of the W(5) and W(2) molecules and the final gradual weight loss to the loss of the strongly hydrogen bonded W(1) molecule.

CHAPTER 5

CHAPTER 5

THE CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPOUNDS $K^+[Ln(edta)].6H_2O$ FOR Ln = Er AND Yb.

5.1 PRELIMINARY X-RAY ANALYSIS

These two compounds crystallized as rhomboidal platelets.

The oscillation, Weissenberg and precession photographs indicated that the two compounds were isomorphous, and showed the crystals to be monoclinic with Z equal to 4.

The approximate unit cell parameters were obtained from the photographs and were similar for both structures.

i.e. for Ln = Er, a = 8.8Å, b = 25.8Å, c = 8.7Å, $\beta = 97.3^o$

Ln = Yb, a = 8.7Å b = 25.9Å, c = 8.7Å $\beta = 97.5^o$

The zero-layer Weissenberg about the unique diad, b, had a paucity of strong reflections, and although the crystals were grossly overexposed, the ensuing photographs made the space group determination difficult.

The general trend showed the condition for non-extinction as $h + k = 2n$, thereby indicating a centred space group. However, there were a few notable exceptions to this trend which thereby forced the space group to be primitive.

5.2 INTENSITY DATA COLLECTIONS

Diffractometer data collections were thus obtained for both crystals as for a primitive unit cell.

Analysis of the diffractometer data confirmed the photographic work, in that the majority of reflections fulfilled the conditions appropriate for the space groups $C2/c$ or Cc, for which the conditions for non-extinction are:

hkl : $h + k = 2n$
$h0l$: $l = 2n$; $(h = 2n)$
$0k0$: $k = 2n$.

However, there were a small number of undoubtedly present reflections which forced the space group to be $P2_1/n$, the conditions for non-extinction being:

hkl : no conditions
$h0l$: $h + l = 2n$
$0k0$: $k = 2n$

At this stage, prior to solving the structure, it appeared likely that there was a problem of pseudo-symmetry in that, somehow, the molecules were indeed arranged in a $P2_1/n$ pattern, but that the motif resembled that for $C2/c$ or Cc, and could be made such by small movements of the molecules.

Therefore, successive attempts were made to solve both of the structures in the space groups $P2_1/n$, Cc and $C2/c$.

The relevant crystal data plus the data collection information for both structures appear in Table 5.1.

5.3 STRUCTURE SOLUTION IN THE SPACE GROUP $P2_1/n$.

The space group $P2_1/n$ is a non-standard setting of the space group $P2_1/c$. The relationship between the two space groups is shown in Figure 5.1.

TABLE 5.1 CRYSTAL DATA AND DATA COLLECTION

Molecular formula:	$K^+[Er(edta)(H_2O)_2].4H_2O$	$K^+[Yb(edta)(H_2O)_2].4H_2O$
Molecular weight:	602.36	608.14
Space group:	*C2/c*	*C2/c*
Z:	4	4
a:	8.802(4)Å	8.723(4)Å
b:	25.810(13)Å	25.886(13)Å
c:	8.704(4)Å	8.720(4)Å
β:	97.29(2)°	97.49(2)°
D_m:	$2.03 g.cm^{-3}$	$2.08 g.cm^{-3}$
D_c:	$2.04 g.cm^{-3}$	$2.07 g.cm^{-3}$
Volume:	$1961.41 Å^3$	$1952.22 Å^3$
F(000):	1172	1180
$\mu(MoK_\alpha)$:	$43.34 cm^{-1}$	$48.37 cm^{-1}$
Crystal dimensions:	0.25x0.25x0.38mm	0.25x0.25x0.38mm
Scan mode:	ω/2θ	ω/2θ
Scan width:	0.6°θ	0.7°θ
Scan speed:	$0.02 \theta s^{-1}$	$0.023 \theta s^{-1}$
Range scanned (2θ):	6 - 52	6 - 52
Stability of standard reflections:	0.91%	0.86%
Number of reflections collected:	3936	3904
Number of observed reflections:	1926 with $I_{(rel)} > 2\sigma I_{(rel)}$	1717 with $I_{(rel)} > 2\sigma I_{(rel)}$
Number of variables:	63	63

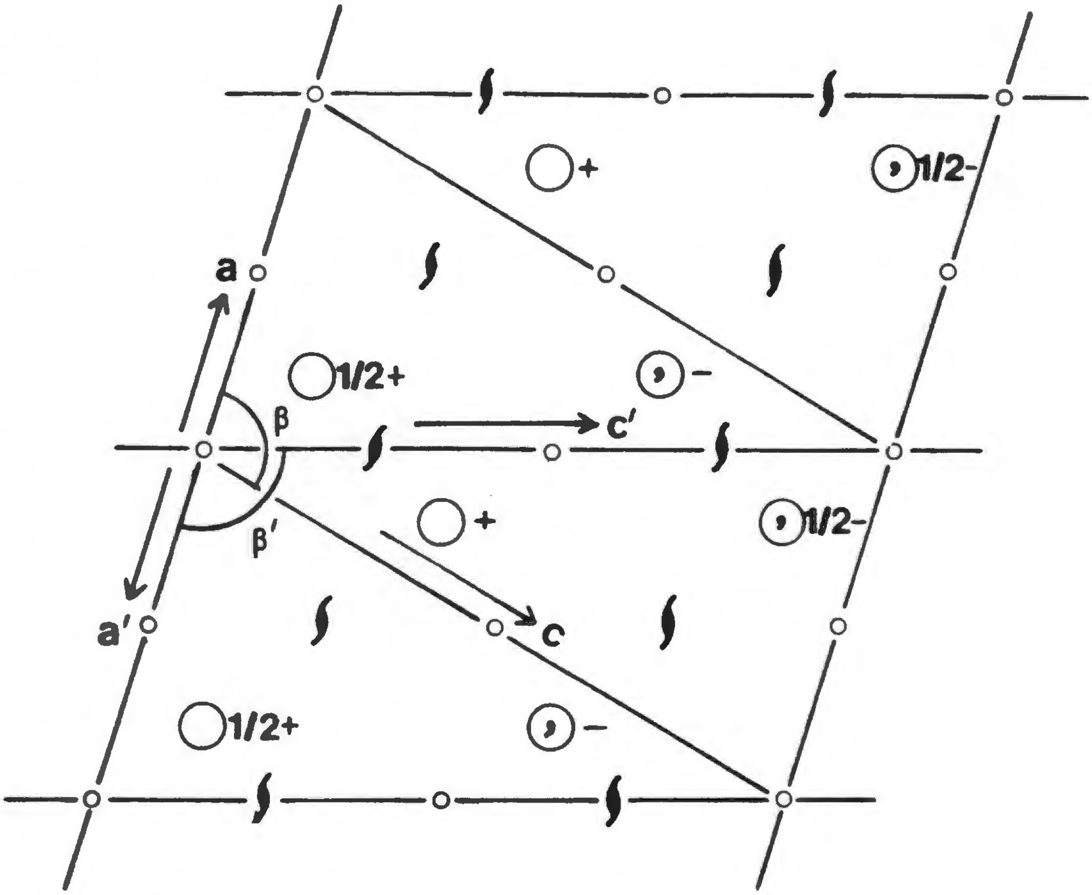


FIGURE 5.1

The relationship (not drawn to scale) between the unit cell (bounded by *a*, *b* and *c*) corresponding to the space group $P2_1/n$, and the unit cell (bounded by *a*', *b*' and *c*') corresponding to the space group $P2_1/c$. The equivalent positions are:

$P2_1/n$: x,y,z; $-x,-y,-z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$

$P2_1/c$: x,y,z; $-x,-y,-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$; $-x,\frac{1}{2}+y,\frac{1}{2}-z$

The two cells are projected down [010].

The position of the Lanthanide ion was located by analysis of a three-dimensional Patterson vector map. A vector grid for the space group $P2_1/n$ was constructed and is shown in Table 5.2.

TABLE 5.2

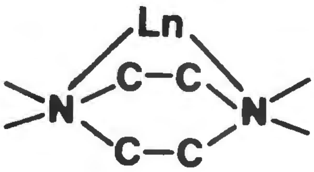
	x,y,z	$-x,-y,-z$	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$
x,y,z	$0,0,0$	$-2x,-2y,-2z$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	$\frac{1}{2}-2x,\frac{1}{2},\frac{1}{2}-2z$
$-x,-y,-z$	$2x,2y,2z$	$0,0,0$	$\frac{1}{2}+2x,\frac{1}{2},\frac{1}{2}+2z$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$
$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	$\frac{1}{2}-2x,\frac{1}{2},\frac{1}{2}-2z$	$0,0,0$	$-2x,-2y,-2z$
$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	$\frac{1}{2}+2x,\frac{1}{2},\frac{1}{2}+2z$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	$2x,-2y,2z$	$0,0,0$

From this vector grid, the vector coordinates were derived. i.e.

Vector position	Multiplicity
$0,0,0$	4
$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	2
$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	2
$\frac{1}{2}+2x,\frac{1}{2},\frac{1}{2}+2z$	2
$\frac{1}{2}-2x,\frac{1}{2},\frac{1}{2}-2z$	2
$2x,2y,2z$	1
$-2x,-2y,-2z$	1
$2x,-2y,2z$	1
$-2x,2y,-2z$	1

The satellite peaks and their corresponding inversion peaks were easily recognised and the heavy atom was located at $x = 0.0$, $y = 0.093$, $z = 0.25$.

The subsequent difference electron density maps, calculated from the structure factors derived from the Ln^{3+} position, yielded peaks which were interpreted as the potassium ion, and twelve possibly coordinated light atoms. Further refinement, with the Ln^{3+} and K^+ ions anisotropic and the light atoms isotropic, yielded very little information which could be chemically interpreted. In particular, in the myriad of rings, a series of peaks were persistently obtained which could be reasonably explained only in terms of:



That is, there appeared to be statistical disorder in the carbon atoms joining the two nitrogen atoms of edta. There also appeared to be disorder in the rest of the structure as no set of peaks could be reasonably interpreted as a molecule.

In an attempt to interpret the disorder, maps of electron density were computed at intervals of $y = 0.02$ phased on the positions of the Ln^{3+} and K^+ ions and transferred onto perspex sheets. No meaningful interpretation could be made from these maps, however. At this point, it was decided to discard this space group.

5.4 STRUCTURE SOLUTION IN THE SPACE GROUP *Cc*.

It was decided to ignore the few reflections which demanded that the space group be primitive and to interpret the reflection data as emanating from a centred lattice. The choice existed between the space groups *Cc* and *C2/c*, both of which have the same conditions limiting the possible reflections. The *E* statistics, however, pointed to the non-centrosymmetric space group *Cc*.

The three-dimensional Patterson vector map was easily interpreted in this space group. The vector grid for the space group appears in Table 5.3.

TABLE 5.3

	x,y,z	$x,-y,\frac{1}{2}+z$	$\frac{1}{2}+x,\frac{1}{2}+y,z$	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$
x,y,z	$0,0,0$	$0,-2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$
$x,-y,\frac{1}{2}+z$	$0,2y,\frac{1}{2}$	$0,0,0$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
$\frac{1}{2}+x,\frac{1}{2}+y,z$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	$0,0,0$	$0,-2y,\frac{1}{2}$
$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,2y,\frac{1}{2}$	$0,0,0$

Hence the vector coordinates were obtained:

Vector position	Multiplicity
$0,0,0$	4
$\frac{1}{2},\frac{1}{2},0$	4
$0,2y,\frac{1}{2}$	2
$0,-2y,\frac{1}{2}$	2

$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	2
$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	2

Thus the Patterson will only yield the *y* coordinate of the Ln^{3+} ion, and since in *Cc* the origin is on the *c* glide plane, the *x* and *z* coordinates of the Ln^{3+} ion were arbitrarily placed at 0. The Ln^{3+} coordinates were thus determined as $x = 0$, $y = 0.093$, $z = 0$. However, subsequent refinements yielded results similar to those described for the space group $P2_1/n$, and no sensible interpretation of the difference electron density map could be obtained.

Again electron density maps were computed phased on the positions of the Ln^{3+} and K^+ ions at intervals of $y = 0.02$ and contoured onto perspex sheets. This is illustrated by photographs in Figures 5.2 and 5.3. However, still no meaningful interpretation could be made of the obvious disorder.

Thus, it was decided to ignore the *E* statistics (which are not generally reliable for heavy metal structures), and to attempt the structure solution in the space group *C*2/*c*.

5.5 STRUCTURE SOLUTION IN THE SPACE GROUP *C*2/*c*

Since $Z = 4$, the Ln^{3+} ion had to be placed on a special position, which in *C*2/*c* is either a centre of inversion (Wyckoff position *a* to *d*), or a diad. (Wyckoff position *e*). Since the anion cannot be centrosymmetric, the Ln^{3+} ion must, in fact, lie on the diad, at $0,y,\frac{1}{4}$, and equivalent positions.

The three-dimensional Patterson vector map was again easily interpreted in this space group. The vector grid for this space group appears in Table 5.4.

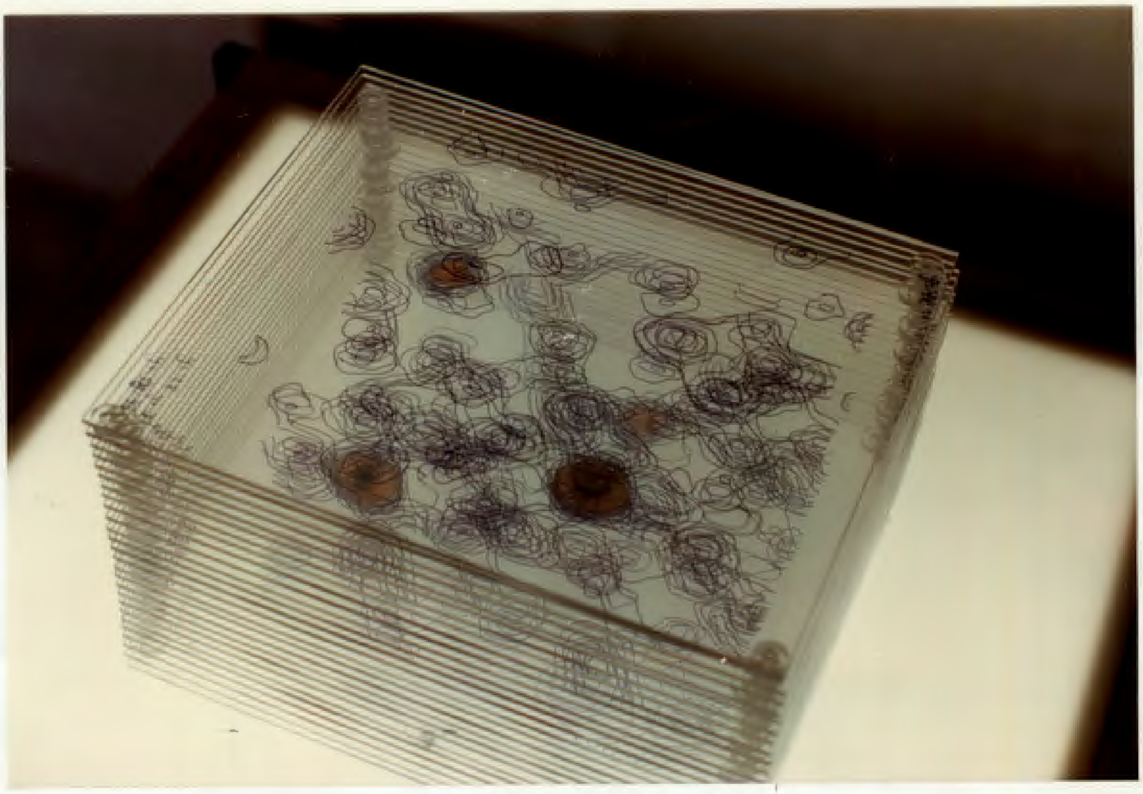


FIGURE 5·2

FIGURE 5·3

TABLE 5.4

	$0,y,\frac{1}{4}$	$0,-y,\frac{3}{4}$	$\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$
$0,y,\frac{1}{4}$	$0,0,0$	$0,-2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$
$0,-y,\frac{3}{4}$	$0,2y,\frac{1}{2}$	$0,0,0$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
$\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	$0,0,0$	$0,-2y,\frac{1}{2}$
$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$	$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,2y,\frac{1}{2}$	$0,0,0$

Hence the vector coordinates were obtained:

Vector position	Multiplicity
$0,0,0$	4
$\frac{1}{2},\frac{1}{2},0$	4
$0,2y,\frac{1}{2}$	2
$0,-2y,\frac{1}{2}$	2
$\frac{1}{2},\frac{1}{2}+2y,\frac{1}{2}$	2
$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	2

Thus the Patterson only yields the y-coordinate of the Ln^{3+} ion. The Ln^{3+} ion coordinates were thus established as $x = 0$, $y = 0.093$, $z = 0.25$. A subsequent refinement yielded the position of the K^+ ion and eight possibly coordinated light atoms. Further least squares refinements followed by appropriate difference electron density maps again yielded what was clearly a disordered structure.

Maps of electron density were again computed phased on the positions of the Ln^{3+} and K^+ ions at intervals of $y = 0.02$, and contoured onto perspex sheets.

Again, a great deal of trouble was experienced in interpreting the disorder.

Eventually, however, two independent structures were identified, one deriving from a set of peaks somewhat stronger than the other. The diad runs through the Ln^{3+} ion and the midpoint of the C - C bond in the N - C - C- N moiety.

The two structures were eventually refined with fractional site occupational factors, such that the sum of the s.o.f. of the corresponding atoms equalled unity. The refinement yielded a chemically 'good' structure, with s.o.f. = 0.66, which had reasonable bond lengths and angles, and a 'lesser' structure, with s.o.f. = 0.33, which had generally worse bond lengths and angles and a nitrogen atom that was clearly suspect and high isotropic temperature factors.

Figure 5.4 is a diagrammatical representation of the two identifiable structures. To simplify the drawing, only half of each structure has been represented. The structure with solid lines represents the 'good' structure, while the structure with dotted lines represents the 'lesser' structure. (The atoms of this structure are also designated with the letter d, for disorder).

It was decided to pursue initially the refinement of the 'good' structure only. This structure obtained showed that there could only be one coordinated water molecule per asymmetric unit i.e. the Ln^{3+} ion could be concluded to be bonded to the hexadentate edta ligand plus two water molecules. Perspective views of this 'good' structure appear in Figures 5.5 and 5.6.

As was the case in the four *Fdd2* structures, trouble was experienced in identifying the positions of the water molecules of crystallization. In fact, these water molecules were also clearly disordered. Taking into account the results of the microanalyses (see Table 2.1) and the thermogravimetric results,

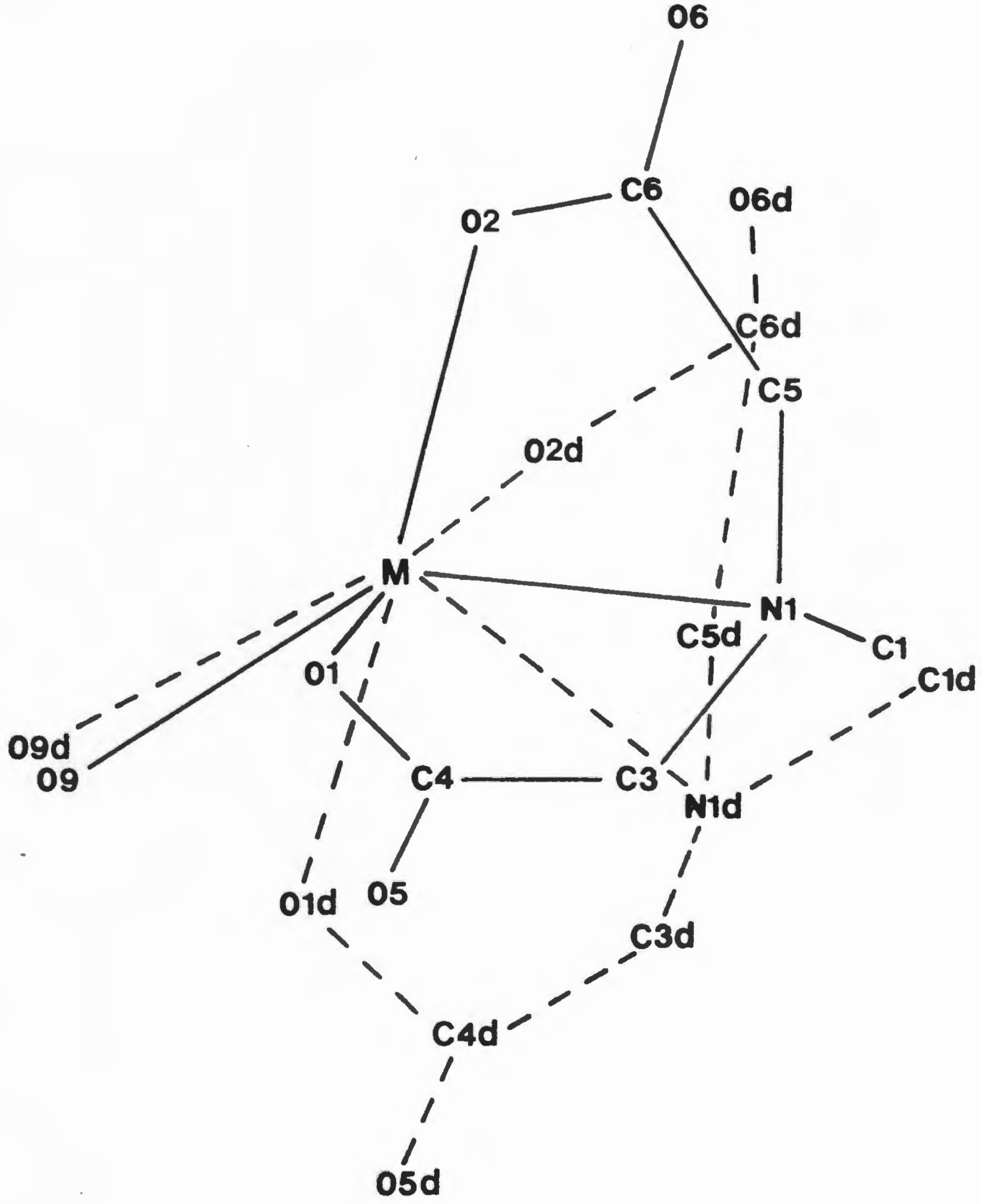

06
C6
02
06d
C6d
C5
02d
M
N1
C5d
C1
C1d
01
09d
09
C4
C3
N1d
01d
05
C3d
C4d
05d

FIGURE 5·4

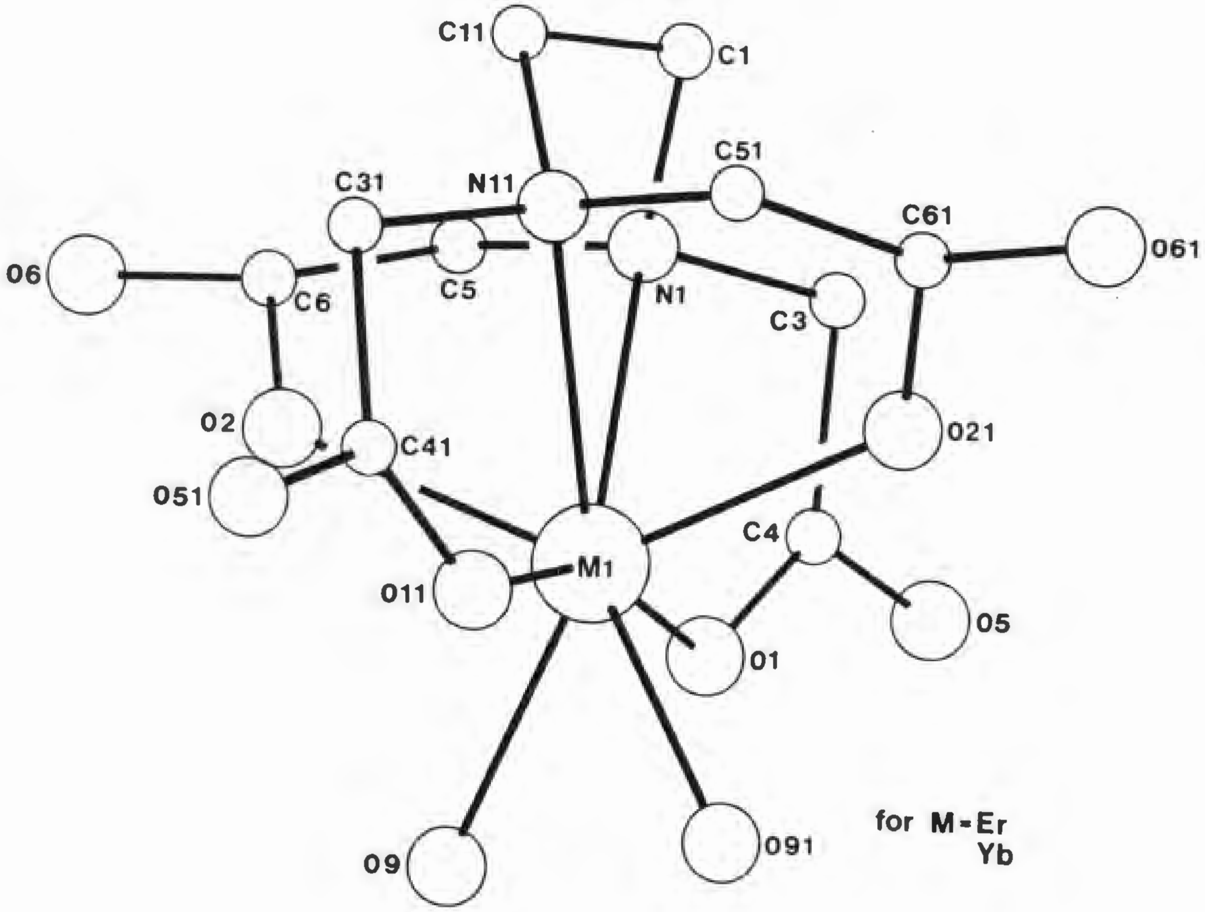

C11
C1
C51
C31
N11
C61
06
C6
C5
N1
061
C3
02
C41
021
051
C4
M1
011
05
01
09
091
for M=Er
Yb

FIGURE 5·5

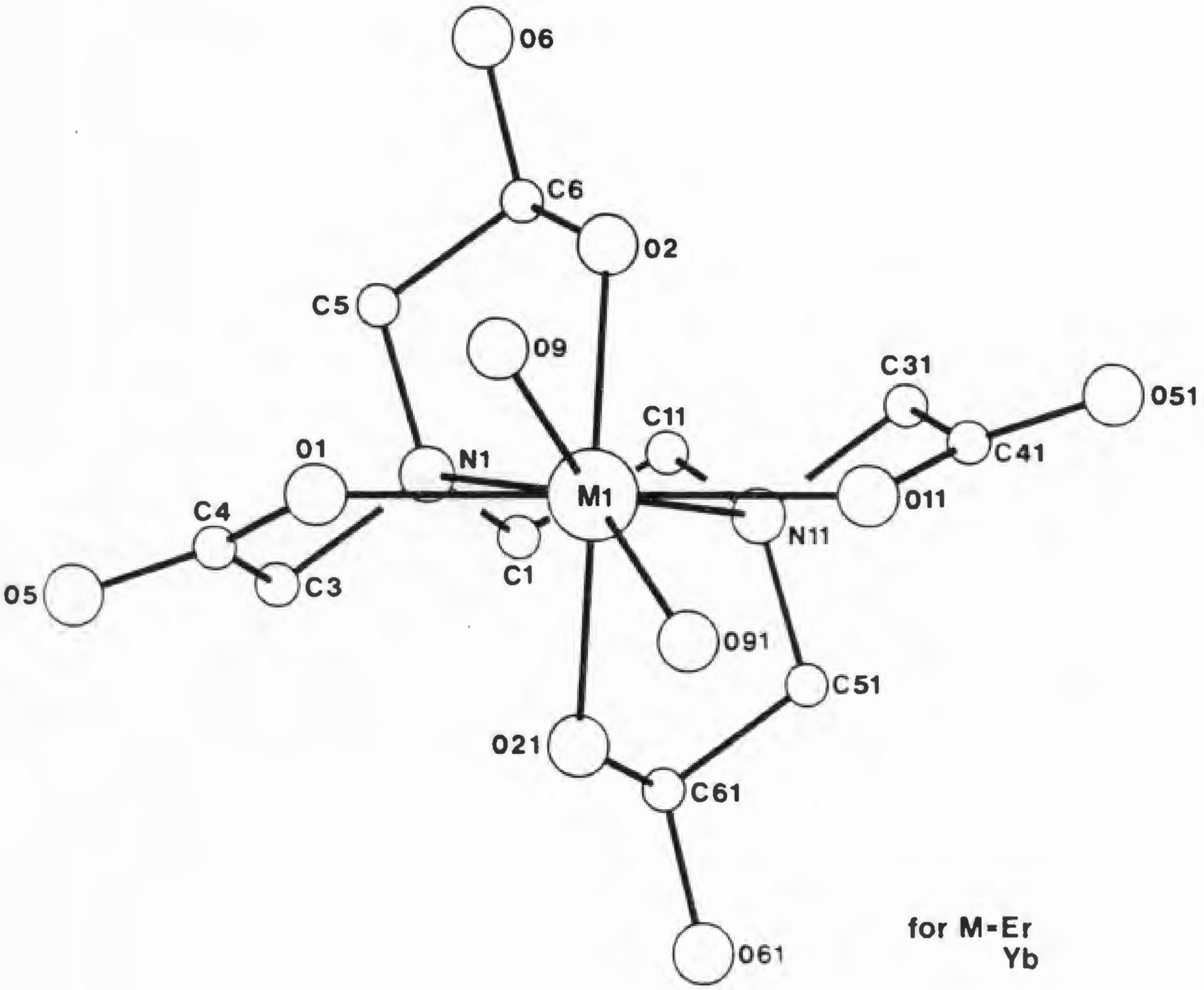

06
C6
02
C5
09
C31
051
C11
C41
01
N1
M1
011
C4
N11
05
C3
C1
091
C51
021
C61
061
for M=Er
Yb

FIGURE 5·6

it was assumed that there were in fact four molecules of water of crystallization i.e. two molecules per asymmetric unit.

A difference map was performed phased on all the atoms of the 'good' structure. Four peaks arose that were possible positions for the water molecules. All four positions were inserted into the program runstream as oxygen atoms and a further difference map was performed phased on all the atoms. The two oxygen atoms with the lower thermal parameters were concluded to be the water molecules of crystallization of the 'good' structure, while the other two were assumed to arise from the disorder and were thus assigned to the 'lesser' structure.

The final model of the 'good' structure, including the appropriate molecules of water of crystallization, and with the Ln^{3+} and K^+ ions anisotropic and the light atoms isotropic, yielded a final R value of 0.147 for the Erbium structure, and a final R value of 0.188 for the Ytterbium structure.

A final refinement of the combination of the two disordered structures, including the water molecules of crystallization, was also performed. The site occupational factors of the corresponding atoms were varied as described above, the Ln^{3+} and K^+ ions were assigned anisotropic thermal parameters while the thermal parameters of the light atoms of the 'good' structure were restricted to the values obtained in the final refinement of the 'good' structure. The thermal parameters of the 'lesser' structure are therefore not recorded in the Tables of final atomic coordinates. This final refinement yielded an R value of 0.131 for the Erbium structure and an R value of 0.176 for the Ytterbium structure. The latter structure also gave unsatisfactorily low temperature factors for the K^+ ion. However, at this point it was decided that the strongly disordered structures obviously gave some peculiar parameters which had doubtful physical meaning and it was decided that refine=

ment of the combination of the two structures could not be pursued further.

[This view, that is, that we had pursued the structure determinations as far as the data would allow us, was independently confirmed at our request by Dr Jerome Karle, President of the International Union of Crystallography, and Dr Isabella Karle, Head of Crystallography, Naval Research Laboratory, Washington D.C., who visited our laboratories in August 1982.]

Tables 5.5 and 5.6 are a list of the final atomic coordinates of both the 'good' structure and the 'lesser' structure (the atoms of the 'lesser' structure are designated by the letter d). The final thermal parameters obtained for the 'good' structure have also been recorded.

Intramolecular bond lengths and angles have been recorded for the 'good' structure only and appear in Tables 5.7 and 5.8 respectively.

5.6 DISCUSSION

It was then decided to insert these final atomic coordinates obtained into the space group $P2_1/n$, since this was the initial space group that was identified. A difference map was performed phased on all the atoms, but the structure failed to refine at all.

An attempt was then made to account for this phenomenon. The packing diagram of the 'good' structure in the [001] projection in the space group $C2/c$ is shown in Figure 5.7. As can be seen from the position of the Ln^{3+} ion, by virtue of its lying on the diad at $0,y,\frac{1}{4}$ (with $y = 0.09$), its position in the unit cell satisfies the equivalent positions of both $P2_1/n$ and $C2/c$.

TABLE 5.5 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) OF THE 'GOOD' STRUCTURE AND FRACTIONAL ATOMIC COORDINATES (Å x 10^4) OF THE 'LESSER' STRUCTURE OF $K^+[Er(edta)(H_2O)_2].4H_2O$. (E.S.D.'S IN PARENTHESES)

Atom	*x*	*y*	*z*	*U*
Er^{3+}	0000(0)	925(1)	2500(0)	*
K^+	0000(0)	3945(4)	2500(0)	*
O(1)	582(44)	820(15)	12(46)	99(11)
O(2)	-2419(68)	1265(24)	1615(72)	147(21)
O(5)	2069(54)	1010(18)	-1831(56)	126(15)
O(6)	-4031(52)	1683(17)	-97(53)	117(14)
O(9)	-1205(51)	208(17)	1460(51)	118(14)
N(1)	26(67)	1803(22)	939(68)	141(18)
C(1)	582(36)	2219(12)	1969(36)	40(7)
C(3)	1517(65)	1666(22)	-172(67)	94(16)
C(4)	1307(59)	1154(20)	-725(60)	81(13)
C(5)	-1452(78)	1740(26)	-118(80)	101(19)
C(6)	-2554(67)	1655(23)	785(68)	93(15)
W(1)	2547(56)	1692(18)	-3516(57)	127(15)
W(2)	3421(59)	220(20)	-4080(60)	143(17)
O(1)d	-863(38)	1246(13)	75(39)	
O(2)d	2300(57)	776(19)	1611(58)	
O(5)d	-2592(75)	1827(26)	1392(76)	
O(6)d	4427(72)	997(25)	422(75)	
O(9)d	-944(57)	219(19)	892(57)	
N(1)d	1606(49)	1741(17)	2347(50)	
C(1)d	520(113)	2222(37)	2047(116)	

TABLE 5.5 CONT/....

TABLE 5.5 CONTINUED

Atom	x	y	z	U
C(3)d	191(75)	1738(26)	798(75)	
C(4)d	-1569(148)	1775(51)	-365(152)	
C(5)d	2550(61)	1636(21)	1032(61)	
C(6)d	94(132)	1064(50)	1219(169)	
W(1)d	1608(108)	201(41)	3155(114)	
W(2)d	4026(119)	995(45)	346(107)	

*Anisotropic parameters:

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Er^{3+}	17(1)	19(1)	15(1)	0(0)	-1(1)	0(0)
K^+	29(5)	59(6)	30(5)	0(0)	3(4)	0(0)

TABLE 5.6 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å x 10^3) OF THE 'GOOD' STRUCTURE AND FRACTIONAL ATOMIC COORDINATES (Å x 10^4) OF THE 'LESSER' STRUCTURE OF $K^+[Yb(edta)(H_2O)_2].4H_2O$ (E.S.D.'S IN PARENTHESES)

Atom	*x*	*y*	*z*	*U*
Yb^{3+}	0000(0)	933(1)	2500(0)	*
K^+	0000(0)	4028(4)	2500(0)	≠
O(1)	641(71)	786(25)	35(73)	109(19)
O(2)	-2540(87)	1263(29)	1765(88)	131(25)
O(5)	2136(86)	944(31)	-1763(86)	138(24)
O(6)	-3951(79)	1676(26)	-60(80)	116(20)
O(9)	-1120(76)	216(25)	1148(75)	110(20)
N(1)	198(96)	1762(31)	949(94)	112(24)
C(1)	562(50)	2215(17)	1984(50)	34(9)
C(3)	1558(105)	1672(35)	13(107)	98(25)
C(4)	1363(92)	1108(31)	-661(93)	81(20)
C(5)	-1242(90)	1779(29)	-69(89)	75(19)
C(6)	-2540(113)	1656(39)	855(115)	104(27)
W(1)	2493(78)	1685(26)	-3668(80)	116(21)
W(2)	3397(92)	230(31)	-3884(92)	143(27)
O(1)d	-903(60)	1234(19)	89(60)	
O(2)d	2213(102)	820(36)	1601(105)	
O(5)d	-2515(103)	1819(34)	1415(104)	
O(6)d	-4793(143)	998(55)	581(159)	
O(9)d	-911(89)	238(31)	746(91)	
N(1)d	1571(77)	1746(26)	2299(79)	

TABLE 5.6 CONT/....

TABLE 5.6 CONTINUED

Atom	x	y	z	U
C(1)d	588(175)	2234(56)	2038(184)	
C(3)d	250(125)	1722(44)	819(125)	
C(4)d	-1880(231)	1689(78)	-541(217)	
C(5)d	2490(92)	1631(31)	1023(95)	
C(6)d	-332(162)	1106(70)	1289(247)	
W(1)d	1616(104)	211(37)	3261(122)	
W(2)d	4195(110)	983(40)	386(112)	

---

*Anisotropic parameters:

(Å x 10^3)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Yb^{3+}	23(1)	15(1)	23(1)	0(0)	6(1)	0(0)

≠unsatisfactorily low values

TABLE 5.7 BOND LENGTHS (Å) WITH E.S.D.'S IN PARENTHESES FOR $K^+[Ln(edta)(H_2O)_2].4H_2O$ FOR Ln = Er AND Yb.

	Ln = Er	Ln = Yb
O(1) - Ln	2.30(4)	2.32(6)
O(2) - Ln	2.34(6)	2.23(8)
O(9) - Ln	2.26(4)	2.34(6)
N(1) - Ln	2.64(6)	2.56(8)
N(1) - C(1)	1.44(6)	1.49(9)
N(1) - C(3)	1.76(18)	1.54(11)
N(1) - C(5)	1.50(8)	1.44(10)
C(1) - C(11)	1.46(6)	1.41(8)
C(3) - C(4)	1.41(7)	1.58(11)
C(5) - C(6)	1.34(8)	1.51(11)
C(4) - O(1)	1.29(6)	1.25(9)
C(4) - O(5)	1.30(6)	1.31(9)
C(6) - O(2)	1.24(7)	1.29(11)
C(6) - O(6)	1.43(7)	1.38(10)

TABLE 5.8 BOND ANGLES (^{o}) WITH E.S.D.'S IN PARENTHESES FOR $K^{+}[Ln(edta)(H_2O)_2]\cdot 4H_2O$ FOR Ln = Er AND Yb.

	Ln = Er	Ln = Yb
O(1) - Ln - O(2)	92(2)	97(3)
O(1) - Ln - O(9)	71(2)	63(2)
O(2) - Ln - O(9)	79(2)	82(3)
N(1) - Ln - O(1)	67(2)	67(2)
N(1) - Ln - O(2)	65(2)	69(3)
N(1) - Ln - O(9)	122(2)	117(2)
C(1) - N(1) - Ln	110(3)	111(5)
C(3) - N(1) - Ln	100(4)	105(5)
C(5) - N(1) - Ln	99(4)	104(5)
C(1) - N(1) - C(3)	106(5)	109(6)
C(1) - N(1) - C(5)	131(5)	117(7)
C(3) - N(1) - C(5)	107(6)	110(7)
C(4) - C(3) - N(1)	108(6)	107(7)
C(3) - C(4) - O(5)	118(5)	122(8)
C(3) - C(4) - O(1)	121(5)	118(7)
C(4) - O(1) - Ln	125(4)	123(6)
C(6) - C(5) - N(1)	107(6)	109(7)
C(5) - C(6) - O(6)	111(6)	111(8)
C(5) - C(6) - O(2)	117(6)	117(9)
C(6) - O(2) - Ln	121(5)	122(7)

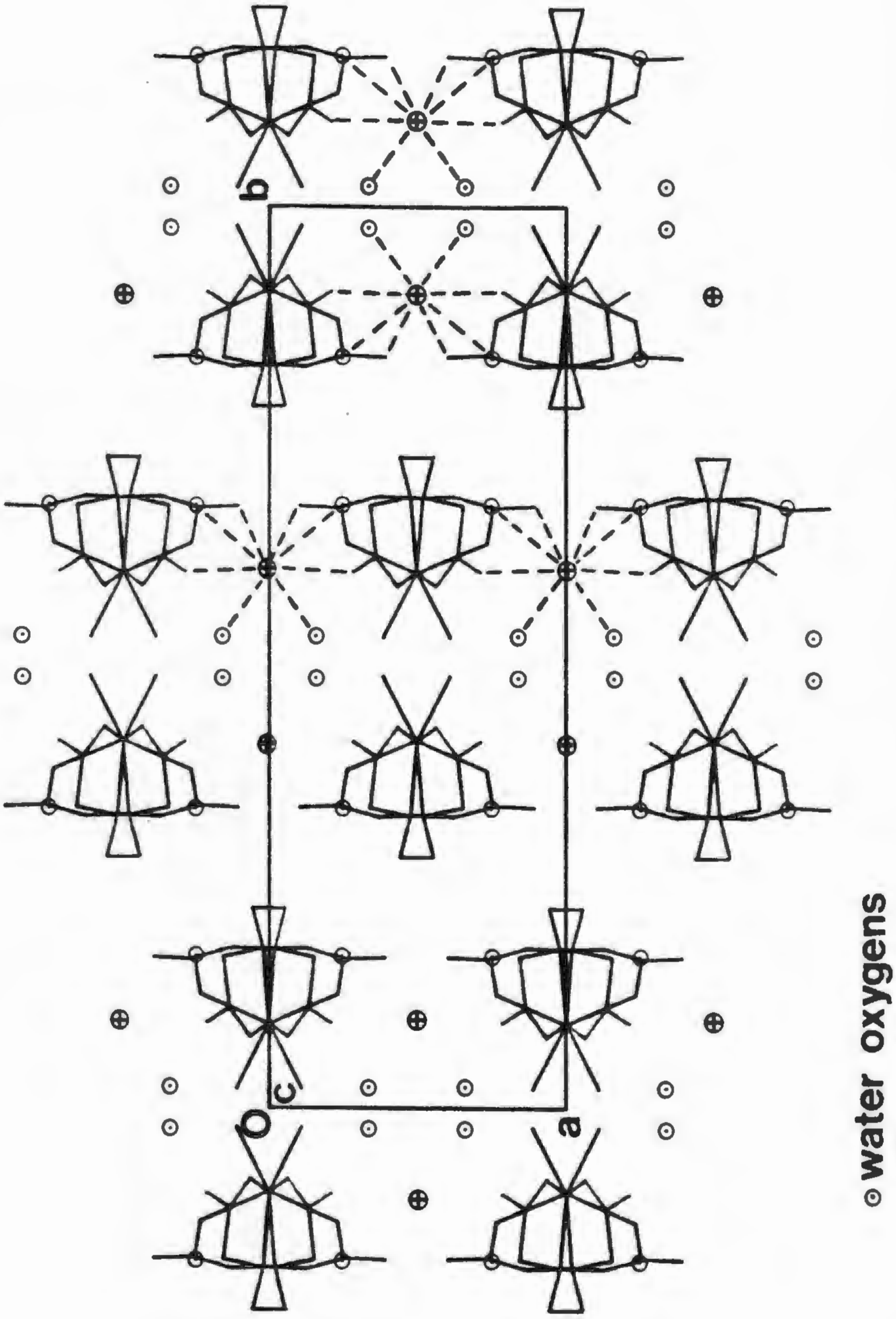


FIGURE 5·7

Namely:

$P2_1/n$	Ln^{3+} ion	$C2/c$ (on diad)
x,y,z	0,0.09,0.25	$0,y,\frac{1}{4}$
$-x,-y,-z$	0,0.91,0.75	$0,-y,\frac{3}{4}$
$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	0.5,0.41,0.75	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$
$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	0.5,0.59,0.25	$\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$

Since the K^+ ion also lies on the diad in the space group $C2/c$, the same applies in this case.

Namely:

$P2_1/n$	K^+ ion	$C2/c$ (on diad)
x,y,z	0,0.40,0.25	$0,y,\frac{1}{4}$
$-x,-y,-z$	0,0.60,0.75	$0,-y,\frac{3}{4}$
$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	0.5,0.10,0.75	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$
$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	0.5,0.90,0.25	$\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$

A large proportion of the scattering power naturally resides in the Ln^{3+} and K^+ ions. That is, for the Erbium structure, the scattering power of the Er^{3+} and K^+ ions is proportional to their respective scattering factors, f_j, which are approximately proportional to the respective Z_i values[58]. i.e. In this structure:

$$(Z_{Er^{3+}} + Z_{K^+})/\Sigma Z_{(\text{all light atoms})}$$

$$= (65 + 18)/206$$

$$= 0.04$$

This gives rise to the problem of pseudo-symmetry described previously i.e. that the molecules are arranged in a $P2_1/n$ pattern but a large concentration of the scattering comes from the heavy atoms arranged in a $C2/c$ pattern. However, although a reasonable explanation can be given for the space group problem, no feasible explanation can be made for the fact that these two edta structures are also disordered.

No Tables of Structure factors or Analyses of Variance have been included since the structures cannot be concluded to have been satisfactorily refined.

5.7 DESCRIPTION OF THE STRUCTURES

Although the compounds $K^+[Ln(edta)(H_2O)_2].4H_2O$ for Ln = Er and Yb were not satisfactorily refined, a certain amount of information could be obtained from the 'good' structures. The structures are isomorphous and were refined in the space group $C2/c$ with four molecule units. In each structure, the metal ion has a coordination number of eight. In these structures, edta again acts as a hexadentate ligand so that the structure around the central metal ion consists of a girdle of four oxygen atoms, one from each of the four acetate groups, and the two nitrogen atoms. In these structures the edta chelate reaches further around the central metal ion than it does in the four *Fdd2* structures, thus leaving space for only two water molecules which are also bonded to the central metal ion. Calculation of the displacement of the Ln^{3+} ion from the mean plane of the coordinated oxygen atoms for each structure shows that the trend (described in Chapter 4, part 4.7) whereby, as the ionic radii of the successive cations decrease, they are enveloped to a greater extent by the edta chelate, has reached the point in these two structures where rejection of one water molecule occurs with a resulting change in coordination number. These displacement values were again calculated using the program XANADU[65]. (The equations of these least squares mean planes and the atomic deviations therefrom are listed in Table 5.9). This displacement value in the Er^{3+} structure was calculated as 0.28Å and in the Yb^{3+} structure as 0.23Å. For the structure of $Cs[Yb(edta)(H_2O)_2].3H_2O$, the other 8-coordinate complex that has been identified[45], this distance was calculated as 0.18Å. Since the Er^{3+} and Yb^{3+} structures with the K^+ counter-ion have been unsatisfactorily refined, these distances can only be taken as being approximate, while the value for the structure of Yb^{3+} with the Cs^+ counter-ion can be taken as being more accurate. (For further discussion, see Chapter 6).

Since the two structures were not well refined, the recorded bond lengths and angles can be taken only as approximate values and thus do not provide much meaningful information. The bond lengths in the chelation framework of the Ytterbium structure should all be slightly shorter than those of the Erbium structure since the size of the Yb^{3+} ion is smaller than that of the Er^{3+} ion. However this trend is not conclusive from the poor results obtained (see Table 5.7). Nevertheless, the mean values of the $Ln - O_{coord.}$ bond lengths in the two structures are close to the sum of the crystal radii for Ln^{3+} and O^{2-}, which are 2.36Å for the Er^{3+} structure and 2.34Å for the Yb^{3+} structure[63].

5.8 PACKING PATTERNS AND CLOSE CONTACTS

Figure 5.7 depicts the [001] projection of the 'good' structures of the two isomorphous structures.

Again, due to the poor refinement of the two structures, not much meaningful information can be obtained about the packing.

TABLE 5.9 LEAST SQUARES PLANES

Equations of least squares planes are expressed in direct space as $pX + qY + rZ = S$. All the least squares planes are calculated through the respective O(1), O(2), O(3) and O(4) atoms.

(1) $K^+[Er(edta)(H_2O)_2].4H_2O$

$0.0X + 25.811Y + 0.0Z = 2.6907$

(2) $K^+[Yb(edta)(H_2O)_2].4H_2O$

$0.0X + 25.886Y + 0.0Z = 2.652$

(3) $Cs^+[Yb(edta)(H_2O)_2].3H_2O$

$12.3469X - 2.1026Y - 1.6710Z = 3.9944$

Atomic deviations expressed in Å ($\sigma < 0.02$Å)

	O(1)	O(2)	O(3)	O(4)	Ln^{3+}
(1)	-0.574	0.574	-0.574	0.574	-0.303
(2)	-0.617	0.617	-0.617	0.617	-0.234
(3)	-0.605	0.692	-0.646	0.559	-0.184

It would appear, however, that the environment of the Potassium ion is such that it is closely surrounded by eight oxygen atoms. Each K^+ ion is shared by two neighbouring molecules and is entrapped by O(5) and O(61) of one molecule and O(51) and O(6) of a neighbouring molecule. Close contacts also exist between the K^+ ion and two symmetry related W(1) molecules as well as between the K^+ ion and two symmetry related W(2) molecules.

The K^+...O distances for both compounds appear in Table 5.10. Although these values are inaccurate, they do lie within the range of values reported in the literature[81,82,83,84,85,86]. These values also agree with the fact that the sum of the ionic radii for potassium and oxygen is 2.73Å[63]. The K^+...O close contacts are depicted by broken lines in the right half of Figure 5.7.

No reasonable hydrogen bonding scheme can be predicted for these two structures due to the disorder in the structures. Hydrogen bonding must, of course, occur, but no estimation could be made thereof.

TABLE 5.10 $K^+ ... O$ CLOSE CONTACTS (Å) FOR $K^+[Ln(edta)(H_2O)_2].4H_2O$ FOR Ln = Er AND Yb. (E.S.D.'S IN PARENTHESES)

Symmetry code:

(i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$

(ii) $\frac{1}{2}-x, \frac{1}{2}-y, z$

	Ln = Er	Ln = Yb
$K^+ ... O(5^{i})$	2.72(14)	2.66(11)
$K^+ ... O(6^{ii})$	2.70(16)	2.86(18)
$K^+ ... W(1^{ii})$	2.77(15)	2.94(21)
$K^+ ... W(2^{ii})$	2.83(19)	2.58(13)

CHAPTER 6

CHAPTER 6

GENERAL DISCUSSION

From the results obtained in this work, it can be seen that the transition from the nine-coordinate $[Ln(H_2O)_3Y]^-$ crystalline complex to the eight-coordinate $[Ln(H_2O)_2Y]^-$ crystalline complex occurs at Erbium. i.e. All the lanthanide metals from Lanthanum to Holmium form 9-coordinate complexes with the edta chelate, and thereafter from Erbium to Lutetium 8-coordinate complexes are formed.

As was stated previously, in all these structures edta acts as a hexadentate ligand. Along the series of the lanthanide ions, as the ionic radii of the successive cations decrease, they are enveloped to a greater extent by the edta chelate, until the point is reached in the case of the Erbium structure where rejection of one water molecule occurs with a resulting change in the coordination number.

From the La^{3+} structure to the Ho^{3+} structure, it can be seen that the $Ln - 4O_{coord.}$ mean plane displacements decrease along the series by an amount comparable to the successive decrease in the crystal radii of the cations (see Chapter 4, part 4.7). For example, the difference in the ionic radii of the Pr^{3+} and Ho^{3+} ions is 0.12Å, while the difference in the $Ln - 4O_{coord.}$ plane distances in their respective structures is 0.10Å.

Now since the change in the ionic radii from Ho^{3+} to Lu^{3+} is even more gradual than it is from La^{3+} to Ho^{3+}, it is surprising that an abrupt change in the $Ln - 4O_{coord.}$ mean plane distance occurs in the Er^{3+} structure corresponding to a change in the coordination number. In fact the difference in the ionic radii of the Ho^{3+} and Yb^{3+} ions is 0.03Å while the difference in the Ln - $4O_{coord.}$ mean plane distances in their respective structures is 0.30Å (using the more reliable value obtained for the Yb^{3+} structure with the Cs^+ counter-ion, see Chapter 5, part 5.7).

It therefore would seem to be an over-simplification to assume that the abrupt change in coordination number in the crystalline Er^{3+} structure is due primarily to the cation size. Other factors, such as the 4f orbital population (described in Chapter 1, part 1.6), almost certainly play a role.

An interesting extension to this work would be in the study of the structure of the Yttrium-edta complex. Since the Y^{3+} and Ho^{3+} ions have almost identical ionic radii, with the Y^{3+} ion having no 4f electrons while the Ho^{3+} ion has ten 4f electrons, a comparison of the two structures would give good information as to whether it is the cation size or the 4f orbital population that plays the dominant role in determining the coordination number. (As was described in Chapter 1, part 1.6, the stability constant of the Ho^{3+} complex is higher than that of the Y^{3+} complex, inferring that the 4f orbital population must certainly play a role in determining the structure).

It would seem that the best explanation of the trends of the thermodynamic data and stability constants of these lanthanide-edta complexes (see part 1.6), is that the dominant species in solution of all these complexes is 9-coordinate (as concluded by Alsaadi *et al.*[55]), with the 8-coordinate species becoming increasingly important in the later part of the series, and with the transition from the sole existence of 9-coordinate complexes in solution to the existence of 9- and 8-coordinate complexes in solution occurring at Gadolinium.

It was also possible to make observations regarding the effect of the counter-ion on the structures of these complexes. This was done by comparison of the two structures of Yb^{3+}. It would appear that while the counter-ion has an effect on the space group and the unit cell parameters, it has a negligible effect on the structure of the anion. i.e. The two Yb^{3+} structures, one with Cs^+ as the counter-ion and the other with K^+ as the counter-ion, crystallize in different space groups with different unit cell parameters, but are both 8-coordinate structures and the general shape of the anions is the same.

APPENDIX A

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	756	799	6	8	0	339	326	18	14	0	141	131	16	22	0	164	161	12	32	0	287	274
8	0	0	376	303	8	8	0	135	169	20	14	0	215	212	18	22	0	244	247	4	34	0	355	336
12	0	0	520	471	10	8	0	351	395	0	16	0	727	706	0	24	0	180	151	8	34	0	363	351
16	0	0	394	360	12	8	0	73	65	2	16	0	246	211	2	24	0	391	395	10	34	0	41	27
20	0	0	63	67	14	8	0	484	475	4	16	0	175	171	4	24	0	271	267	0	36	0	400	364
4	2	0	552	662	16	8	0	37	23	6	16	0	114	103	8	24	0	62	55	2	36	0	185	183
6	2	0	483	500	18	8	0	209	180	8	16	0	247	233	10	24	0	391	409	4	36	0	191	179
8	2	0	439	430	20	8	0	41	18	10	16	0	134	136	12	24	0	154	144	6	36	0	102	95
10	2	0	395	392	2	10	0	385	344	12	16	0	463	474	14	24	0	360	346	8	36	0	75	70
12	2	0	50	38	4	10	0	188	187	14	16	0	77	75	16	24	0	65	64	2	38	0	58	72
16	2	0	431	386	6	10	0	763	863	16	16	0	300	290	2	26	0	204	204	4	38	0	214	216
18	2	0	130	105	8	10	0	285	272	2	18	0	140	114	6	26	0	510	511	6	38	0	171	179
20	2	0	320	278	10	10	0	391	434	4	18	0	357	354	8	26	0	42	57	3	1	1	420	380
2	4	0	655	769	12	10	0	126	123	8	18	0	336	332	10	26	0	214	213	5	1	1	491	480
4	4	0	249	281	14	10	0	52	39	10	18	0	136	145	14	26	0	77	69	7	1	1	314	300
6	4	0	181	186	16	10	0	44	45	12	18	0	134	129	16	26	0	40	34	9	1	1	576	511
8	4	0	302	261	18	10	0	342	318	16	18	0	300	308	0	28	0	81	57	11	1	1	282	245
10	4	0	139	165	0	12	0	823	753	18	18	0	67	59	2	28	0	350	344	13	1	1	270	257
12	4	0	241	218	2	12	0	325	367	0	20	0	281	264	4	28	0	92	101	15	1	1	317	281
14	4	0	407	355	4	12	0	217	200	2	20	0	104	80	10	28	0	317	310	17	1	1	203	197
16	4	0	178	167	8	12	0	78	82	4	20	0	425	431	12	28	0	109	108	19	1	1	247	208
18	4	0	213	185	10	12	0	468	498	6	20	0	84	86	14	28	0	294	274	21	1	1	161	134
2	6	0	188	203	12	12	0	342	360	8	20	0	127	139	2	30	0	82	84	3	3	1	70	85
6	6	0	585	622	14	12	0	300	304	10	20	0	127	139	4	30	0	218	221	5	3	1	474	529
8	6	0	92	89	16	12	0	222	229	12	20	0	417	412	6	30	0	452	445	7	3	1	465	478
10	6	0	411	424	18	12	0	139	131	14	20	0	168	170	8	30	0	233	223	9	3	1	286	312
12	6	0	32	18	2	14	0	60	51	16	20	0	262	275	10	30	0	268	268	11	3	1	395	414
14	6	0	81	65	4	14	0	562	579	18	20	0	53	45	12	30	0	115	117	13	3	1	255	229
16	6	0	260	245	6	14	0	502	512	2	22	0	165	177	14	30	0	50	53	15	3	1	249	228
18	6	0	370	323	8	14	0	453	480	4	22	0	194	205	0	32	0	287	265	17	3	1	340	294
20	6	0	282	259	10	14	0	128	138	6	22	0	403	416	2	32	0	45	34	19	3	1	122	95
0	8	0	150	161	12	14	0	142	143	8	22	0	243	247	4	32	0	314	323	21	3	1	104	81
2	8	0	488	531	14	14	0	47	11	10	22	0	247	257	8	32	0	86	76	1	5	1	393	412
4	8	0	461	513	16	14	0	189	195	12	22	0	58	52	10	32	0	124	125	3	5	1	260	278

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC
5	5	1	108	115
7	5	1	224	227
9	5	1	432	445
11	5	1	133	151
13	5	1	256	280
15	5	1	323	340
17	5	1	78	86
19	5	1	252	250
21	5	1	188	156
1	7	1	373	383
3	7	1	160	169
5	7	1	404	390
7	7	1	453	502
9	7	1	404	436
11	7	1	235	249
13	7	1	200	226
15	7	1	122	128
17	7	1	211	237
19	7	1	152	160
21	7	1	81	98
1	9	1	95	134
3	9	1	605	619
5	9	1	385	408
7	9	1	343	323
9	9	1	486	530
11	9	1	262	274
13	9	1	253	287
15	9	1	195	206
17	9	1	236	256
19	9	1	149	160
21	9	1	124	128
1	11	1	703	710
3	11	1	524	525
5	11	1	226	245
7	11	1	486	501
9	11	1	410	421
11	11	1	133	156
13	11	1	266	281
15	11	1	195	211
19	11	1	203	216
21	11	1	173	177
1	13	1	521	503
3	13	1	151	162
5	13	1	315	337
7	13	1	287	305
9	13	1	73	75
11	13	1	423	454
13	13	1	214	225
15	13	1	75	77
17	13	1	278	296
19	13	1	89	96
1	15	1	458	429
3	15	1	451	443
5	15	1	249	256
7	15	1	302	302
9	15	1	369	375
11	15	1	91	82
13	15	1	245	267
15	15	1	213	224
17	15	1	104	101
19	15	1	116	117
1	17	1	305	286
3	17	1	387	375
5	17	1	274	265
7	17	1	296	284
9	17	1	143	129
11	17	1	348	353
13	17	1	101	86
15	17	1	166	179
17	17	1	183	184
19	17	1	146	149
1	19	1	422	429
3	19	1	348	345
5	19	1	271	240
7	19	1	330	338
9	19	1	195	213
11	19	1	230	230
13	19	1	195	200
15	19	1	153	157
17	19	1	193	192
19	19	1	131	136
1	21	1	209	199
3	21	1	547	558
5	21	1	41	28
7	21	1	252	256
9	21	1	232	229
11	21	1	73	70
13	21	1	210	228
15	21	1	285	297
17	21	1	66	55
1	23	1	400	381
3	23	1	205	202
5	23	1	356	352
7	23	1	150	140
9	23	1	108	114
11	23	1	236	236
13	23	1	210	220
15	23	1	122	116
17	23	1	196	203
3	25	1	321	325
5	25	1	268	308
7	25	1	169	170
9	25	1	160	158
11	25	1	199	201
13	25	1	89	90
15	25	1	186	181
3	27	1	284	278
5	27	1	330	350
7	27	1	138	132
9	27	1	231	229
11	27	1	176	181
13	27	1	158	155
15	27	1	215	224
1	29	1	239	246
5	29	1	296	284
7	29	1	196	190
11	29	1	225	232
13	29	1	108	106
1	31	1	96	100
3	31	1	296	304
5	31	1	111	117
7	31	1	169	174
9	31	1	242	242
11	31	1	71	72
13	31	1	213	210
1	33	1	217	207
3	33	1	202	198
5	33	1	264	251
7	33	1	195	195
9	33	1	172	151
11	33	1	193	195
1	35	1	168	162
3	35	1	100	119
5	35	1	210	209
7	35	1	162	158
9	35	1	153	163
1	37	1	137	131
3	37	1	233	227
5	37	1	73	93
7	37	1	145	134
1	39	1	168	167
2	0	2	418	391
6	0	2	696	719
10	0	2	504	444
14	0	2	193	225
18	0	2	423	388
0	2	2	361	317
2	2	2	561	540
4	2	2	248	249
6	2	2	51	62
8	2	2	286	289
10	2	2	561	558
12	2	2	191	209
14	2	2	492	463
16	2	2	72	70
18	2	2	191	163
2	4	2	166	132
4	4	2	392	408
6	4	2	509	543
8	4	2	567	596
10	4	2	377	405
12	4	2	134	143
16	4	2	196	196
18	4	2	270	240
20	4	2	215	215
0	6	2	540	555
2	6	2	429	457
4	6	2	343	347
6	6	2	166	177
8	6	2	335	335

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	6	2	87	78	0	14	2	224	242	18	20	2	199	197	4	30	2	240	225	9	3	3	171	184
12	6	2	399	420	2	14	2	652	690	0	22	2	456	450	8	30	2	111	120	11	3	3	339	331
14	6	2	271	283	4	14	2	192	197	2	22	2	376	356	10	30	2	165	169	13	3	3	251	232
16	6	2	278	291	6	14	2	196	200	4	22	2	365	353	12	30	2	209	216	15	3	3	115	99
18	6	2	123	126	8	14	2	134	124	6	22	2	54	33	2	32	2	196	207	17	3	3	234	221
2	8	2	386	353	10	14	2	282	296	8	22	2	73	72	4	32	2	118	122	19	3	3	143	128
4	8	2	531	523	12	14	2	194	191	10	22	2	173	189	6	32	2	308	293	21	3	3	107	91
6	8	2	127	124	14	14	2	283	309	12	22	2	241	229	8	32	2	129	133	1	5	3	180	191
8	8	2	738	843	16	14	2	189	200	14	22	2	225	237	10	32	2	196	185	3	5	3	549	545
10	8	2	76	77	18	14	2	120	129	16	22	2	230	249	12	32	2	63	54	5	5	3	139	122
12	8	2	149	153	2	16	2	334	320	2	24	2	167	172	0	34	2	63	85	7	5	3	303	323
14	8	2	45	44	4	16	2	144	134	4	24	2	385	381	2	34	2	320	308	9	5	3	391	372
16	8	2	182	183	6	16	2	475	496	6	24	2	115	105	10	34	2	202	217	11	5	3	133	133
18	8	2	44	39	8	16	2	75	78	8	24	2	415	434	4	36	2	75	77	13	5	3	234	224
20	8	2	266	290	10	16	2	321	339	10	24	2	70	56	6	36	2	253	247	15	5	3	281	298
0	10	2	797	829	12	16	2	175	187	12	24	2	133	138	8	36	2	67	58	17	5	3	104	94
2	10	2	353	336	14	16	2	162	179	14	24	2	52	62	0	38	2	120	116	19	5	3	222	225
4	10	2	418	475	18	16	2	234	252	16	24	2	145	144	2	38	2	205	221	21	5	3	169	164
6	10	2	303	315	0	18	2	224	236	0	26	2	446	407	4	38	2	75	86	1	7	3	623	596
8	10	2	242	255	2	18	2	744	756	2	26	2	90	98	1	1	3	578	596	3	7	3	500	469
12	10	2	453	476	4	18	2	75	87	4	26	2	301	292	3	1	3	442	437	5	7	3	556	569
14	10	2	118	115	6	18	2	162	173	8	26	2	175	180	5	1	3	255	260	7	7	3	206	203
16	10	2	289	324	8	18	2	62	56	10	26	2	47	50	7	1	3	215	209	9	7	3	202	207
18	10	2	67	74	10	18	2	240	230	12	26	2	315	319	9	1	3	534	527	11	7	3	279	307
2	12	2	111	90	14	18	2	385	404	16	26	2	235	246	11	1	3	234	216	13	7	3	156	155
4	12	2	506	512	18	18	2	102	109	2	28	2	161	171	13	1	3	286	281	15	7	3	162	168
6	12	2	392	415	2	20	2	376	392	4	28	2	377	367	15	1	3	189	169	17	7	3	307	307
8	12	2	459	498	4	20	2	246	240	6	28	2	157	166	17	1	3	148	139	19	7	3	188	179
10	12	2	284	307	6	20	2	432	444	8	28	2	281	268	19	1	3	174	143	21	7	3	132	135
12	12	2	107	115	8	20	2	292	294	10	28	2	119	118	21	1	3	183	172	1	9	3	318	327
14	12	2	95	102	10	20	2	308	323	12	28	2	70	81	1	3	3	408	404	3	9	3	492	479
16	12	2	138	140	12	20	2	102	120	14	28	2	51	47	3	3	3	169	150	5	9	3	387	376
18	12	2	221	224	14	20	2	60	53	0	30	2	210	190	5	3	3	518	487	7	9	3	364	368
20	12	2	220	244	16	20	2	115	103	2	30	2	261	265	7	3	3	292	290	9	9	3	146	163

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
11	9	3	254	255	19	15	3	157	174	11	23	3	353	348	3	33	3	136	131	10	4	4	297	290
13	9	3	212	210	1	17	3	283	260	13	23	3	149	140	5	33	3	156	168	12	4	4	451	470
15	9	3	215	212	3	17	3	304	273	15	23	3	149	154	7	33	3	131	132	14	4	4	187	180
17	9	3	254	259	5	17	3	341	325	17	23	3	177	190	9	33	3	75	93	16	4	4	300	298
19	9	3	161	163	7	17	3	219	236	1	25	3	167	164	11	33	3	172	174	18	4	4	144	135
1	11	3	532	501	9	17	3	399	412	3	25	3	311	318	1	35	3	156	163	20	4	4	58	56
3	11	3	515	511	11	17	3	156	165	5	25	3	283	276	3	35	3	201	202	2	6	4	50	41
5	11	3	302	292	13	17	3	294	306	7	25	3	252	268	5	35	3	154	155	4	6	4	224	198
7	11	3	278	283	15	17	3	188	196	9	25	3	304	297	7	35	3	122	130	6	6	4	746	729
9	11	3	351	362	17	17	3	190	201	11	25	3	162	153	9	35	3	116	113	8	6	4	260	265
11	11	3	109	127	19	17	3	152	149	13	25	3	191	191	1	37	3	173	163	10	6	4	304	298
13	11	3	82	80	1	19	3	143	133	15	25	3	145	146	3	37	3	208	214	12	6	4	116	106
15	11	3	258	276	3	19	3	207	194	1	27	3	171	181	5	37	3	115	109	14	6	4	80	82
17	11	3	147	156	5	19	3	258	237	3	27	3	307	286	0	0	4	655	675	16	6	4	117	106
19	11	3	197	209	7	19	3	385	389	5	27	3	166	165	4	0	4	55	53	18	6	4	332	324
1	13	3	572	526	9	19	3	123	114	7	27	3	248	255	8	0	4	378	369	20	6	4	86	83
3	13	3	286	259	11	19	3	335	346	9	27	3	246	247	12	0	4	529	515	0	8	4	376	312
5	13	3	540	542	13	19	3	184	196	11	27	3	157	160	16	0	4	229	219	2	8	4	571	560
7	13	3	404	416	15	19	3	196	200	13	27	3	135	134	20	0	4	65	65	4	8	4	380	358
9	13	3	120	134	17	19	3	232	233	15	27	3	162	165	2	2	4	122	118	6	8	4	286	289
11	13	3	324	339	1	21	3	74	98	1	29	3	263	229	4	2	4	772	754	8	8	4	207	202
13	13	3	308	316	3	21	3	348	310	3	29	3	44	67	6	2	4	371	361	10	8	4	325	328
15	13	3	118	129	5	21	3	160	154	5	29	3	297	293	8	2	4	720	707	12	8	4	145	149
17	13	3	181	179	7	21	3	227	243	7	29	3	277	282	10	2	4	130	115	14	8	4	389	393
19	13	3	100	103	9	21	3	386	388	9	29	3	87	80	12	2	4	297	301	16	8	4	126	113
1	15	3	389	363	11	21	3	117	132	11	29	3	226	225	14	2	4	63	51	18	8	4	197	212
3	15	3	519	498	13	21	3	247	248	13	29	3	125	128	16	2	4	155	150	20	8	4	43	40
5	15	3	214	207	15	21	3	221	223	1	31	3	112	107	18	2	4	92	82	2	10	4	193	187
7	15	3	274	287	17	21	3	54	23	3	31	3	292	298	20	2	4	243	231	4	10	4	305	270
9	15	3	363	380	1	23	3	339	317	5	31	3	115	105	0	4	4	565	546	6	10	4	572	601
11	15	3	241	253	3	23	3	104	99	7	31	3	124	137	2	4	4	687	609	8	10	4	72	58
13	15	3	188	201	5	23	3	324	324	9	31	3	203	194	4	4	4	265	246	10	10	4	290	304
15	15	3	261	263	7	23	3	358	360	11	31	3	66	77	6	4	4	92	70	12	10	4	54	56
17	15	3	109	98	9	23	3	138	140	1	33	3	149	149	8	4	4	329	328	14	10	4	85	95

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
16	10	4	90	90	8	18	4	463	469	14	26	4	52	61	19	1	5	156	149	7	9	5	233	229
18	10	4	304	315	10	18	4	105	106	0	28	4	308	298	1	3	5	311	303	9	9	5	203	207
20	10	4	96	93	12	18	4	183	197	2	28	4	418	412	3	3	5	226	186	11	9	5	220	237
0	12	4	675	642	16	18	4	217	227	4	28	4	138	129	5	3	5	402	402	13	9	5	149	158
2	12	4	588	569	0	20	4	360	361	6	28	4	167	163	7	3	5	494	486	15	9	5	188	188
4	12	4	285	294	2	20	4	342	329	8	28	4	59	59	9	3	5	166	163	17	9	5	226	220
6	12	4	113	119	4	20	4	150	157	10	28	4	224	218	11	3	5	366	356	19	9	5	103	111
8	12	4	146	154	6	20	4	64	63	12	28	4	139	143	13	3	5	317	296	1	11	5	210	195
10	12	4	341	337	10	20	4	180	187	14	28	4	254	255	15	3	5	142	125	3	11	5	339	320
12	12	4	180	185	12	20	4	375	379	2	30	4	133	139	17	3	5	274	253	5	11	5	119	95
14	12	4	301	297	14	20	4	202	212	4	30	4	234	214	19	3	5	110	92	7	11	5	176	189
16	12	4	164	157	16	20	4	219	227	6	30	4	233	217	1	5	5	587	542	9	11	5	319	321
18	12	4	112	111	2	22	4	86	90	8	30	4	260	258	3	5	5	668	641	11	11	5	194	179
2	14	4	217	207	4	22	4	308	294	10	30	4	99	93	5	5	5	539	511	13	11	5	171	160
4	14	4	417	414	6	22	4	329	330	0	32	4	383	366	7	5	5	395	391	15	11	5	276	267
6	14	4	328	344	8	22	4	284	283	2	32	4	215	207	9	5	5	431	428	17	11	5	125	126
8	14	4	444	462	10	22	4	204	210	4	32	4	229	220	11	5	5	44	32	19	11	5	183	191
10	14	4	133	150	12	22	4	131	127	6	32	4	81	90	13	5	5	357	360	1	13	5	493	470
12	14	4	63	59	14	22	4	109	118	10	32	4	77	73	15	5	5	278	263	3	13	5	65	68
14	14	4	104	105	16	22	4	93	99	2	34	4	45	37	17	5	5	51	46	5	13	5	385	381
16	14	4	211	206	0	24	4	266	231	4	34	4	239	238	19	5	5	186	184	7	13	5	315	308
18	14	4	169	169	2	24	4	356	358	6	34	4	41	43	1	7	5	453	431	9	13	5	109	98
0	16	4	697	688	4	24	4	40	42	8	34	4	241	240	3	7	5	213	212	11	13	5	236	240
2	16	4	211	205	6	24	4	69	68	0	36	4	349	339	5	7	5	297	309	13	13	5	119	123
4	16	4	308	329	8	24	4	50	54	4	36	4	166	173	7	7	5	319	341	15	13	5	104	87
6	16	4	112	114	10	24	4	258	260	1	1	5	236	236	9	7	5	108	104	17	13	5	209	205
8	16	4	113	125	12	24	4	161	165	3	1	5	365	395	11	7	5	317	321	19	13	5	158	158
10	16	4	70	74	14	24	4	273	269	5	1	5	240	224	13	7	5	228	235	1	15	5	160	162
12	16	4	415	435	2	26	4	256	262	7	1	5	354	334	15	7	5	201	188	3	15	5	462	432
14	16	4	147	149	4	26	4	81	71	9	1	5	372	361	17	7	5	254	263	5	15	5	102	102
16	16	4	266	278	6	26	4	466	471	11	1	5	306	303	19	7	5	133	146	7	15	5	238	222
2	18	4	75	85	8	26	4	43	39	13	1	5	266	245	1	9	5	412	387	9	15	5	375	378
4	18	4	387	387	10	26	4	294	296	15	1	5	306	278	3	9	5	296	263	11	15	5	105	106
6	18	4	167	153	12	26	4	78	82	17	1	5	188	174	5	9	5	476	463	13	15	5	211	216

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
15	15	5	258	257	13	23	5	154	162	5	35	5	153	153	2	8	6	108	104	16	14	6	145	147
17	15	5	60	68	1	25	5	180	182	2	0	6	331	323	4	8	6	435	445	18	14	6	59	63
1	17	5	438	437	3	25	5	297	289	6	0	6	437	399	6	8	6	42	46	2	16	6	359	354
3	17	5	328	318	5	25	5	94	94	10	0	6	448	439	8	8	6	480	491	4	16	6	150	146
5	17	5	369	381	7	25	5	239	246	14	0	6	258	221	10	8	6	146	142	6	16	6	539	514
7	17	5	224	228	9	25	5	268	261	18	0	6	316	279	12	8	6	217	222	10	16	6	345	369
9	17	5	237	227	11	25	5	101	85	0	2	6	412	394	16	8	6	291	276	12	16	6	55	66
11	17	5	206	204	13	25	5	176	184	2	2	6	817	797	18	8	6	55	66	0	18	6	111	104
13	17	5	245	252	1	27	5	162	155	4	2	6	193	191	0	10	6	536	534	2	18	6	342	336
15	17	5	160	160	3	27	5	320	315	6	2	6	108	98	2	10	6	96	100	6	18	6	67	38
17	17	5	140	147	5	27	5	172	176	8	2	6	82	70	4	10	6	312	335	8	18	6	87	88
1	19	5	299	278	7	27	5	194	197	10	2	6	110	119	6	10	6	135	140	10	18	6	295	311
3	19	5	90	83	9	27	5	219	219	12	2	6	221	197	8	10	6	157	146	12	18	6	105	92
5	19	5	304	293	11	27	5	99	103	14	2	6	452	443	10	10	6	65	67	14	18	6	315	339
7	19	5	228	234	13	27	5	143	148	16	2	6	103	98	12	10	6	294	286	2	20	6	192	199
9	19	5	136	131	1	29	5	312	299	18	2	6	116	110	14	10	6	277	268	4	20	6	234	249
11	19	5	307	323	3	29	5	100	78	2	4	6	221	228	16	10	6	253	246	6	20	6	341	327
13	19	5	215	223	5	29	5	268	256	4	4	6	339	349	2	12	6	181	196	8	20	6	213	210
15	19	5	85	101	7	29	5	220	231	6	4	6	408	387	4	12	6	384	367	10	20	6	202	210
17	19	5	182	183	9	29	5	87	81	8	4	6	319	291	6	12	6	269	250	12	20	6	130	134
1	21	5	237	246	11	29	5	205	210	10	4	6	302	288	8	12	6	357	365	16	20	6	71	80
3	21	5	351	341	1	31	5	204	190	12	4	6	70	77	10	12	6	252	244	0	22	6	219	214
5	21	5	196	201	3	31	5	311	299	14	4	6	112	103	12	12	6	40	57	2	22	6	224	233
7	21	5	222	213	5	31	5	62	69	16	4	6	210	203	14	12	6	81	83	4	22	6	148	163
9	21	5	223	212	7	31	5	224	229	18	4	6	253	248	16	12	6	144	152	6	22	6	37	47
11	21	5	54	62	9	31	5	171	169	0	6	6	755	685	18	12	6	107	104	8	22	6	147	142
13	21	5	151	159	11	31	5	100	95	2	6	6	355	373	0	14	6	407	373	10	22	6	282	281
15	21	5	176	178	1	33	5	202	200	4	6	6	416	403	2	14	6	324	321	12	22	6	243	244
1	23	5	264	255	3	33	5	94	99	6	6	6	191	194	4	14	6	356	358	14	22	6	192	193
3	23	5	146	130	5	33	5	162	152	8	6	6	110	126	6	14	6	128	123	2	24	6	133	119
5	23	5	241	238	7	33	5	165	170	10	6	6	141	128	8	14	6	118	113	4	24	6	331	331
7	23	5	236	234	9	33	5	109	104	12	6	6	411	392	10	14	6	282	288	6	24	6	166	160
9	23	5	56	62	1	35	5	204	205	14	6	6	120	135	12	14	6	204	208	8	24	6	316	330
11	23	5	287	289	3	35	5	169	167	16	6	6	331	329	14	14	6	353	349	10	24	6	69	64

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
12	24	6	82	89	5	3	7	366	349	3	11	7	414	373	3	19	7	128	120	3	29	7	47	50
0	26	6	425	393	7	3	7	334	336	5	11	7	200	194	5	19	7	288	294	5	29	7	226	219
2	26	6	44	51	9	3	7	102	90	7	11	7	167	164	7	19	7	136	141	7	29	7	169	169
4	26	6	220	221	11	3	7	312	322	9	11	7	365	367	9	19	7	162	152	9	29	7	60	75
6	26	6	52	49	13	3	7	214	205	11	11	7	219	227	11	19	7	234	235	1	31	7	107	114
8	26	6	177	181	15	3	7	107	106	13	11	7	131	146	13	19	7	166	163	3	31	7	205	205
12	26	6	317	318	17	3	7	253	237	15	11	7	276	277	15	19	7	93	91	5	31	7	56	65
2	28	6	126	114	1	5	7	137	142	17	11	7	83	67	1	21	7	200	198	7	31	7	139	148
4	28	6	292	285	3	5	7	418	407	1	13	7	485	454	3	21	7	279	269	1	33	7	135	144
6	28	6	150	147	5	5	7	298	284	3	13	7	71	79	5	21	7	100	100	3	33	7	54	69
8	28	6	368	376	7	5	7	238	243	5	13	7	414	398	7	21	7	217	215	0	0	8	593	568
12	28	6	68	69	9	5	7	388	386	7	13	7	301	306	9	21	7	207	214	4	0	8	386	358
0	30	6	216	191	13	5	7	292	282	9	13	7	168	162	11	21	7	78	73	8	0	8	210	240
2	30	6	311	283	15	5	7	272	264	11	13	7	286	292	13	21	7	156	162	12	0	8	391	395
4	30	6	133	139	17	5	7	40	38	13	13	7	170	178	1	23	7	325	331	16	0	8	247	243
6	30	6	49	56	1	7	7	209	192	15	13	7	88	97	3	23	7	118	129	2	2	8	142	141
8	30	6	113	111	3	7	7	111	97	17	13	7	141	140	5	23	7	268	262	4	2	8	397	400
10	30	6	180	186	5	7	7	293	296	1	15	7	248	226	7	23	7	157	143	6	2	8	191	184
2	32	6	168	170	7	7	7	295	290	3	15	7	337	319	9	23	7	93	90	8	2	8	354	340
4	32	6	100	98	9	7	7	162	156	5	15	7	260	273	11	23	7	199	201	10	2	8	103	100
6	32	6	297	296	11	7	7	217	217	7	15	7	73	80	13	23	7	122	129	12	2	8	111	107
8	32	6	162	166	13	7	7	160	159	9	15	7	345	340	1	25	7	262	253	14	2	8	70	87
2	34	6	241	241	15	7	7	199	205	11	15	7	105	101	3	25	7	297	287	16	2	8	226	223
1	1	7	330	324	17	7	7	245	245	13	15	7	180	188	5	25	7	131	126	0	4	8	449	404
3	1	7	486	451	1	9	7	239	247	15	15	7	196	210	7	25	7	184	189	2	4	8	278	276
5	1	7	210	204	3	9	7	157	158	1	17	7	268	266	9	25	7	217	211	4	4	8	240	240
7	1	7	223	223	5	9	7	355	373	3	17	7	253	235	11	25	7	169	172	6	4	8	168	149
9	1	7	210	206	7	9	7	378	369	5	17	7	239	239	1	27	7	211	212	8	4	8	139	141
11	1	7	222	193	9	9	7	294	291	7	17	7	180	167	3	27	7	308	299	10	4	8	226	212
13	1	7	217	216	11	9	7	241	241	9	17	7	191	184	5	27	7	175	177	12	4	8	278	264
15	1	7	255	238	13	9	7	233	224	11	17	7	238	235	7	27	7	175	164	14	4	8	218	214
17	1	7	92	96	15	9	7	192	200	13	17	7	184	186	9	27	7	216	213	16	4	8	205	210
1	3	7	440	406	17	9	7	100	110	15	17	7	192	201	11	27	7	78	89	2	6	8	158	175
3	3	7	289	275	1	11	7	139	137	1	19	7	333	320	1	29	7	216	224	4	6	8	187	189

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	6	8	493	482	10	14	8	180	196	8	26	8	79	63	3	7	9	224	209	11	15	9	143	139
8	6	8	245	245	12	14	8	96	101	10	26	8	165	184	5	7	9	300	302	13	15	9	191	191
10	6	8	286	288	0	16	8	559	545	0	28	8	142	136	7	7	9	173	165	1	17	9	215	211
12	6	8	102	96	2	16	8	86	81	2	28	8	269	267	9	7	9	200	199	3	17	9	214	204
14	6	8	46	43	4	16	8	310	313	6	28	8	80	81	11	7	9	232	227	5	17	9	227	221
16	6	8	99	99	6	16	8	47	45	8	28	8	69	63	13	7	9	195	182	7	17	9	183	170
0	8	8	184	171	8	16	8	103	99	2	30	8	100	116	15	7	9	95	99	9	17	9	205	198
2	8	8	421	421	10	16	8	87	85	4	30	8	181	182	1	9	9	228	220	11	17	9	164	156
4	8	8	69	98	12	16	8	343	343	6	30	8	219	217	3	9	9	398	375	13	17	9	107	124
6	8	8	65	45	14	16	8	95	85	1	1	9	315	309	5	9	9	199	203	1	19	9	251	240
8	8	8	81	87	2	18	8	43	33	3	1	9	337	337	7	9	9	300	312	3	19	9	115	104
10	8	8	340	322	4	18	8	339	340	5	1	9	159	161	9	9	9	162	163	5	19	9	250	257
12	8	8	117	106	8	18	8	396	392	7	1	9	249	260	11	9	9	258	254	7	19	9	219	213
14	8	8	365	357	10	18	8	40	33	9	1	9	222	207	13	9	9	146	142	9	19	9	127	131
2	10	8	208	216	12	18	8	119	122	11	1	9	173	165	15	9	9	107	119	11	19	9	209	209
4	10	8	129	128	14	18	8	88	92	13	1	9	133	136	1	11	9	224	244	1	21	9	184	177
6	10	8	537	519	0	20	8	503	486	15	1	9	219	218	3	11	9	234	231	3	21	9	282	281
8	10	8	107	94	2	20	8	226	223	1	3	9	373	354	5	11	9	206	195	5	21	9	96	116
10	10	8	286	302	4	20	8	245	239	3	3	9	93	100	7	11	9	255	254	7	21	9	180	180
12	10	8	113	104	10	20	8	111	90	5	3	9	350	352	9	11	9	285	280	9	21	9	243	249
14	10	8	47	35	12	20	8	266	280	7	3	9	187	198	11	11	9	60	77	11	21	9	63	60
16	10	8	74	72	2	22	8	123	114	9	3	9	74	69	13	11	9	217	215	1	23	9	186	183
0	12	8	321	325	4	22	8	218	211	11	3	9	237	230	15	11	9	200	196	5	23	9	228	226
2	12	8	321	317	6	22	8	307	308	13	3	9	200	199	1	13	9	267	275	7	23	9	225	223
4	12	8	255	248	8	22	8	222	223	15	3	9	116	108	3	13	9	42	49	9	23	9	116	107
8	12	8	74	70	10	22	8	215	210	1	5	9	150	151	5	13	9	291	289	1	25	9	173	167
10	12	8	319	317	12	22	8	56	40	3	5	9	393	365	7	13	9	215	204	3	25	9	131	130
12	12	8	150	164	0	24	8	243	228	5	5	9	81	80	11	13	9	252	249	5	25	9	216	224
14	12	8	305	299	2	24	8	397	375	7	5	9	249	243	13	13	9	168	171	7	25	9	186	186
16	12	8	135	145	4	24	8	93	92	9	5	9	233	233	1	15	9	282	278	1	27	9	133	126
2	14	8	120	117	6	24	8	131	126	11	5	9	127	120	3	15	9	238	237	3	27	9	120	121
4	14	8	323	328	10	24	8	213	224	13	5	9	162	191	5	15	9	123	142	5	27	9	180	176
6	14	8	273	283	2	26	8	160	152	15	5	9	170	162	7	15	9	274	275	1	29	9	170	174
8	14	8	316	310	6	26	8	345	346	1	7	9	286	276	9	15	9	241	237	3	29	9	43	17

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	10	288	303	2	10	10	54	50	2	22	10	197	188	5	9	11	169	168	6	2	12	117	121
6	0	10	563	554	4	10	10	304	300	4	22	10	168	174	7	9	11	168	158	8	2	12	285	286
10	0	10	346	350	6	10	10	128	118	8	22	10	66	54	9	9	11	199	191	0	4	12	328	326
14	0	10	69	81	8	10	10	150	158	2	24	10	71	69	11	9	11	172	180	2	4	12	289	290
0	2	10	120	121	10	10	10	68	80	4	24	10	262	267	1	11	11	181	170	4	4	12	188	187
2	2	10	346	354	12	10	10	335	334	6	24	10	92	97	3	11	11	375	373	6	4	12	63	50
4	2	10	172	171	2	12	10	92	93	0	26	10	385	391	5	11	11	121	113	2	6	12	224	212
6	2	10	60	46	4	12	10	333	324	2	26	10	41	33	7	11	11	219	231	4	6	12	155	147
8	2	10	66	65	6	12	10	246	254	1	1	11	175	168	9	11	11	190	207	6	6	12	247	243
10	2	10	355	339	8	12	10	321	321	3	1	11	322	304	1	13	11	189	177	8	6	12	157	147
12	2	10	119	114	10	12	10	167	167	5	1	11	251	248	3	13	11	51	31	2	8	12	429	419
14	2	10	292	295	12	12	10	78	76	7	1	11	197	196	5	13	11	232	243	4	8	12	64	67
2	4	10	133	144	0	14	10	290	257	9	1	11	267	270	7	13	11	169	173	6	8	12	104	111
4	4	10	228	228	2	14	10	400	374	11	1	11	190	186	1	15	11	234	239	2	10	12	166	170
6	4	10	277	272	6	14	10	134	123	1	3	11	350	320	3	15	11	229	243	4	10	12	75	74
8	4	10	355	348	8	14	10	66	60	3	3	11	69	47	5	15	11	121	117	6	10	12	313	322
10	4	10	217	223	10	14	10	203	206	5	3	11	270	270	7	15	11	147	166	8	10	12	90	78
12	4	10	105	110	12	14	10	135	143	7	3	11	190	195	9	15	11	165	180	0	12	12	165	180
14	4	10	64	42	2	16	10	182	176	9	3	11	81	82	1	17	11	108	114	2	12	12	255	271
0	6	10	171	191	4	16	10	62	62	11	3	11	220	224	3	17	11	191	189	4	12	12	46	52
2	6	10	96	97	6	16	10	342	334	1	5	11	84	83	5	17	11	153	161	6	12	12	71	70
4	6	10	260	281	8	16	10	62	77	3	5	11	256	251	7	17	11	128	134	4	14	12	271	283
6	6	10	122	96	10	16	10	207	199	5	5	11	80	67	1	19	11	217	213	6	14	12	172	159
8	6	10	150	150	0	18	10	46	58	7	5	11	153	154	3	19	11	136	141	0	16	12	237	242
10	6	10	107	104	2	18	10	373	357	9	5	11	279	265	5	19	11	109	128	2	16	12	121	108
12	6	10	290	278	4	18	10	130	131	11	5	11	67	56	7	19	11	172	181	4	16	12	90	102
14	6	10	143	154	6	18	10	60	56	1	7	11	272	256	1	21	11	133	131	1	1	13	142	155
2	8	10	75	79	8	18	10	44	50	3	7	11	243	230	3	21	11	214	217	3	1	13	139	132
4	8	10	276	295	10	18	10	189	195	5	7	11	171	167	5	21	11	41	41	5	1	13	170	178
6	8	10	73	70	2	20	10	164	167	7	7	11	259	271	0	0	12	502	498	1	3	13	223	227
8	8	10	345	348	4	20	10	92	90	9	7	11	129	129	4	0	12	173	201	3	3	13	40	23
10	8	10	81	71	6	20	10	287	290	11	7	11	175	186	8	0	12	87	90	5	3	13	201	202
12	8	10	69	69	8	20	10	143	140	1	9	11	173	166	2	2	12	119	118	1	5	13	71	88
0	10	10	472	449	0	22	10	324	324	3	9	11	182	178	4	2	12	281	285	3	5	13	191	196

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PR-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	5	13	108	119	1	7	13	180	189	3	7	13	150	140	1	9	13	130	139	3	9	13	160	164

APPENDIX B

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	754	737	6	8	0	343	334	0	16	0	852	821	2	24	0	437	435	2	36	0	198	212
8	0	0	306	290	8	8	0	134	156	2	16	0	279	243	4	24	0	258	252	4	36	0	194	182
12	0	0	509	510	10	8	0	422	470	4	16	0	197	192	6	24	0	46	37	6	36	0	97	77
16	0	0	327	329	12	8	0	45	29	6	16	0	68	71	8	24	0	73	69	8	36	0	92	94
4	2	0	608	712	14	8	0	521	533	8	16	0	272	268	10	24	0	422	439	2	38	0	86	98
6	2	0	445	466	16	8	0	56	40	10	16	0	130	141	12	24	0	106	110	4	38	0	207	218
8	2	0	454	474	18	8	0	180	171	12	16	0	523	530	14	24	0	375	373	3	1	1	504	466
10	2	0	346	377	20	8	0	53	53	14	16	0	79	78	2	26	0	223	231	5	1	1	528	526
12	2	0	52	25	2	10	0	431	396	16	16	0	297	284	6	26	0	533	531	7	1	1	330	348
16	2	0	421	418	4	10	0	212	191	2	18	0	168	161	8	26	0	67	73	9	1	1	569	580
18	2	0	143	136	6	10	0	843	874	4	18	0	422	427	10	26	0	194	192	11	1	1	280	273
20	2	0	311	316	8	10	0	310	269	8	18	0	384	372	12	26	0	59	38	13	1	1	256	279
2	4	0	822	779	10	10	0	389	423	10	18	0	166	178	14	26	0	112	109	15	1	1	309	317
4	4	0	271	271	12	10	0	132	135	12	18	0	123	115	0	28	0	123	111	17	1	1	198	204
6	4	0	173	161	14	10	0	104	96	14	18	0	47	6	2	28	0	395	394	19	1	1	238	230
8	4	0	275	240	18	10	0	379	379	16	18	0	337	360	4	28	0	79	90	21	1	1	160	151
10	4	0	186	205	0	12	0	954	816	18	18	0	99	81	8	28	0	81	101	3	3	1	76	76
12	4	0	254	258	2	12	0	405	450	0	20	0	337	327	10	28	0	324	332	5	3	1	518	575
14	4	0	387	388	4	12	0	227	228	4	20	0	440	436	12	28	0	155	154	7	3	1	500	532
16	4	0	145	160	8	12	0	119	129	6	20	0	75	77	14	28	0	291	294	9	3	1	266	280
18	4	0	176	181	10	12	0	509	532	8	20	0	164	173	2	30	0	87	78	11	3	1	404	446
20	4	0	60	67	12	12	0	391	415	10	20	0	158	167	4	30	0	257	276	13	3	1	272	283
2	6	0	259	281	14	12	0	320	329	12	20	0	433	440	6	30	0	436	439	15	3	1	189	191
4	6	0	81	72	16	12	0	220	242	14	20	0	198	202	8	30	0	283	282	17	3	1	320	320
6	6	0	632	628	18	12	0	133	127	16	20	0	269	278	10	30	0	233	234	19	3	1	146	146
8	6	0	125	127	2	14	0	51	40	2	22	0	207	218	12	30	0	107	113	21	3	1	78	84
10	6	0	446	473	4	14	0	670	649	4	22	0	198	191	0	32	0	303	294	1	5	1	455	455
12	6	0	48	38	6	14	0	519	520	6	22	0	462	478	4	32	0	309	311	3	5	1	341	340
16	6	0	237	253	8	14	0	516	541	8	22	0	224	219	8	32	0	139	134	5	5	1	84	72
18	6	0	371	373	10	14	0	107	107	10	22	0	274	278	10	32	0	105	114	7	5	1	246	260
20	6	0	236	247	12	14	0	129	124	14	22	0	61	48	12	32	0	328	329	9	5	1	515	527
0	8	0	158	166	16	14	0	237	238	16	22	0	197	193	4	34	0	379	378	11	5	1	137	141
2	8	0	592	602	18	14	0	155	149	18	22	0	295	301	8	34	0	384	385	13	5	1	282	301
4	8	0	483	544	20	14	0	242	247	0	24	0	150	125	0	36	0	380	353	15	5	1	375	383

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
17	5	1	94	101	19	11	1	222	234	7	19	1	371	356	3	27	1	327	316	7	37	1	148	148
19	5	1	235	250	1	13	1	555	517	9	19	1	223	230	5	27	1	315	324	1	39	1	180	193
21	5	1	185	182	3	13	1	137	132	11	19	1	284	280	7	27	1	157	157	2	0	2	418	383
1	7	1	425	412	5	13	1	355	351	13	19	1	217	219	9	27	1	280	269	6	0	2	763	739
3	7	1	204	218	7	13	1	362	357	15	19	1	153	146	11	27	1	168	182	10	0	2	488	437
5	7	1	455	417	9	13	1	100	98	17	19	1	203	204	13	27	1	171	169	14	0	2	225	257
7	7	1	490	501	11	13	1	477	480	19	19	1	169	167	15	27	1	232	243	18	0	2	461	450
9	7	1	436	462	13	13	1	261	266	1	21	1	229	210	1	29	1	251	266	0	2	2	351	334
11	7	1	269	275	15	13	1	77	78	3	21	1	597	591	3	29	1	56	48	2	2	2	581	586
13	7	1	257	268	17	13	1	301	319	5	21	1	44	41	5	29	1	312	303	4	2	2	237	235
15	7	1	122	118	19	13	1	107	123	7	21	1	275	264	7	29	1	224	216	8	2	2	315	300
17	7	1	254	264	1	15	1	522	461	9	21	1	283	268	11	29	1	241	246	10	2	2	616	605
19	7	1	196	198	3	15	1	471	455	11	21	1	76	65	13	29	1	138	135	12	2	2	206	216
21	7	1	104	98	5	15	1	317	302	13	21	1	206	219	1	31	1	132	137	14	2	2	510	498
1	9	1	82	110	7	15	1	331	301	15	21	1	315	324	3	31	1	327	341	16	2	2	75	78
3	9	1	678	596	9	15	1	422	406	17	21	1	75	85	5	31	1	125	122	18	2	2	144	139
5	9	1	459	456	11	15	1	117	117	1	23	1	443	422	7	31	1	179	189	20	2	2	48	43
7	9	1	427	402	13	15	1	258	274	3	23	1	195	180	9	31	1	265	266	2	4	2	183	166
9	9	1	537	560	15	15	1	248	250	5	23	1	391	368	11	31	1	113	111	4	4	2	444	438
11	9	1	311	325	17	15	1	118	119	7	23	1	190	174	13	31	1	217	221	6	4	2	521	548
13	9	1	294	325	19	15	1	134	144	9	23	1	152	148	1	33	1	210	206	8	4	2	594	591
15	9	1	211	232	1	17	1	334	321	11	23	1	249	250	3	33	1	229	232	10	4	2	391	405
17	9	1	260	272	3	17	1	441	407	13	23	1	229	239	5	33	1	274	264	12	4	2	125	120
19	9	1	181	180	5	17	1	312	274	15	23	1	129	127	7	33	1	201	209	14	4	2	51	54
21	9	1	137	135	7	17	1	330	309	17	23	1	200	213	9	33	1	179	163	16	4	2	227	229
1	11	1	752	704	9	17	1	218	204	1	25	1	339	330	11	33	1	189	193	18	4	2	304	282
3	11	1	602	564	11	17	1	374	358	3	25	1	337	338	1	35	1	197	186	20	4	2	238	242
5	11	1	272	244	13	17	1	108	106	5	25	1	345	325	3	35	1	112	117	0	6	2	617	630
7	11	1	534	499	15	17	1	195	203	7	25	1	200	194	5	35	1	224	222	2	6	2	474	491
9	11	1	499	489	17	17	1	193	198	9	25	1	179	171	7	35	1	191	188	4	6	2	388	326
11	11	1	118	145	19	17	1	151	156	11	25	1	218	220	9	35	1	150	154	6	6	2	154	158
13	11	1	288	305	1	19	1	455	452	13	25	1	113	114	1	37	1	132	122	8	6	2	379	373
15	11	1	236	248	3	19	1	310	305	15	25	1	186	191	3	37	1	244	256	10	6	2	105	106
17	11	1	55	55	5	19	1	313	291	1	27	1	210	204	5	37	1	102	104	12	6	2	452	450

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
14	6	2	280	287	6	14	2	190	175	6	22	2	54	32	10	30	2	216	222	13	3	3	302	284
16	6	2	285	292	10	14	2	365	368	8	22	2	115	105	12	30	2	222	221	15	3	3	125	114
18	6	2	117	110	12	14	2	226	221	10	22	2	194	204	2	32	2	217	237	17	3	3	243	243
2	8	2	412	349	14	14	2	330	349	12	22	2	297	289	4	32	2	101	109	19	3	3	156	152
4	8	2	651	596	16	14	2	200	197	14	22	2	241	240	6	32	2	355	351	21	3	3	105	90
6	8	2	112	120	18	14	2	110	124	16	22	2	246	255	8	32	2	102	111	1	5	3	188	204
8	8	2	825	849	2	16	2	398	374	2	24	2	170	174	10	32	2	198	207	3	5	3	567	617
10	8	2	83	82	4	16	2	131	128	4	24	2	442	437	12	32	2	65	53	5	5	3	155	135
12	8	2	126	142	6	16	2	569	567	6	24	2	95	86	2	34	2	348	339	7	5	3	322	331
16	8	2	251	252	10	16	2	374	369	8	24	2	486	491	10	34	2	231	246	9	5	3	453	426
18	8	2	52	35	12	16	2	162	169	12	24	2	134	135	2	36	2	179	190	11	5	3	150	156
20	8	2	319	330	14	16	2	177	193	14	24	2	69	67	4	36	2	125	109	13	5	3	247	237
0	10	2	904	917	18	16	2	287	295	16	24	2	194	193	6	36	2	263	269	15	5	3	308	324
2	10	2	350	310	0	18	2	272	282	0	26	2	496	475	8	36	2	109	96	17	5	3	115	110
4	10	2	491	493	2	18	2	794	785	2	26	2	133	131	0	38	2	175	174	19	5	3	220	229
6	10	2	332	328	4	18	2	94	97	4	26	2	311	309	2	38	2	210	213	21	5	3	187	196
8	10	2	299	308	6	18	2	137	141	6	26	2	42	32	4	38	2	115	117	1	7	3	633	594
10	10	2	60	61	8	18	2	90	82	8	26	2	195	197	1	1	3	547	641	3	7	3	482	447
12	10	2	519	519	10	18	2	311	299	10	26	2	56	60	3	1	3	418	446	5	7	3	614	599
14	10	2	158	147	12	18	2	65	62	12	26	2	354	358	5	1	3	280	299	7	7	3	287	289
16	10	2	312	338	14	18	2	426	433	14	26	2	50	33	7	1	3	253	234	9	7	3	231	260
18	10	2	58	56	18	18	2	102	108	16	26	2	246	257	9	1	3	579	554	11	7	3	316	339
2	12	2	123	119	2	20	2	395	398	2	28	2	172	184	11	1	3	271	264	13	7	3	185	190
4	12	2	570	551	4	20	2	294	288	4	28	2	401	381	13	1	3	296	289	15	7	3	165	173
6	12	2	471	448	6	20	2	483	480	6	28	2	208	218	15	1	3	198	182	17	7	3	322	318
8	12	2	541	547	8	20	2	345	329	8	28	2	296	293	17	1	3	165	155	19	7	3	207	204
10	12	2	325	326	10	20	2	328	335	10	28	2	152	150	19	1	3	187	163	1	9	3	346	358
12	12	2	91	88	12	20	2	113	121	12	28	2	58	59	21	1	3	184	191	3	9	3	499	479
16	12	2	161	175	14	20	2	101	87	14	28	2	61	52	1	3	3	411	452	5	9	3	455	427
18	12	2	271	267	16	20	2	149	143	0	30	2	187	171	3	3	3	161	144	7	9	3	399	370
20	12	2	245	263	18	20	2	209	213	2	30	2	305	315	5	3	3	536	541	9	9	3	179	180
0	14	2	245	259	0	22	2	541	538	4	30	2	226	217	7	3	3	343	348	11	9	3	285	301
2	14	2	718	721	2	22	2	379	362	6	30	2	49	45	9	3	3	141	151	13	9	3	229	234
4	14	2	223	223	4	22	2	392	373	8	30	2	120	130	11	3	3	381	369	15	9	3	219	221

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
17	9	3	271	273	5	17	3	373	352	1	25	3	184	171	1	35	3	180	193	4	6	4	227	211
19	9	3	169	166	7	17	3	242	238	3	25	3	318	316	3	35	3	176	193	6	6	4	762	785
1	11	3	551	515	9	17	3	445	439	5	25	3	303	290	5	35	3	183	190	8	6	4	255	271
3	11	3	543	507	11	17	3	169	171	7	25	3	295	302	7	35	3	142	152	10	6	4	346	325
5	11	3	340	306	13	17	3	322	322	9	25	3	299	292	1	37	3	164	153	12	6	4	95	88
7	11	3	312	297	15	17	3	230	217	11	25	3	200	188	3	37	3	215	232	14	6	4	73	91
9	11	3	407	385	17	17	3	205	210	13	25	3	202	196	5	37	3	115	111	16	6	4	138	133
11	11	3	156	162	19	17	3	177	175	15	25	3	155	162	0	0	4	589	638	18	6	4	379	374
13	11	3	55	68	1	19	3	208	195	1	27	3	193	206	4	0	4	49	48	20	6	4	99	93
15	11	3	285	302	3	19	3	222	206	3	27	3	352	333	8	0	4	459	432	0	8	4	332	274
17	11	3	156	163	5	19	3	295	263	5	27	3	190	188	12	0	4	604	582	2	8	4	604	612
19	11	3	217	226	7	19	3	432	429	7	27	3	250	261	16	0	4	254	247	4	8	4	348	336
1	13	3	617	566	9	19	3	113	101	9	27	3	292	290	20	0	4	73	70	6	8	4	266	267
3	13	3	269	247	11	19	3	363	372	11	27	3	177	172	2	2	4	127	125	8	8	4	202	203
5	13	3	604	583	13	19	3	229	224	13	27	3	147	148	4	2	4	769	791	10	8	4	390	370
7	13	3	462	438	15	19	3	193	193	15	27	3	179	182	6	2	4	375	371	12	8	4	140	153
9	13	3	135	139	17	19	3	272	267	1	29	3	296	273	8	2	4	754	720	14	8	4	411	424
11	13	3	359	364	1	21	3	109	123	3	29	3	47	65	10	2	4	141	129	16	8	4	107	104
13	13	3	326	324	3	21	3	399	365	5	29	3	330	326	12	2	4	280	276	18	8	4	174	179
15	13	3	110	114	5	21	3	187	174	7	29	3	334	326	14	2	4	55	43	20	8	4	57	36
17	13	3	214	214	7	21	3	221	236	9	29	3	92	77	16	2	4	195	188	2	10	4	193	190
19	13	3	137	142	9	21	3	432	410	11	29	3	249	245	18	2	4	123	108	4	10	4	319	280
1	15	3	432	405	11	21	3	119	122	13	29	3	147	150	20	2	4	258	252	6	10	4	665	668
3	15	3	548	497	13	21	3	271	263	1	31	3	163	145	0	4	4	514	545	8	10	4	79	70
5	15	3	238	225	15	21	3	282	281	3	31	3	301	312	2	4	4	664	631	10	10	4	329	314
7	15	3	307	295	1	23	3	351	331	5	31	3	142	141	4	4	4	216	226	14	10	4	100	115
9	15	3	392	387	3	23	3	135	117	7	31	3	134	153	6	4	4	78	56	16	10	4	106	116
11	15	3	273	267	5	23	3	341	332	9	31	3	211	217	8	4	4	365	371	18	10	4	339	356
13	15	3	208	211	7	23	3	397	391	11	31	3	84	104	10	4	4	334	316	20	10	4	98	114
15	15	3	294	285	9	23	3	180	178	1	33	3	146	156	12	4	4	515	528	0	12	4	701	680
17	15	3	132	121	11	23	3	382	358	3	33	3	166	171	14	4	4	225	212	2	12	4	602	582
19	15	3	158	175	13	23	3	184	173	5	33	3	167	183	16	4	4	311	308	4	12	4	320	330
1	17	3	322	293	15	23	3	153	150	7	33	3	157	160	18	4	4	121	111	6	12	4	102	113
3	17	3	354	323	17	23	3	211	218	9	33	3	114	125	20	4	4	54	50	8	12	4	180	177

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	12	4	386	364	6	20	4	42	58	2	30	4	150	150	17	3	5	293	276	5	11	5	102	88
12	12	4	208	212	8	20	4	54	58	4	30	4	260	250	19	3	5	150	121	7	11	5	200	202
14	12	4	285	280	10	20	4	235	232	6	30	4	248	236	1	5	5	551	558	9	11	5	370	364
16	12	4	161	161	12	20	4	420	409	8	30	4	296	297	3	5	5	639	675	11	11	5	201	182
18	12	4	99	86	14	20	4	238	242	10	30	4	103	97	5	5	5	511	538	13	11	5	187	172
2	14	4	221	215	16	20	4	221	226	0	32	4	411	418	7	5	5	375	392	15	11	5	314	302
4	14	4	469	452	2	22	4	91	97	2	32	4	171	179	9	5	5	451	457	17	11	5	138	138
6	14	4	374	379	4	22	4	309	294	4	32	4	251	257	11	5	5	60	48	19	11	5	184	189
8	14	4	504	488	6	22	4	395	382	6	32	4	97	87	13	5	5	358	349	1	13	5	492	489
10	14	4	139	149	8	22	4	304	294	8	32	4	67	55	15	5	5	293	277	3	13	5	55	58
12	14	4	46	32	10	22	4	236	224	10	32	4	52	53	17	5	5	71	60	5	13	5	432	428
14	14	4	128	123	12	22	4	114	111	4	34	4	255	260	19	5	5	196	195	7	13	5	361	352
16	14	4	255	244	14	22	4	126	133	8	34	4	262	266	1	7	5	439	456	9	13	5	100	98
18	14	4	174	171	16	22	4	101	110	0	36	4	353	363	3	7	5	229	242	11	13	5	265	265
0	16	4	761	762	0	24	4	225	202	2	36	4	62	74	5	7	5	313	326	13	13	5	161	155
2	16	4	198	196	2	24	4	387	397	4	36	4	166	182	7	7	5	323	350	15	13	5	76	73
4	16	4	352	361	6	24	4	49	52	1	1	5	244	270	9	7	5	135	131	17	13	5	215	216
6	16	4	123	117	10	24	4	320	316	3	1	5	380	445	11	7	5	336	336	1	15	5	182	188
8	16	4	163	166	12	24	4	167	160	5	1	5	239	243	13	7	5	261	261	3	15	5	487	469
10	16	4	70	72	14	24	4	308	300	7	1	5	366	346	15	7	5	207	190	5	15	5	111	110
12	16	4	475	479	2	26	4	271	278	9	1	5	396	386	17	7	5	276	275	7	15	5	258	249
14	16	4	120	126	4	26	4	58	33	11	1	5	308	306	19	7	5	154	164	9	15	5	410	397
16	16	4	270	281	6	26	4	514	512	13	1	5	276	252	1	9	5	406	409	11	15	5	134	133
2	18	4	88	81	8	26	4	51	62	15	1	5	319	292	3	9	5	294	282	13	15	5	232	224
4	18	4	431	425	10	26	4	321	307	17	1	5	202	190	5	9	5	509	532	15	15	5	299	286
6	18	4	200	185	12	26	4	75	80	19	1	5	172	166	7	9	5	265	268	17	15	5	96	101
8	18	4	531	512	14	26	4	81	84	1	3	5	288	322	9	9	5	189	200	1	17	5	432	437
10	18	4	102	104	0	28	4	325	327	3	3	5	208	201	11	9	5	244	251	3	17	5	363	344
12	18	4	175	163	2	28	4	403	409	5	3	5	427	450	13	9	5	167	167	5	17	5	373	381
16	18	4	265	267	4	28	4	169	159	7	3	5	503	515	15	9	5	179	176	7	17	5	238	225
18	18	4	60	55	6	28	4	133	135	9	3	5	154	146	17	9	5	236	231	9	17	5	285	266
0	20	4	352	361	8	28	4	94	77	11	3	5	388	368	19	9	5	139	142	11	17	5	213	203
2	20	4	379	370	10	28	4	250	247	13	3	5	349	332	1	11	5	254	248	13	17	5	284	275
4	20	4	146	157	12	28	4	172	165	15	3	5	169	161	3	11	5	368	369	15	17	5	178	166

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
17	17	5	151	151	3	27	5	335	334	10	2	6	176	198	8	10	6	172	168	14	18	6	366	363
1	19	5	323	309	5	27	5	151	148	12	2	6	237	208	10	10	6	95	95	16	18	6	58	47
3	19	5	106	95	7	27	5	202	205	14	2	6	475	457	12	10	6	325	320	2	20	6	209	223
5	19	5	309	295	9	27	5	262	255	16	2	6	110	95	14	10	6	276	267	4	20	6	276	285
7	19	5	268	266	11	27	5	120	119	18	2	6	105	92	16	10	6	254	243	6	20	6	359	341
9	19	5	126	113	13	27	5	141	154	2	4	6	236	253	2	12	6	186	197	8	20	6	237	236
11	19	5	350	340	1	29	5	320	323	4	4	6	355	377	4	12	6	388	394	10	20	6	216	205
13	19	5	261	258	3	29	5	55	53	6	4	6	433	430	6	12	6	303	286	12	20	6	136	134
15	19	5	102	104	5	29	5	282	275	8	4	6	332	322	8	12	6	368	369	16	20	6	120	115
17	19	5	209	202	7	29	5	241	248	10	4	6	319	316	10	12	6	265	258	0	22	6	267	269
1	21	5	244	247	9	29	5	68	63	12	4	6	42	50	12	12	6	61	65	2	22	6	211	230
3	21	5	376	358	11	29	5	225	227	14	4	6	139	125	14	12	6	106	104	4	22	6	177	196
5	21	5	217	228	1	31	5	186	181	16	4	6	244	236	16	12	6	179	182	8	22	6	163	161
7	21	5	237	220	3	31	5	312	307	18	4	6	258	258	18	12	6	136	139	10	22	6	271	264
9	21	5	255	249	5	31	5	70	83	0	6	6	748	747	0	14	6	394	391	12	22	6	301	288
11	21	5	95	91	7	31	5	219	219	2	6	6	310	356	2	14	6	360	369	14	22	6	202	190
13	21	5	177	179	9	31	5	194	192	4	6	6	417	444	4	14	6	352	351	2	24	6	119	115
15	21	5	207	203	1	33	5	220	222	6	6	6	145	149	6	14	6	129	117	4	24	6	355	355
1	23	5	263	259	3	33	5	137	130	8	6	6	142	156	8	14	6	115	120	6	24	6	134	130
3	23	5	162	152	5	33	5	178	167	10	6	6	141	140	10	14	6	327	330	8	24	6	335	337
5	23	5	226	225	7	33	5	175	182	12	6	6	453	449	12	14	6	190	190	10	24	6	55	60
7	23	5	262	260	1	35	5	211	224	14	6	6	146	154	14	14	6	400	378	12	24	6	90	84
9	23	5	82	90	3	35	5	163	158	16	6	6	313	307	16	14	6	139	147	0	26	6	430	415
11	23	5	334	324	5	35	5	165	173	2	8	6	110	106	2	16	6	362	366	2	26	6	59	56
13	23	5	188	181	2	0	6	337	330	4	8	6	446	472	4	16	6	136	126	4	26	6	230	235
15	23	5	53	74	6	0	6	489	477	8	8	6	495	521	6	16	6	573	545	8	26	6	188	197
1	25	5	182	184	10	0	6	487	483	10	8	6	140	145	10	16	6	355	366	12	26	6	346	337
3	25	5	288	286	14	0	6	285	249	12	8	6	187	199	12	16	6	84	66	2	28	6	130	128
5	25	5	150	156	18	0	6	336	303	16	8	6	342	320	14	16	6	59	63	4	28	6	300	302
7	25	5	255	256	0	2	6	401	423	18	8	6	54	57	0	18	6	152	145	6	28	6	191	189
9	25	5	265	266	2	2	6	759	781	0	10	6	538	575	2	18	6	366	372	8	28	6	364	365
11	25	5	122	120	4	2	6	191	202	2	10	6	122	124	8	18	6	115	107	10	28	6	70	71
13	25	5	187	193	6	2	6	80	81	4	10	6	328	355	10	18	6	325	335	0	30	6	228	201
1	27	5	157	151	8	2	6	93	78	6	10	6	122	123	12	18	6	132	120	2	30	6	331	318

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	30	6	131	132	17	5	7	74	70	13	13	7	190	197	1	23	7	323	334	16	0	8	245	236
8	30	6	117	117	1	7	7	211	215	15	13	7	71	72	3	23	7	136	142	2	2	8	133	138
10	30	6	207	210	3	7	7	128	125	17	13	7	164	162	5	23	7	277	270	4	2	8	413	432
2	32	6	184	186	5	7	7	286	305	1	15	7	258	249	7	23	7	183	168	6	2	8	191	194
4	32	6	89	78	7	7	7	321	325	3	15	7	362	361	9	23	7	101	90	8	2	8	351	344
6	32	6	325	323	9	7	7	167	170	5	15	7	281	284	11	23	7	202	199	10	2	8	88	86
8	32	6	145	151	11	7	7	221	226	7	15	7	104	101	13	23	7	145	145	12	2	8	79	82
0	34	6	55	41	13	7	7	215	212	9	15	7	374	369	1	25	7	266	264	14	2	8	70	81
2	34	6	253	265	15	7	7	205	211	11	15	7	113	107	3	25	7	284	285	16	2	8	257	262
1	1	7	328	339	17	7	7	241	250	13	15	7	189	192	5	25	7	159	164	0	4	8	449	443
3	1	7	465	477	1	9	7	235	255	15	15	7	231	215	7	25	7	187	193	2	4	8	299	306
5	1	7	221	224	3	9	7	160	156	1	17	7	255	262	9	25	7	214	209	4	4	8	259	258
7	1	7	207	211	5	9	7	351	379	3	17	7	278	273	11	25	7	193	197	6	4	8	147	140
9	1	7	235	225	7	9	7	376	377	5	17	7	232	239	1	27	7	211	213	8	4	8	132	139
11	1	7	244	208	9	9	7	285	291	7	17	7	213	199	3	27	7	330	319	10	4	8	248	241
13	1	7	225	227	11	9	7	261	266	9	17	7	179	178	5	27	7	175	176	12	4	8	286	269
15	1	7	273	259	13	9	7	253	243	11	17	7	251	237	7	27	7	166	159	14	4	8	255	241
17	1	7	110	108	15	9	7	188	187	13	17	7	214	213	9	27	7	241	227	16	4	8	195	185
1	3	7	434	438	17	9	7	132	139	15	17	7	204	206	11	27	7	107	102	2	6	8	168	185
3	3	7	241	259	1	11	7	146	141	1	19	7	352	356	1	29	7	240	243	4	6	8	180	186
5	3	7	357	356	3	11	7	429	416	3	19	7	126	121	3	29	7	49	49	6	6	8	492	498
7	3	7	321	353	5	11	7	197	199	5	19	7	302	312	5	29	7	233	237	8	6	8	223	231
9	3	7	111	101	7	11	7	182	186	7	19	7	171	169	7	29	7	175	182	10	6	8	261	269
11	3	7	326	346	9	11	7	389	390	9	19	7	163	150	9	29	7	56	64	12	6	8	76	75
13	3	7	233	224	11	11	7	195	202	11	19	7	255	244	1	31	7	129	133	14	6	8	55	53
15	3	7	99	99	13	11	7	158	164	13	19	7	189	178	3	31	7	215	219	16	6	8	128	121
17	3	7	270	250	15	11	7	298	298	15	19	7	88	74	5	31	7	92	93	0	8	8	165	176
1	5	7	148	160	17	11	7	54	60	1	21	7	178	186	7	31	7	155	155	2	8	8	442	451
3	5	7	403	423	1	13	7	457	452	3	21	7	299	293	1	33	7	145	155	4	8	8	78	100
5	5	7	297	304	3	13	7	78	90	5	21	7	96	100	3	33	7	95	113	6	8	8	49	36
7	5	7	230	240	5	13	7	397	382	7	21	7	222	226	0	0	8	620	637	8	8	8	88	84
9	5	7	399	404	7	13	7	316	320	9	21	7	225	226	4	0	8	388	386	10	8	8	361	352
13	5	7	298	298	9	13	7	125	119	11	21	7	85	83	8	0	8	215	243	12	8	8	84	87
15	5	7	296	288	11	13	7	308	308	13	21	7	176	171	12	0	8	384	390	14	8	8	385	380

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
16	8	8	52	39	8	18	8	410	408	7	1	9	228	248	11	9	9	267	262	7	19	9	229	224
2	10	8	210	221	12	18	8	116	111	9	1	9	227	220	13	9	9	174	165	9	19	9	120	128
4	10	8	149	149	14	18	8	89	87	11	1	9	191	182	15	9	9	115	117	11	19	9	227	207
6	10	8	521	526	0	20	8	467	479	13	1	9	137	134	1	11	9	212	237	1	21	9	171	175
8	10	8	123	118	2	20	8	242	244	15	1	9	221	225	3	11	9	248	251	3	21	9	303	306
10	10	8	262	279	4	20	8	228	227	1	3	9	377	378	5	11	9	204	200	5	21	9	108	121
12	10	8	117	112	6	20	8	45	42	3	3	9	69	73	7	11	9	253	251	7	21	9	177	180
14	10	8	73	64	10	20	8	130	116	5	3	9	363	366	9	11	9	295	298	9	21	9	256	255
16	10	8	73	66	12	20	8	304	299	7	3	9	191	205	11	11	9	78	89	11	21	9	67	73
0	12	8	310	315	2	22	8	152	149	9	3	9	70	70	13	11	9	208	212	1	23	9	198	203
2	12	8	329	334	4	22	8	206	200	11	3	9	242	231	15	11	9	221	216	3	23	9	59	45
4	12	8	237	237	6	22	8	336	339	13	3	9	196	203	1	13	9	253	261	5	23	9	225	240
8	12	8	104	109	8	22	8	230	224	15	3	9	119	114	3	13	9	53	51	7	23	9	230	219
10	12	8	336	339	10	22	8	220	221	1	5	9	135	142	5	13	9	295	297	9	23	9	125	124
12	12	8	193	198	0	24	8	203	205	3	5	9	378	361	7	13	9	246	236	1	25	9	179	178
14	12	8	314	315	2	24	8	416	400	5	5	9	117	113	11	13	9	273	258	3	25	9	146	147
16	12	8	151	158	4	24	8	67	84	7	5	9	223	225	13	13	9	186	192	5	25	9	233	233
2	14	8	113	113	6	24	8	112	108	9	5	9	258	257	1	15	9	277	291	7	25	9	192	196
4	14	8	360	375	10	24	8	239	248	11	5	9	137	137	3	15	9	232	238	1	27	9	134	135
6	14	8	252	269	2	26	8	167	165	13	5	9	162	180	5	15	9	145	166	3	27	9	135	130
8	14	8	337	336	4	26	8	47	60	15	5	9	168	171	7	15	9	262	264	5	27	9	190	186
10	14	8	164	170	6	26	8	362	363	1	7	9	289	298	9	15	9	246	239	1	29	9	177	185
12	14	8	89	97	8	26	8	92	74	3	7	9	218	219	11	15	9	148	149	2	0	10	287	310
0	16	8	528	546	10	26	8	185	187	5	7	9	301	314	13	15	9	202	194	6	0	10	556	552
2	16	8	99	95	0	28	8	166	163	7	7	9	177	177	1	17	9	199	207	10	0	10	325	322
4	16	8	280	283	2	28	8	281	277	9	7	9	206	214	3	17	9	224	223	14	0	10	77	77
6	16	8	45	46	4	28	8	58	56	11	7	9	236	241	5	17	9	221	221	0	2	10	121	121
8	16	8	133	136	6	28	8	79	73	13	7	9	211	187	7	17	9	199	187	2	2	10	327	341
10	16	8	102	91	8	28	8	70	79	15	7	9	93	93	9	17	9	208	198	4	2	10	156	158
12	16	8	378	373	2	30	8	103	106	1	9	9	209	199	11	17	9	175	174	6	2	10	66	53
14	16	8	93	84	4	30	8	205	215	3	9	9	372	370	13	17	9	126	126	8	2	10	78	83
2	18	8	56	46	1	1	9	302	312	5	9	9	203	211	1	19	9	274	270	10	2	10	378	353
4	18	8	351	369	3	1	9	324	334	7	9	9	300	315	3	19	9	104	92	12	2	10	132	125
6	18	8	59	66	5	1	9	178	185	9	9	9	169	172	5	19	9	261	274	14	2	10	304	297

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EU-EDTA STRUCTURE

H	K	L	FO	FC
2	4	10	144	154
4	4	10	241	248
6	4	10	286	280
8	4	10	349	344
10	4	10	205	212
12	4	10	92	94
14	4	10	71	55
0	6	10	189	201
2	6	10	103	97
4	6	10	251	269
6	6	10	85	70
8	6	10	169	178
10	6	10	127	109
12	6	10	311	302
14	6	10	147	150
2	8	10	71	76
4	8	10	308	322
6	8	10	69	63
8	8	10	370	366
10	8	10	74	66
12	8	10	58	53
0	10	10	429	435
2	10	10	54	60
4	10	10	298	294
6	10	10	111	104
8	10	10	176	181
10	10	10	97	99
12	10	10	353	349
2	12	10	102	112
4	12	10	319	315
6	12	10	263	268
8	12	10	321	312
10	12	10	161	167
12	12	10	61	59
0	14	10	260	235
2	14	10	394	380
6	14	10	119	114
8	14	10	79	73
10	14	10	229	226
12	14	10	146	143
2	16	10	179	183
4	16	10	54	55
6	16	10	368	360
8	16	10	66	78
10	16	10	192	198
0	18	10	72	81
2	18	10	375	367
4	18	10	149	144
6	18	10	59	51
8	18	10	46	51
10	18	10	210	209
2	20	10	167	164
4	20	10	118	114
6	20	10	287	293
8	20	10	164	162
0	22	10	335	339
2	22	10	185	177
4	22	10	183	188
8	22	10	65	68
2	24	10	68	62
4	24	10	264	274
6	24	10	73	74
0	26	10	384	384
2	26	10	54	41
1	1	11	173	177
3	1	11	307	305
5	1	11	246	239
7	1	11	195	196
9	1	11	268	271
11	1	11	180	179
1	3	11	324	308
3	3	11	57	57
5	3	11	289	282
9	3	11	62	60
11	3	11	213	223
1	5	11	72	75
3	5	11	260	264
5	5	11	77	55
7	5	11	179	172
9	5	11	281	269
11	5	11	81	77
1	7	11	265	257
3	7	11	236	222
5	7	11	186	181
7	7	11	247	261
9	7	11	140	136
11	7	11	171	174
1	9	11	171	166
3	9	11	181	178
5	9	11	178	179
7	9	11	175	172
9	9	11	181	176
11	9	11	191	185
1	11	11	175	169
3	11	11	369	369
5	11	11	128	111
7	11	11	212	223
9	11	11	216	216
11	11	11	50	30
1	13	11	195	185
3	13	11	50	28
5	13	11	243	246
7	13	11	173	184
1	15	11	234	231
3	15	11	235	238
5	15	11	136	135
7	15	11	160	156
9	15	11	166	168
1	17	11	125	130
3	17	11	206	195
5	17	11	149	155
7	17	11	139	137
1	19	11	222	208
3	19	11	126	124
5	19	11	124	131
1	21	11	117	119
3	21	11	216	218
0	0	12	481	476
4	0	12	155	174
8	0	12	115	110
2	2	12	120	120
4	2	12	295	295
6	2	12	125	128
8	2	12	302	293
0	4	12	315	304
2	4	12	284	284
4	4	12	158	155
2	6	12	219	220
4	6	12	154	144
6	6	12	262	249
8	6	12	157	144
2	8	12	416	403
6	8	12	101	103
2	10	12	173	172
4	10	12	71	76
6	10	12	329	324
8	10	12	93	81
0	12	12	197	209
2	12	12	240	254
4	12	12	75	72
4	14	12	283	282
6	14	12	169	161
0	16	12	245	257
2	16	12	97	89
4	16	12	95	112
1	1	13	146	141
3	1	13	150	141
5	1	13	171	167
1	3	13	224	219
5	3	13	196	183
1	5	13	103	101
3	5	13	218	204
1	7	13	185	185
3	7	13	158	140
1	9	13	155	162

APPENDIX C

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC
4	0	0	844	743
8	0	0	323	287
12	0	0	560	518
16	0	0	350	336
24	0	0	239	248
4	2	0	715	745
6	2	0	482	461
8	2	0	519	500
10	2	0	381	376
16	2	0	456	445
18	2	0	169	157
20	2	0	346	349
22	2	0	73	81
24	2	0	172	162
2	4	0	824	789
4	4	0	299	290
6	4	0	186	164
8	4	0	301	234
10	4	0	222	221
12	4	0	296	281
14	4	0	435	410
16	4	0	162	167
18	4	0	184	181
20	4	0	87	84
22	4	0	116	122
24	4	0	206	233
2	6	0	270	295
4	6	0	101	91
6	6	0	715	633
8	6	0	161	147
10	6	0	518	480
12	6	0	69	54
16	6	0	262	265
18	6	0	425	405
20	6	0	258	258
22	6	0	182	206
24	6	0	98	109
0	8	0	143	160
2	8	0	579	614
4	8	0	487	546
6	8	0	358	336
8	8	0	138	152
10	8	0	475	497
14	8	0	590	561
16	8	0	50	46
18	8	0	192	181
20	8	0	56	63
22	8	0	235	235
2	10	0	412	391
4	10	0	207	186
6	10	0	878	884
8	10	0	326	266
10	10	0	424	422
12	10	0	142	134
14	10	0	129	124
16	10	0	61	73
18	10	0	436	420
20	10	0	54	67
22	10	0	190	209
0	12	0	886	838
2	12	0	392	445
4	12	0	224	245
8	12	0	135	136
10	12	0	555	560
12	12	0	448	442
14	12	0	358	342
16	12	0	242	252
18	12	0	139	130
22	12	0	143	154
4	14	0	632	659
6	14	0	522	526
8	14	0	537	535
10	14	0	116	109
12	14	0	130	119
14	14	0	50	24
16	14	0	279	271
18	14	0	169	172
20	14	0	277	280
22	14	0	122	129
0	16	0	805	837
2	16	0	254	237
4	16	0	194	186
6	16	0	59	60
8	16	0	278	279
10	16	0	147	154
12	16	0	560	545
14	16	0	94	84
16	16	0	322	300
20	16	0	65	39
2	18	0	160	158
4	18	0	405	417
8	18	0	390	382
10	18	0	178	182
12	18	0	114	108
16	18	0	377	377
18	18	0	97	81
20	18	0	305	311
0	20	0	323	331
4	20	0	420	428
6	20	0	79	76
8	20	0	170	176
10	20	0	170	173
12	20	0	455	448
14	20	0	225	210
16	20	0	277	289
2	22	0	201	217
4	22	0	184	180
6	22	0	454	473
8	22	0	227	220
10	22	0	278	276
14	22	0	61	60
16	22	0	196	208
18	22	0	317	309
20	22	0	207	213
0	24	0	139	128
2	24	0	403	437
4	24	0	239	241
8	24	0	60	67
10	24	0	433	444
12	24	0	125	107
14	24	0	388	371
16	24	0	55	49
18	24	0	112	107
2	26	0	120	207
6	26	0	512	518
8	26	0	68	81
10	26	0	180	180
12	26	0	49	35
14	26	0	127	123
18	26	0	242	241
0	28	0	135	104
2	28	0	351	378
4	28	0	85	78
8	28	0	89	107
10	28	0	329	322
12	28	0	156	152
14	28	0	300	287
16	28	0	109	115
18	28	0	118	98
4	30	0	252	251
6	30	0	416	423
8	30	0	279	269
10	30	0	233	219
12	30	0	100	97
16	30	0	139	147
0	32	0	276	277
4	32	0	268	284
8	32	0	144	137
10	32	0	98	111
12	32	0	341	319
14	32	0	146	142
16	32	0	215	202
4	34	0	343	353
8	34	0	377	365
12	34	0	145	139
14	34	0	69	58
0	36	0	345	331
2	36	0	193	195
4	36	0	139	166
6	36	0	80	59
8	36	0	74	86
12	36	0	273	271
14	36	0	100	87
4	38	0	187	205
6	38	0	203	213
8	38	0	184	197
10	38	0	163	143
0	40	0	147	148
2	40	0	264	255
10	40	0	131	144

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	42	0	110	128	17	5	1	101	115	15	11	1	266	273	13	17	1	121	117	15	23	1	128	126
6	42	0	307	290	19	5	1	268	263	17	11	1	73	74	15	17	1	205	212	17	23	1	218	215
0	44	0	59	58	21	5	1	210	209	19	11	1	246	248	17	17	1	208	215	19	23	1	149	158
2	44	0	233	211	1	7	1	400	417	21	11	1	221	221	19	17	1	162	164	1	25	1	308	327
3	1	1	518	478	3	7	1	203	221	23	11	1	83	72	21	17	1	181	176	3	25	1	318	324
5	1	1	565	531	5	7	1	463	418	1	13	1	501	509	1	19	1	423	446	5	25	1	321	306
7	1	1	359	358	7	7	1	523	507	3	13	1	128	117	3	19	1	286	288	7	25	1	197	186
9	1	1	613	599	9	7	1	483	464	5	13	1	353	352	5	19	1	310	288	9	25	1	178	173
11	1	1	305	291	11	7	1	303	297	7	13	1	374	386	7	19	1	365	359	11	25	1	205	212
13	1	1	282	297	13	7	1	281	293	9	13	1	104	101	9	19	1	226	232	13	25	1	110	119
15	1	1	335	337	15	7	1	134	127	11	13	1	495	495	11	19	1	294	293	15	25	1	192	193
17	1	1	216	217	17	7	1	279	282	13	13	1	279	284	13	19	1	221	219	17	25	1	186	195
19	1	1	263	245	19	7	1	222	212	15	13	1	86	79	15	19	1	160	145	19	25	1	154	156
21	1	1	168	176	21	7	1	101	109	17	13	1	336	340	17	19	1	211	208	1	27	1	196	198
23	1	1	133	122	23	7	1	195	195	19	13	1	120	143	19	19	1	191	176	3	27	1	311	308
3	3	1	76	79	1	9	1	77	110	21	13	1	86	78	21	19	1	107	108	5	27	1	288	308
5	3	1	592	582	3	9	1	643	598	23	13	1	184	188	1	21	1	203	214	7	27	1	161	155
7	3	1	553	551	5	9	1	450	462	1	15	1	484	456	3	21	1	560	583	9	27	1	277	269
9	3	1	284	282	7	9	1	460	410	3	15	1	448	447	5	21	1	52	42	11	27	1	165	179
11	3	1	442	460	9	9	1	600	569	5	15	1	312	302	7	21	1	268	259	13	27	1	159	161
13	3	1	305	309	11	9	1	355	341	7	15	1	328	304	9	21	1	288	278	15	27	1	246	244
15	3	1	203	188	13	9	1	335	340	9	15	1	445	417	11	21	1	85	70	17	27	1	62	71
17	3	1	349	343	15	9	1	247	244	11	15	1	131	128	13	21	1	214	212	19	27	1	141	155
19	3	1	169	167	17	9	1	287	287	13	15	1	278	273	15	21	1	337	335	1	29	1	240	250
21	3	1	93	88	19	9	1	199	200	15	15	1	257	267	17	21	1	89	93	5	29	1	288	282
23	3	1	213	217	21	9	1	147	152	17	15	1	137	126	19	21	1	182	185	7	29	1	223	215
1	5	1	426	455	23	9	1	145	155	19	15	1	161	157	21	21	1	219	220	11	29	1	228	233
3	5	1	345	353	1	11	1	692	685	21	15	1	178	169	1	23	1	406	411	13	29	1	143	140
5	5	1	87	66	3	11	1	578	574	1	17	1	292	312	3	23	1	176	163	15	29	1	53	29
7	5	1	276	268	5	11	1	268	244	3	17	1	420	417	5	23	1	365	359	17	29	1	183	181
9	5	1	590	554	7	11	1	532	498	5	17	1	303	276	7	23	1	188	188	1	31	1	120	132
11	5	1	154	144	9	11	1	531	504	7	17	1	331	314	9	23	1	159	155	3	31	1	322	328
13	5	1	311	314	11	11	1	136	146	9	17	1	230	221	11	23	1	252	258	5	31	1	112	114
15	5	1	419	409	13	11	1	310	311	11	17	1	383	361	13	23	1	239	237	7	31	1	175	180

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
9	31	1	265	255	5	43	1	108	127	8	6	2	430	388	16	12	2	191	197	22	18	2	167	155
11	31	1	110	111	2	0	2	426	389	10	6	2	111	117	18	12	2	313	281	2	20	2	363	393
13	31	1	213	211	6	0	2	757	747	12	6	2	497	477	20	12	2	274	289	4	20	2	277	280
15	31	1	240	239	10	0	2	498	429	14	6	2	302	298	22	12	2	111	131	6	20	2	460	474
1	33	1	197	188	14	0	2	245	273	16	6	2	300	304	0	14	2	230	258	8	20	2	335	322
3	33	1	140	212	18	0	2	488	493	18	6	2	119	113	2	14	2	677	720	10	20	2	335	336
5	33	1	263	250	22	0	2	228	252	22	6	2	52	62	4	14	2	214	227	12	20	2	108	121
7	33	1	197	202	0	2	2	367	349	24	6	2	238	248	6	14	2	183	171	14	20	2	127	97
9	33	1	168	153	2	2	2	632	607	2	8	2	380	352	8	14	2	148	150	16	20	2	161	157
11	33	1	191	182	4	2	2	228	236	4	8	2	636	610	10	14	2	380	380	18	20	2	234	235
13	33	1	163	159	8	2	2	331	311	6	8	2	102	114	12	14	2	236	228	20	20	2	162	159
15	33	1	133	133	10	2	2	645	627	8	8	2	878	851	14	14	2	367	365	0	22	2	509	530
1	35	1	175	177	12	2	2	216	230	10	8	2	98	90	16	14	2	216	205	2	22	2	360	360
5	35	1	209	203	14	2	2	549	526	12	8	2	148	139	18	14	2	123	124	4	22	2	352	347
7	35	1	183	174	16	2	2	77	89	16	8	2	293	285	22	14	2	164	157	6	22	2	68	36
9	35	1	128	145	18	2	2	145	144	20	8	2	345	361	2	16	2	362	374	8	22	2	104	108
11	35	1	217	216	22	2	2	185	183	0	10	2	865	954	4	16	2	123	116	10	22	2	199	207
13	35	1	176	172	24	2	2	71	103	2	10	2	320	318	6	16	2	567	576	12	22	2	308	295
1	37	1	116	110	2	4	2	181	167	4	10	2	471	493	8	16	2	95	102	14	22	2	246	245
3	37	1	220	230	4	4	2	447	454	6	10	2	322	325	10	16	2	377	367	16	22	2	256	255
5	37	1	96	104	6	4	2	567	553	8	10	2	309	319	12	16	2	166	166	18	22	2	75	67
7	37	1	136	138	8	4	2	633	602	10	10	2	58	65	14	16	2	182	199	2	24	2	157	168
9	37	1	175	175	10	4	2	415	405	12	10	2	564	541	18	16	2	323	323	4	24	2	424	421
13	37	1	132	139	12	4	2	128	121	14	10	2	176	156	20	16	2	74	78	6	24	2	97	87
1	39	1	162	175	14	4	2	74	76	16	10	2	351	355	22	16	2	222	227	8	24	2	472	489
5	39	1	186	196	16	4	2	245	255	18	10	2	68	49	0	18	2	257	289	10	24	2	66	48
7	39	1	139	139	18	4	2	330	310	20	10	2	56	48	2	18	2	747	782	12	24	2	128	133
11	39	1	170	156	20	4	2	255	265	2	12	2	116	118	4	18	2	86	88	16	24	2	213	206
1	41	1	133	133	22	4	2	186	196	4	12	2	545	555	6	18	2	116	127	18	24	2	68	57
3	41	1	163	163	24	4	2	98	79	6	12	2	461	455	8	18	2	92	89	20	24	2	289	289
5	41	1	98	94	0	6	2	596	652	8	12	2	541	554	10	18	2	324	308	0	26	2	467	468
7	41	1	130	144	2	6	2	449	497	10	12	2	340	330	12	18	2	74	64	2	26	2	112	129
1	43	1	116	112	4	6	2	367	324	12	12	2	107	86	14	18	2	450	441	4	26	2	292	293
3	43	1	170	165	6	6	2	157	157	14	12	2	109	102	18	18	2	111	105	8	26	2	195	196

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	26	2	59	60	8	36	2	111	89	19	3	3	179	175	17	9	3	294	287	17	15	3	147	134
12	26	2	348	359	10	36	2	158	158	21	3	3	106	96	19	9	3	185	178	19	15	3	187	186
16	26	2	267	261	0	38	2	167	159	23	3	3	229	232	21	9	3	181	189	21	15	3	206	212
2	28	2	161	179	2	38	2	190	189	1	5	3	182	199	23	9	3	162	170	1	17	3	313	304
4	28	2	369	371	4	38	2	87	101	3	5	3	592	625	1	11	3	513	516	3	17	3	332	326
6	28	2	210	213	8	38	2	58	75	5	5	3	159	141	3	11	3	514	509	5	17	3	359	341
8	28	2	292	288	10	38	2	149	150	7	5	3	330	326	5	11	3	330	304	7	17	3	240	231
10	28	2	151	149	12	38	2	182	177	9	5	3	476	442	7	11	3	307	301	9	17	3	443	434
12	28	2	59	60	4	40	2	211	216	11	5	3	162	159	9	11	3	412	401	11	17	3	178	175
14	28	2	62	51	6	40	2	129	131	13	5	3	256	249	11	11	3	173	175	13	17	3	331	323
16	28	2	179	183	8	40	2	225	201	15	5	3	327	342	13	11	3	63	74	15	17	3	231	228
18	28	2	93	95	0	42	2	250	247	17	5	3	123	123	15	11	3	314	322	17	17	3	222	217
0	30	2	166	153	4	42	2	89	166	19	5	3	234	243	17	11	3	169	166	19	17	3	188	192
2	30	2	288	304	1	1	3	566	644	21	5	3	211	224	19	11	3	234	239	21	17	3	122	129
4	30	2	213	201	3	1	3	437	458	1	7	3	603	589	21	11	3	204	214	1	19	3	187	188
8	30	2	114	129	5	1	3	288	309	3	7	3	462	441	1	13	3	585	575	3	19	3	216	209
10	30	2	221	217	7	1	3	255	255	5	7	3	614	590	3	13	3	245	236	5	19	3	284	252
12	30	2	213	222	9	1	3	585	571	7	7	3	294	311	5	13	3	578	576	7	19	3	422	432
14	30	2	225	219	11	1	3	282	268	9	7	3	256	279	7	13	3	454	441	9	19	3	104	107
16	30	2	163	146	13	1	3	302	302	11	7	3	349	344	9	13	3	135	136	11	19	3	366	367
2	32	2	202	223	15	1	3	209	198	13	7	3	200	205	11	13	3	375	371	13	19	3	229	241
4	32	2	100	104	17	1	3	177	172	15	7	3	180	182	13	13	3	344	328	15	19	3	193	188
6	32	2	353	335	19	1	3	188	181	17	7	3	346	335	15	13	3	110	109	17	19	3	285	280
8	32	2	105	104	21	1	3	204	212	19	7	3	224	224	17	13	3	240	235	19	19	3	76	97
10	32	2	202	197	23	1	3	111	127	21	7	3	159	162	19	13	3	167	163	21	19	3	97	110
12	32	2	54	51	1	3	3	420	440	23	7	3	214	223	21	13	3	135	115	1	21	3	103	123
14	32	2	113	104	3	3	3	174	143	1	9	3	323	354	1	15	3	401	402	3	21	3	375	364
16	32	2	69	66	5	3	3	577	548	3	9	3	483	488	3	15	3	515	496	5	21	3	180	168
2	34	2	317	311	7	3	3	352	365	5	9	3	451	427	5	15	3	229	231	7	21	3	211	229
10	34	2	227	240	9	3	3	133	142	7	9	3	390	382	7	15	3	286	289	9	21	3	420	403
14	34	2	310	299	11	3	3	396	384	9	9	3	186	198	9	15	3	381	388	11	21	3	104	120
2	36	2	156	174	13	3	3	323	311	11	9	3	312	311	11	15	3	272	263	13	21	3	275	256
4	36	2	116	98	15	3	3	135	120	13	9	3	249	253	13	15	3	222	222	15	21	3	292	298
6	36	2	249	245	17	3	3	258	267	15	9	3	246	227	15	15	3	305	304	17	21	3	56	14

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
19	21	3	158	168	13	29	3	141	146	7	39	3	120	114	4	6	4	234	210	10	12	4	378	379
1	23	3	327	328	15	29	3	94	93	1	41	3	125	109	6	6	4	834	801	12	12	4	211	216
3	23	3	113	112	17	29	3	186	183	3	41	3	187	180	8	6	4	266	269	14	12	4	299	292
5	23	3	323	317	1	31	3	157	140	5	41	3	116	133	12	6	4	90	83	16	12	4	181	163
7	23	3	384	383	3	31	3	280	301	7	41	3	110	112	14	6	4	81	97	18	12	4	100	89
9	23	3	177	177	5	31	3	133	135	1	43	3	108	106	16	6	4	159	148	22	12	4	151	147
11	23	3	371	359	7	31	3	139	142	0	0	4	619	641	18	6	4	403	403	2	14	4	204	214
13	23	3	188	175	9	31	3	210	205	8	0	4	466	454	20	6	4	102	111	4	14	4	454	448
15	23	3	152	151	11	31	3	101	105	12	0	4	615	621	22	6	4	239	242	6	14	4	358	390
17	23	3	215	226	13	31	3	167	159	16	0	4	268	276	0	8	4	316	284	8	14	4	485	493
19	23	3	122	130	15	31	3	187	179	20	0	4	66	71	2	8	4	608	606	10	14	4	140	159
1	25	3	163	168	1	33	3	141	144	2	2	4	128	134	4	8	4	335	336	14	14	4	131	122
3	25	3	295	320	3	33	3	159	160	4	2	4	813	799	6	8	4	261	262	16	14	4	281	258
5	25	3	278	278	5	33	3	163	174	6	2	4	383	379	8	8	4	205	207	18	14	4	174	172
7	25	3	284	298	7	33	3	152	151	8	2	4	755	723	10	8	4	398	395	20	14	4	278	267
9	25	3	291	284	9	33	3	107	125	10	2	4	144	133	12	8	4	163	159	22	14	4	126	128
11	25	3	197	190	11	33	3	170	169	12	2	4	271	270	14	8	4	444	444	0	16	4	727	760
15	25	3	158	167	13	33	3	130	144	14	2	4	50	36	16	8	4	128	111	2	16	4	193	188
17	25	3	124	122	15	33	3	133	133	16	2	4	216	218	18	8	4	182	173	4	16	4	340	358
19	25	3	118	120	1	35	3	161	186	18	2	4	128	118	22	8	4	221	222	8	16	4	164	174
1	27	3	180	193	3	35	3	163	175	20	2	4	276	282	2	10	4	184	183	10	16	4	64	72
3	27	3	329	320	5	35	3	177	176	22	2	4	67	68	4	10	4	312	285	12	16	4	481	486
5	27	3	186	186	7	35	3	117	138	0	4	4	521	537	6	10	4	664	685	14	16	4	117	121
7	27	3	244	250	9	35	3	103	88	2	4	4	674	630	8	10	4	70	69	16	16	4	292	285
9	27	3	282	289	11	35	3	152	154	4	4	4	216	222	14	10	4	117	124	2	18	4	61	57
11	27	3	164	167	13	35	3	151	138	6	4	4	71	47	16	10	4	107	128	4	18	4	421	424
13	27	3	150	151	1	37	3	137	138	8	4	4	382	386	18	10	4	371	378	6	18	4	187	176
15	27	3	187	181	3	37	3	207	206	10	4	4	341	322	20	10	4	121	126	8	18	4	527	517
17	27	3	95	89	5	37	3	99	102	12	4	4	519	550	22	10	4	257	257	16	18	4	287	287
1	29	3	271	265	7	37	3	109	106	14	4	4	240	228	0	12	4	659	679	18	18	4	68	66
5	29	3	307	314	9	37	3	215	200	16	4	4	319	322	2	12	4	575	578	20	18	4	285	290
7	29	3	322	317	11	37	3	86	76	18	4	4	125	113	4	12	4	310	321	0	20	4	330	360
9	29	3	68	76	1	39	3	224	217	20	4	4	62	46	6	12	4	97	103	2	20	4	363	365
11	29	3	246	241	5	39	3	183	175	22	4	4	176	172	8	12	4	175	175	4	20	4	152	152

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	20	4	50	50	4	28	4	162	151	0	40	4	158	157	17	5	5	91	67	21	11	5	205	206
8	20	4	48	63	6	28	4	120	121	4	40	4	59	61	19	5	5	213	212	1	13	5	460	473
10	20	4	227	229	8	28	4	78	78	8	40	4	62	39	21	5	5	196	198	3	13	5	43	46
12	20	4	420	413	10	28	4	246	247	2	42	4	129	124	1	7	5	439	457	5	13	5	414	426
14	20	4	246	242	12	28	4	166	155	1	1	5	254	278	3	7	5	232	246	7	13	5	360	356
16	20	4	231	226	14	28	4	256	247	3	1	5	391	443	5	7	5	323	337	9	13	5	107	102
18	20	4	114	108	16	28	4	89	78	5	1	5	245	242	7	7	5	335	341	11	13	5	259	267
20	20	4	80	81	2	30	4	145	145	7	1	5	365	342	9	7	5	147	145	13	13	5	167	162
2	22	4	81	91	4	30	4	250	235	13	1	5	275	263	11	7	5	347	334	15	13	5	78	68
4	22	4	285	285	6	30	4	235	229	15	1	5	324	302	13	7	5	264	281	17	13	5	229	226
6	22	4	384	382	8	30	4	281	282	17	1	5	208	207	17	7	5	276	296	19	13	5	188	191
8	22	4	289	287	10	30	4	116	94	19	1	5	169	183	19	7	5	166	176	21	13	5	76	71
10	22	4	228	223	16	30	4	175	172	21	1	5	144	154	21	7	5	163	163	1	15	5	176	186
12	22	4	129	112	0	32	4	389	393	23	1	5	111	107	1	9	5	400	406	3	15	5	466	472
14	22	4	139	141	2	32	4	159	166	1	3	5	289	324	3	9	5	290	283	5	15	5	105	111
16	22	4	109	114	4	32	4	236	244	3	3	5	209	202	5	9	5	534	538	7	15	5	248	251
18	22	4	224	237	6	32	4	87	87	5	3	5	445	457	7	9	5	276	273	9	15	5	403	400
20	22	4	110	127	8	32	4	60	55	7	3	5	514	525	9	9	5	205	214	11	15	5	137	135
0	24	4	196	188	12	32	4	264	265	9	3	5	147	140	11	9	5	262	260	13	15	5	228	231
2	24	4	363	382	14	32	4	69	80	11	3	5	384	374	13	9	5	169	175	15	15	5	311	299
4	24	4	45	41	4	34	4	231	244	13	3	5	356	343	15	9	5	187	179	17	15	5	95	107
10	24	4	316	319	6	34	4	58	26	15	3	5	187	169	17	9	5	246	239	19	15	5	182	182
12	24	4	172	156	8	34	4	261	249	17	3	5	305	297	19	9	5	150	163	21	15	5	164	157
14	24	4	313	297	12	34	4	70	72	19	3	5	147	140	21	9	5	159	168	1	17	5	410	432
18	24	4	101	84	0	36	4	329	339	21	3	5	74	83	1	11	5	250	259	3	17	5	341	343
2	26	4	252	267	2	36	4	58	73	23	3	5	199	197	3	11	5	364	375	5	17	5	359	380
6	26	4	485	495	4	36	4	159	166	1	5	5	556	560	5	11	5	104	90	7	17	5	227	225
8	26	4	76	66	10	36	4	109	113	3	5	5	668	677	7	11	5	202	206	9	17	5	269	271
10	26	4	305	296	12	36	4	249	243	5	5	5	530	535	9	11	5	374	369	11	17	5	208	198
12	26	4	68	75	2	38	4	136	127	7	5	5	388	391	11	11	5	199	189	13	17	5	285	275
14	26	4	71	93	4	38	4	211	217	9	5	5	478	462	13	11	5	182	177	15	17	5	180	168
18	26	4	251	255	6	38	4	194	192	11	5	5	64	60	15	11	5	334	314	17	17	5	157	154
0	28	4	299	310	8	38	4	167	138	13	5	5	353	346	17	11	5	136	142	19	17	5	164	163
2	28	4	372	386	10	38	4	136	136	15	5	5	299	294	19	11	5	206	198	21	17	5	122	113

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC
1	19	5	307	310
3	19	5	104	106
5	19	5	292	288
7	19	5	267	273
9	19	5	107	105
11	19	5	344	343
13	19	5	266	266
15	19	5	85	111
17	19	5	216	216
19	19	5	128	129
1	21	5	230	242
3	21	5	357	348
5	21	5	212	220
7	21	5	226	217
9	21	5	259	250
11	21	5	99	93
13	21	5	179	179
15	21	5	217	210
17	21	5	55	49
19	21	5	125	133
1	23	5	249	240
3	23	5	151	148
5	23	5	215	203
7	23	5	258	251
9	23	5	81	88
11	23	5	323	321
13	23	5	187	187
15	23	5	62	76
17	23	5	212	209
19	23	5	132	137
1	25	5	170	177
3	25	5	267	268
5	25	5	148	150
7	25	5	235	247
9	25	5	258	254
11	25	5	127	128
13	25	5	184	190
15	25	5	142	158
17	25	5	152	156
1	27	5	135	133
3	27	5	311	309
5	27	5	153	136
7	27	5	174	185
9	27	5	252	248
11	27	5	105	121
13	27	5	149	152
15	27	5	168	174
17	27	5	142	131
1	29	5	300	302
3	29	5	56	53
5	29	5	267	255
7	29	5	241	244
9	29	5	69	57
11	29	5	224	218
13	29	5	181	186
1	31	5	172	166
3	31	5	283	282
5	31	5	68	79
7	31	5	204	204
9	31	5	181	183
11	31	5	119	109
13	31	5	132	134
15	31	5	162	150
1	33	5	205	210
3	33	5	122	120
5	33	5	155	158
7	33	5	159	170
9	33	5	118	116
11	33	5	162	162
13	33	5	153	141
1	35	5	181	201
3	35	5	144	144
5	35	5	162	157
7	35	5	147	144
9	35	5	67	84
11	35	5	182	187
1	37	5	97	95
3	37	5	193	196
5	37	5	97	103
7	37	5	132	128
9	37	5	199	204
1	39	5	175	156
5	39	5	184	190
7	39	5	154	143
1	41	5	126	120
3	41	5	149	131
2	0	6	331	317
6	0	6	516	500
10	0	6	490	485
14	0	6	284	255
18	0	6	337	327
0	2	6	410	418
2	2	6	762	768
4	2	6	190	193
6	2	6	84	79
8	2	6	91	81
10	2	6	196	220
12	2	6	231	212
14	2	6	466	461
16	2	6	97	93
18	2	6	94	87
22	2	6	139	139
2	4	6	244	250
4	4	6	371	376
6	4	6	459	449
8	4	6	346	324
10	4	6	337	326
14	4	6	140	127
16	4	6	249	245
18	4	6	271	274
20	4	6	168	195
22	4	6	184	192
0	6	6	778	759
2	6	6	317	353
4	6	6	425	440
6	6	6	137	144
8	6	6	163	161
10	6	6	144	143
12	6	6	467	467
14	6	6	157	159
16	6	6	306	304
22	6	6	114	97
2	8	6	112	113
4	8	6	454	475
6	8	6	57	47
8	8	6	525	536
10	8	6	136	137
12	8	6	180	187
14	8	6	59	39
16	8	6	348	338
18	8	6	66	60
20	8	6	320	325
0	10	6	541	569
2	10	6	121	126
4	10	6	330	350
6	10	6	125	119
8	10	6	188	172
10	10	6	100	107
12	10	6	347	333
14	10	6	281	265
16	10	6	247	248
20	10	6	56	70
2	12	6	181	187
4	12	6	385	388
6	12	6	301	283
8	12	6	375	369
10	12	6	252	253
12	12	6	69	66
14	12	6	113	105
16	12	6	196	198
18	12	6	151	156
20	12	6	264	261
0	14	6	377	383
2	14	6	362	361
4	14	6	334	338
6	14	6	116	117
8	14	6	127	125
10	14	6	329	340
12	14	6	197	187
14	14	6	397	379
16	14	6	147	148
18	14	6	74	61
20	14	6	74	51
2	16	6	347	357
4	16	6	125	120
6	16	6	558	542
10	16	6	349	355
14	16	6	81	76
18	16	6	300	300
20	16	6	121	113

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	18	6	148	145	0	26	6	405	394	4	38	6	110	99	1	7	7	222	222	7	13	7	311	318
2	18	6	356	363	4	26	6	216	228	1	1	7	329	337	3	7	7	133	133	9	13	7	112	106
6	18	6	54	28	6	26	6	63	41	3	1	7	464	464	7	7	7	330	337	11	13	7	311	312
8	18	6	107	108	8	26	6	181	193	5	1	7	231	230	9	7	7	181	178	13	13	7	201	199
10	18	6	330	340	12	26	6	340	326	7	1	7	207	206	11	7	7	234	237	15	13	7	61	64
12	18	6	130	121	2	28	6	124	116	9	1	7	235	227	13	7	7	228	222	17	13	7	162	168
14	18	6	365	373	4	28	6	286	282	11	1	7	251	229	15	7	7	211	221	19	13	7	150	145
16	18	6	52	45	6	28	6	189	179	13	1	7	216	225	17	7	7	250	252	1	15	7	253	245
18	18	6	111	115	8	28	6	352	342	15	1	7	272	270	19	7	7	148	149	3	15	7	353	358
2	20	6	199	213	10	28	6	72	65	17	1	7	115	118	21	7	7	104	118	5	15	7	278	284
4	20	6	268	278	14	28	6	62	46	19	1	7	141	148	1	9	7	229	251	7	15	7	85	92
6	20	6	349	333	16	28	6	121	131	21	1	7	145	159	3	9	7	164	148	9	15	7	366	370
8	20	6	240	229	0	30	6	203	191	1	3	7	438	438	5	9	7	346	365	11	15	7	123	110
10	20	6	210	199	2	30	6	325	300	3	3	7	234	244	7	9	7	375	367	13	15	7	176	188
12	20	6	128	129	4	30	6	122	125	5	3	7	356	359	9	9	7	285	289	15	15	7	228	228
16	20	6	124	122	8	30	6	110	112	7	3	7	335	359	11	9	7	270	270	17	15	7	111	112
18	20	6	255	255	10	30	6	199	199	9	3	7	111	108	13	9	7	265	243	19	15	7	170	165
0	22	6	261	264	12	30	6	182	184	11	3	7	332	348	15	9	7	194	190	1	17	7	232	242
2	22	6	196	217	14	30	6	195	184	13	3	7	246	230	17	9	7	140	152	3	17	7	269	263
4	22	6	175	196	2	32	6	175	170	15	3	7	95	107	19	9	7	147	152	5	17	7	227	235
8	22	6	155	160	4	32	6	80	71	17	3	7	269	260	21	9	7	116	116	7	17	7	201	194
10	22	6	254	253	6	32	6	311	299	19	3	7	118	139	1	11	7	143	138	9	17	7	171	176
12	22	6	299	287	8	32	6	147	140	21	3	7	98	90	3	11	7	422	409	11	17	7	246	236
14	22	6	192	195	10	32	6	167	155	1	5	7	145	153	5	11	7	202	200	13	17	7	222	218
16	22	6	214	200	2	34	6	240	238	3	5	7	408	420	7	11	7	188	190	15	17	7	197	197
18	22	6	98	96	6	34	6	65	52	5	5	7	309	299	9	11	7	401	394	17	17	7	141	148
2	24	6	126	112	10	34	6	193	196	7	5	7	232	226	11	11	7	186	195	19	17	7	133	141
4	24	6	344	334	2	36	6	133	142	9	5	7	406	412	13	11	7	160	163	1	19	7	341	348
6	24	6	113	122	4	36	6	84	69	11	5	7	57	22	15	11	7	305	304	3	19	7	118	114
8	24	6	324	318	6	36	6	280	271	13	5	7	309	303	17	11	7	74	63	5	19	7	291	302
10	24	6	58	62	8	36	6	92	78	15	5	7	303	301	19	11	7	148	157	7	19	7	167	167
12	24	6	77	78	10	36	6	208	203	17	5	7	87	77	1	13	7	443	440	9	19	7	158	153
14	24	6	55	45	0	38	6	246	217	19	5	7	165	154	3	13	7	92	93	11	19	7	240	235
16	24	6	167	166	2	38	6	184	176	21	5	7	181	195	5	13	7	385	369	13	19	7	188	184

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC
15	19	7	84	77
17	19	7	220	226
1	21	7	152	168
3	21	7	275	279
5	21	7	103	98
7	21	7	205	209
9	21	7	218	222
11	21	7	86	84
13	21	7	161	165
15	21	7	227	225
17	21	7	109	80
1	23	7	309	324
3	23	7	116	137
5	23	7	262	261
7	23	7	187	166
9	23	7	88	90
11	23	7	188	190
13	23	7	145	140
15	23	7	101	102
17	23	7	170	161
1	25	7	244	240
3	25	7	261	271
5	25	7	139	154
7	25	7	177	181
9	25	7	211	207
11	25	7	186	185
13	25	7	139	140
15	25	7	160	171
1	27	7	186	213
3	27	7	305	307
5	27	7	175	173
7	27	7	157	155
9	27	7	231	210
11	27	7	102	98
13	27	7	145	136
15	27	7	159	139
1	29	7	222	227
3	29	7	60	50
5	29	7	223	225
7	29	7	170	173
11	29	7	159	175
13	29	7	172	178
1	31	7	127	120
3	31	7	192	201
5	31	7	78	87
7	31	7	145	144
9	31	7	183	185
11	31	7	98	93
13	31	7	116	114
1	33	7	133	142
3	33	7	103	109
5	33	7	136	150
7	33	7	188	173
9	33	7	104	110
11	33	7	139	147
1	35	7	152	167
3	35	7	92	103
5	35	7	92	107
7	35	7	128	132
9	35	7	96	95
1	37	7	98	98
3	37	7	163	170
5	37	7	80	76
7	37	7	118	124
1	39	7	179	176
0	0	8	625	645
4	0	8	389	369
8	0	8	225	239
12	0	8	381	391
16	0	8	223	241
2	2	8	116	132
4	2	8	418	427
6	2	8	196	186
8	2	8	340	340
10	2	8	69	79
12	2	8	79	77
14	2	8	67	82
16	2	8	280	278
18	2	8	107	110
20	2	8	273	284
0	4	8	456	452
2	4	8	306	314
4	4	8	260	257
6	4	8	142	134
8	4	8	140	147
10	4	8	256	241
12	4	8	286	277
14	4	8	256	249
16	4	8	177	192
18	4	8	81	83
20	4	8	68	49
2	6	8	168	179
4	6	8	184	178
6	6	8	494	485
8	6	8	224	224
10	6	8	251	262
12	6	8	50	65
14	6	8	92	66
16	6	8	119	131
18	6	8	255	265
20	6	8	144	144
0	8	8	153	167
2	8	8	444	450
4	8	8	93	104
6	8	8	51	38
8	8	8	88	85
10	8	8	370	348
12	8	8	97	82
14	8	8	385	390
18	8	8	134	129
2	10	8	203	214
4	10	8	95	144
6	10	8	519	500
8	10	8	123	120
10	10	8	252	262
12	10	8	119	111
14	10	8	101	80
16	10	8	68	62
18	10	8	271	265
0	12	8	302	307
2	12	8	335	340
4	12	8	217	220
8	12	8	121	112
10	12	8	341	332
12	12	8	193	204
14	12	8	309	313
16	12	8	148	160
18	12	8	105	113
2	14	8	101	108
4	14	8	359	365
6	14	8	244	260
8	14	8	327	330
10	14	8	138	157
12	14	8	68	91
16	14	8	205	206
18	14	8	128	136
0	16	8	508	526
2	16	8	79	90
4	16	8	262	267
6	16	8	65	50
8	16	8	157	138
10	16	8	95	90
12	16	8	389	373
14	16	8	98	84
16	16	8	189	201
2	18	8	53	53
4	18	8	347	358
6	18	8	67	70
8	18	8	390	395
12	18	8	99	109
14	18	8	77	78
16	18	8	229	213
0	20	8	452	445
2	20	8	222	224
4	20	8	222	216
10	20	8	132	121
12	20	8	297	294
14	20	8	155	162
16	20	8	152	153
2	22	8	152	145
4	22	8	204	193
6	22	8	311	318
8	22	8	219	215
10	22	8	204	212
14	22	8	77	75
16	22	8	116	122
0	24	8	199	199
2	24	8	389	368
4	24	8	81	89
6	24	8	117	94

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	24	8	250	241	7	1	9	224	243	15	7	9	89	92	15	15	9	211	200	3	25	9	105	135
14	24	8	274	270	9	1	9	219	217	17	7	9	195	195	17	15	9	81	75	5	25	9	211	218
2	26	8	162	157	11	1	9	194	186	19	7	9	123	128	1	17	9	198	196	7	25	9	191	177
6	26	8	334	344	13	1	9	133	127	1	9	9	197	188	3	17	9	216	212	9	25	9	136	132
8	26	8	79	63	15	1	9	229	225	3	9	9	362	357	5	17	9	222	217	11	25	9	151	146
10	26	8	169	181	17	1	9	133	118	5	9	9	193	189	7	17	9	175	183	13	25	9	106	112
12	26	8	65	51	19	1	9	164	156	7	9	9	294	301	9	17	9	193	191	1	27	9	111	122
14	26	8	80	82	1	3	9	374	374	9	9	9	178	166	11	17	9	179	179	3	27	9	122	119
0	28	8	143	150	3	3	9	66	58	11	9	9	268	258	13	17	9	121	124	5	27	9	176	177
2	28	8	261	261	5	3	9	353	354	13	9	9	175	174	15	17	9	140	147	7	27	9	171	159
4	28	8	62	50	7	3	9	193	207	15	9	9	108	113	17	17	9	150	152	9	27	9	229	224
6	28	8	72	68	9	3	9	51	71	17	9	9	166	171	1	19	9	259	264	11	27	9	108	111
8	28	8	77	78	11	3	9	237	236	1	11	9	191	227	3	19	9	87	88	1	29	9	143	171
10	28	8	207	216	13	3	9	211	200	3	11	9	248	237	5	19	9	268	261	5	29	9	156	174
12	28	8	167	172	15	3	9	120	115	5	11	9	193	194	7	19	9	222	216	7	29	9	192	178
2	30	8	112	99	17	3	9	215	210	7	11	9	241	245	9	19	9	130	123	11	29	9	155	156
4	30	8	193	203	19	3	9	134	132	9	11	9	298	285	11	19	9	210	198	1	31	9	97	88
6	30	8	200	197	1	5	9	130	135	11	11	9	85	92	13	19	9	181	171	3	31	9	178	165
8	30	8	239	238	3	5	9	365	354	13	11	9	189	206	15	19	9	98	79	5	31	9	128	123
10	30	8	115	108	5	5	9	133	121	15	11	9	237	222	1	21	9	157	156	7	31	9	136	144
0	32	8	246	245	7	5	9	219	221	1	13	9	239	245	3	21	9	302	287	9	31	9	199	189
2	32	8	83	64	9	5	9	258	258	5	13	9	294	283	5	21	9	104	121	1	33	9	139	149
4	32	8	80	92	11	5	9	144	137	7	13	9	246	235	7	21	9	167	163	3	33	9	138	135
8	32	8	113	101	13	5	9	165	181	11	13	9	275	258	9	21	9	245	244	5	33	9	131	121
10	32	8	73	71	15	5	9	180	175	13	13	9	193	193	11	21	9	50	72	7	33	9	130	126
4	34	8	225	210	17	5	9	88	77	15	13	9	107	116	13	21	9	151	168	1	35	9	117	112
6	34	8	65	41	19	5	9	127	139	17	13	9	221	215	15	21	9	175	172	2	0	10	275	295
8	34	8	252	246	1	7	9	297	290	1	15	9	264	292	1	23	9	193	189	6	0	10	537	537
0	36	8	234	221	3	7	9	216	207	3	15	9	233	233	5	23	9	235	232	10	0	10	303	307
2	36	8	93	96	5	7	9	295	301	5	15	9	147	159	7	23	9	191	201	14	0	10	86	77
4	36	8	114	98	7	7	9	182	181	7	15	9	250	256	9	23	9	87	115	18	0	10	214	210
1	1	9	294	302	9	7	9	214	211	9	15	9	251	233	11	23	9	190	212	0	2	10	126	117
3	1	9	315	320	11	7	9	228	241	11	15	9	144	136	13	23	9	137	139	2	2	10	316	320
5	1	9	183	192	13	7	9	202	191	13	15	9	186	193	1	25	9	155	158	4	2	10	156	148

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC
6	2	10	53	48
8	2	10	88	86
10	2	10	372	353
12	2	10	123	126
14	2	10	294	296
16	2	10	80	86
2	4	10	132	146
4	4	10	245	240
6	4	10	277	277
8	4	10	340	335
10	4	10	196	206
12	4	10	74	83
14	4	10	62	57
16	4	10	120	118
18	4	10	178	172
0	6	10	197	189
2	6	10	90	89
4	6	10	247	250
6	6	10	82	62
8	6	10	182	179
10	6	10	129	111
12	6	10	321	305
14	6	10	150	155
16	6	10	182	203
18	6	10	59	56
2	8	10	56	72
4	8	10	297	304
6	8	10	68	60
8	8	10	363	356
10	8	10	65	63
12	8	10	62	48
16	8	10	191	189
0	10	10	423	409
4	10	10	278	275
6	10	10	100	101
8	10	10	183	182
10	10	10	97	97
12	10	10	352	347
14	10	10	63	57
16	10	10	226	220
4	12	10	305	304
6	12	10	258	255
8	12	10	313	298
10	12	10	160	154
12	12	10	76	54
14	12	10	97	85
16	12	10	128	117
0	14	10	244	227
2	14	10	373	365
4	14	10	58	40
6	14	10	102	106
8	14	10	78	76
10	14	10	232	222
12	14	10	132	148
14	14	10	209	215
16	14	10	104	109
2	16	10	179	173
6	16	10	366	346
8	16	10	70	72
10	16	10	193	188
12	16	10	50	52
14	16	10	98	89
0	18	10	88	85
2	18	10	372	346
4	18	10	132	139
10	18	10	216	197
12	18	10	56	36
14	18	10	258	258
2	20	10	164	155
4	20	10	115	108
6	20	10	280	275
8	20	10	164	157
10	20	10	169	180
4	22	10	167	178
8	22	10	82	60
10	22	10	94	98
12	22	10	194	195
2	24	10	58	60
4	24	10	254	255
6	24	10	70	68
8	24	10	273	262
10	24	10	82	64
0	26	10	355	349
4	26	10	154	157
10	26	10	35	41
2	32	10	122	111
4	32	10	61	60
1	1	11	178	171
3	1	11	295	296
5	1	11	233	219
7	1	11	191	186
9	1	11	262	258
11	1	11	165	167
13	1	11	167	158
15	1	11	177	170
1	3	11	318	291
3	3	11	82	63
5	3	11	274	268
7	3	11	186	186
9	3	11	56	48
11	3	11	195	208
13	3	11	145	143
15	3	11	69	82
1	5	11	81	73
3	5	11	264	255
5	5	11	80	43
7	5	11	180	170
9	5	11	271	260
11	5	11	77	76
13	5	11	143	133
15	5	11	232	214
1	7	11	252	237
3	7	11	220	211
5	7	11	181	175
7	7	11	245	249
9	7	11	110	127
11	7	11	157	161
13	7	11	160	157
15	7	11	138	119
1	9	11	168	153
3	9	11	182	178
5	9	11	169	170
7	9	11	185	169
9	9	11	169	165
11	9	11	179	182
13	9	11	157	149
15	9	11	157	148
1	11	11	175	166
3	11	11	347	352
5	11	11	121	102
7	11	11	211	215
9	11	11	200	210
11	11	11	63	30
13	11	11	118	133
15	11	11	157	154
1	13	11	189	179
5	13	11	228	231
7	13	11	176	177
13	13	11	180	181
1	15	11	214	213
3	15	11	233	224
5	15	11	133	130
7	15	11	148	154
9	15	11	156	156
1	17	11	99	121
3	17	11	187	183
5	17	11	135	136
7	17	11	131	124
11	17	11	128	135
13	17	11	155	154
1	19	11	210	188
3	19	11	107	125
5	19	11	112	121
11	19	11	130	128
1	21	11	120	105
3	21	11	210	200
5	21	11	59	56
7	21	11	142	131
9	21	11	213	207
1	23	11	173	167
3	23	11	53	31
9	23	11	82	88
1	25	11	139	133
3	25	11	147	151
7	25	11	129	114
7	27	11	116	108
0	0	12	461	448
4	0	12	156	165
8	0	12	116	111
12	0	12	275	270

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GD-EDTA STRUCTURE

H	K	L	FO	FC
2	2	12	118	117
4	2	12	284	279
6	2	12	121	124
8	2	12	288	279
12	2	12	71	80
0	4	12	280	274
2	4	12	261	263
4	4	12	151	146
6	4	12	55	46
12	4	12	208	196
14	4	12	173	169
2	6	12	217	209
4	6	12	134	137
6	6	12	270	235
8	6	12	151	141
10	6	12	170	164
2	8	12	379	371
4	8	12	66	44
6	8	12	92	96
2	10	12	166	165
4	10	12	65	68
6	10	12	311	312
8	10	12	68	76
10	10	12	168	179
0	12	12	193	193
2	12	12	225	226
4	12	12	74	74
4	14	12	261	264
6	14	12	159	150
0	16	12	204	225
2	16	12	43	70
4	16	12	74	98
6	18	12	33	48
10	18	12	30	51
1	1	13	129	126
3	1	13	144	136
5	1	13	154	156
7	1	13	137	124
9	1	13	158	160
11	1	13	169	159
1	3	13	207	205
5	3	13	179	166
7	3	13	186	170
9	3	13	83	66
11	3	13	175	172
1	5	13	105	90
3	5	13	164	181
5	5	13	120	120
1	7	13	176	169
3	7	13	144	124
5	7	13	193	182
9	7	13	62	81
11	7	13	184	175
1	9	13	129	150
3	9	13	139	141
5	11	13	136	136
7	11	13	149	156
1	13	13	199	193
7	13	13	140	130
5	15	13	88	92
7	15	13	152	145
3	17	13	187	177
5	17	13	135	126
1	19	13	167	158
3	19	13	61	55
5	19	13	154	143
1	21	13	107	101
3	21	13	201	181
2	0	14	143	147
6	0	14	246	240
0	2	14	93	97
2	2	14	216	206
4	2	14	66	70
2	4	14	119	111
4	4	14	144	130
6	4	14	182	176
8	4	14	139	142
4	8	14	218	192
8	8	14	33	217
0	10	14	278	254
6	10	14	56	31
2	12	14	105	95
4	12	14	200	185
6	12	14	152	132
0	14	14	218	203
2	14	14	212	201
2	16	14	141	134
1	1	15	123	105
1	3	15	162	159

APPENDIX D

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	814	714	6	8	0	355	348	18	14	0	187	171	0	24	0	154	132	0	36	0	360	350
8	0	0	226	220	8	8	0	103	122	20	14	0	278	264	2	24	0	489	488	2	36	0	204	204
12	0	0	597	550	10	8	0	564	575	0	16	0	949	934	4	24	0	255	249	4	36	0	178	181
16	0	0	294	268	12	8	0	31	17	2	16	0	295	242	8	24	0	73	71	6	36	0	70	46
4	2	0	777	756	14	8	0	617	563	4	16	0	229	214	10	24	0	479	471	8	36	0	120	122
6	2	0	496	467	18	8	0	123	113	8	16	0	317	300	12	24	0	82	84	4	38	0	207	216
8	2	0	570	553	20	8	0	91	80	10	16	0	134	138	14	24	0	369	367	3	1	1	493	524
10	2	0	355	363	2	10	0	493	441	12	16	0	571	563	16	24	0	57	30	5	1	1	558	575
12	2	0	51	48	4	10	0	197	163	16	16	0	234	240	2	26	0	247	257	7	1	1	367	362
16	2	0	508	457	6	10	0	852	866	18	16	0	66	18	6	26	0	548	544	9	1	1	632	612
18	2	0	194	172	8	10	0	309	276	2	18	0	170	165	8	26	0	89	87	11	1	1	322	305
20	2	0	346	320	10	10	0	335	361	4	18	0	478	470	10	26	0	131	146	13	1	1	276	279
2	4	0	892	820	12	10	0	126	115	6	18	0	55	35	12	26	0	59	30	15	1	1	338	340
4	4	0	265	267	14	10	0	224	208	8	18	0	404	382	14	26	0	180	171	17	1	1	225	218
6	4	0	157	152	16	10	0	95	97	10	18	0	189	203	16	26	0	76	73	19	1	1	234	221
8	4	0	234	181	18	10	0	489	442	14	18	0	55	12	0	28	0	173	153	21	1	1	178	172
10	4	0	304	285	20	10	0	62	81	16	18	0	378	412	2	28	0	421	425	3	3	1	75	71
12	4	0	350	325	0	12	0	1038	917	18	18	0	101	92	4	28	0	72	74	5	3	1	548	606
14	4	0	444	415	2	12	0	463	503	0	20	0	420	404	8	28	0	131	140	7	3	1	573	587
16	4	0	141	136	4	12	0	235	230	2	20	0	120	139	10	28	0	352	337	9	3	1	232	230
18	4	0	134	130	6	12	0	60	53	4	20	0	451	444	12	28	0	182	193	11	3	1	426	455
20	4	0	131	125	8	12	0	183	176	6	20	0	70	74	14	28	0	297	279	13	3	1	345	325
2	6	0	326	335	10	12	0	544	572	8	20	0	193	203	4	30	0	280	296	15	3	1	132	116
4	6	0	153	134	12	12	0	427	471	10	20	0	192	202	6	30	0	420	410	17	3	1	339	323
6	6	0	652	641	14	12	0	356	345	12	20	0	469	460	8	30	0	305	290	19	3	1	218	206
8	6	0	175	160	16	12	0	237	226	14	20	0	211	213	10	30	0	185	187	21	3	1	76	74
10	6	0	530	480	18	12	0	97	83	16	20	0	227	235	0	32	0	333	315	1	5	1	484	480
14	6	0	121	110	20	12	0	89	47	2	22	0	246	265	2	32	0	67	64	3	5	1	400	406
16	6	0	271	256	4	14	0	706	694	4	22	0	194	206	4	32	0	268	279	5	5	1	91	92
18	6	0	472	425	6	14	0	511	492	6	22	0	509	514	8	32	0	199	188	7	5	1	253	273
20	6	0	222	217	8	14	0	552	554	8	22	0	215	209	10	32	0	74	106	9	5	1	630	594
0	8	0	165	165	10	14	0	61	59	10	22	0	256	263	12	32	0	373	367	11	5	1	178	162
2	8	0	662	665	14	14	0	58	51	14	22	0	114	112	4	34	0	398	401	13	5	1	292	285
4	8	0	477	495	16	14	0	317	306	16	22	0	215	225	8	34	0	384	378	15	5	1	429	413

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
17	5	1	131	150	19	11	1	226	225	9	19	1	215	231	13	27	1	172	162	4	2	2	205	221
19	5	1	215	218	1	13	1	536	516	13	19	1	247	238	15	27	1	241	245	8	2	2	341	336
21	5	1	221	206	3	13	1	119	117	15	19	1	148	134	1	29	1	242	267	10	2	2	663	665
1	7	1	446	428	5	13	1	389	375	17	19	1	204	194	5	29	1	287	303	12	2	2	221	233
3	7	1	219	231	7	13	1	444	424	1	21	1	215	209	7	29	1	241	247	14	2	2	533	504
5	7	1	484	443	9	13	1	135	134	3	21	1	613	603	11	29	1	237	241	16	2	2	80	74
7	7	1	511	504	11	13	1	520	492	5	21	1	85	77	13	29	1	171	174	20	2	2	70	63
9	7	1	448	456	13	13	1	320	324	7	21	1	269	265	1	31	1	132	159	2	4	2	209	193
11	7	1	308	294	17	13	1	337	323	9	21	1	335	321	3	31	1	356	365	4	4	2	457	470
13	7	1	325	323	19	13	1	183	173	11	21	1	121	103	5	31	1	95	125	6	4	2	513	561
15	7	1	133	118	1	15	1	561	493	13	21	1	190	192	7	31	1	180	188	8	4	2	561	598
17	7	1	294	277	3	15	1	464	451	15	21	1	358	335	9	31	1	284	272	10	4	2	372	388
19	7	1	249	232	5	15	1	379	350	17	21	1	134	128	11	31	1	129	143	12	4	2	118	124
21	7	1	74	87	7	15	1	339	313	1	23	1	455	440	13	31	1	211	205	14	4	2	126	135
1	9	1	113	119	9	15	1	468	439	5	23	1	409	383	1	33	1	187	197	16	4	2	280	284
3	9	1	693	622	11	15	1	175	171	7	23	1	235	232	3	33	1	217	236	18	4	2	341	315
5	9	1	485	476	13	15	1	266	259	9	23	1	165	164	5	33	1	265	261	20	4	2	254	243
7	9	1	524	461	15	15	1	287	277	11	23	1	268	262	7	33	1	223	227	0	6	2	690	706
9	9	1	603	583	17	15	1	139	134	13	23	1	259	258	9	33	1	175	166	2	6	2	490	514
11	9	1	360	358	19	15	1	164	152	15	23	1	131	130	11	33	1	196	191	4	6	2	369	333
13	9	1	353	350	1	17	1	351	327	17	23	1	205	207	1	35	1	198	212	6	6	2	108	113
15	9	1	232	229	3	17	1	456	437	1	25	1	303	348	3	35	1	66	125	8	6	2	448	442
17	9	1	271	263	5	17	1	346	311	3	25	1	291	337	5	35	1	190	229	10	6	2	142	144
19	9	1	205	202	7	17	1	351	323	5	25	1	310	325	7	35	1	182	198	12	6	2	503	484
21	9	1	157	142	9	17	1	292	269	7	25	1	211	216	9	35	1	139	144	14	6	2	272	272
1	11	1	730	674	11	17	1	394	362	9	25	1	203	196	1	37	1	88	115	16	6	2	255	255
3	11	1	619	592	13	17	1	133	130	11	25	1	223	228	3	37	1	249	264	18	6	2	87	75
5	11	1	322	301	15	17	1	212	216	13	25	1	150	146	2	0	2	404	413	20	6	2	98	102
7	11	1	528	486	17	17	1	212	207	15	25	1	195	192	6	0	2	700	778	2	8	2	421	370
9	11	1	589	549	19	17	1	159	155	3	27	1	297	343	10	0	2	418	384	4	8	2	730	671
11	11	1	156	160	1	19	1	463	464	5	27	1	287	296	14	0	2	308	347	6	8	2	95	102
13	11	1	308	295	3	19	1	260	260	7	27	1	172	179	18	0	2	517	501	8	8	2	839	834
15	11	1	299	295	5	19	1	347	329	9	27	1	310	295	0	2	2	395	362	10	8	2	76	76
17	11	1	111	120	7	19	1	409	381	11	27	1	165	188	2	2	2	660	646	12	8	2	66	85

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
16	8	2	361	343	6	16	2	619	617	6	24	2	83	81	0	38	2	208	208	3	7	3	439	410
20	8	2	351	332	8	16	2	105	107	8	24	2	512	508	2	38	2	172	198	5	7	3	635	626
0	10	2	983	1028	10	16	2	365	357	12	24	2	91	93	1	1	3	580	657	7	7	3	350	353
2	10	2	310	287	12	16	2	143	146	14	24	2	78	67	3	1	3	413	446	9	7	3	259	287
4	10	2	511	492	14	16	2	224	232	16	24	2	259	251	5	1	3	273	327	11	7	3	332	356
6	10	2	313	316	18	16	2	304	334	0	26	2	543	526	7	1	3	240	260	13	7	3	212	225
8	10	2	387	374	0	18	2	294	300	2	26	2	152	143	9	1	3	542	577	15	7	3	159	167
10	10	2	82	99	2	18	2	799	792	4	26	2	315	303	11	1	3	292	294	17	7	3	334	319
12	10	2	530	551	4	18	2	69	84	8	26	2	231	235	13	1	3	285	299	19	7	3	223	228
14	10	2	176	165	6	18	2	64	79	10	26	2	65	70	15	1	3	199	195	1	9	3	373	387
16	10	2	301	309	8	18	2	112	102	12	26	2	382	389	17	1	3	186	179	3	9	3	485	483
20	10	2	106	106	10	18	2	401	371	14	26	2	61	43	19	1	3	178	176	5	9	3	475	454
2	12	2	142	133	12	18	2	90	85	2	28	2	187	199	21	1	3	203	199	7	9	3	393	387
4	12	2	604	594	14	18	2	443	433	4	28	2	411	402	1	3	3	448	471	9	9	3	205	216
6	12	2	500	482	18	18	2	80	76	6	28	2	243	246	3	3	3	186	158	11	9	3	320	331
8	12	2	563	556	2	20	2	410	426	8	28	2	304	299	5	3	3	557	558	13	9	3	240	261
10	12	2	319	320	4	20	2	318	313	10	28	2	158	151	7	3	3	366	402	15	9	3	228	233
12	12	2	57	39	6	20	2	499	498	14	28	2	72	65	9	3	3	60	75	17	9	3	274	274
14	12	2	122	130	8	20	2	359	343	0	30	2	177	168	11	3	3	375	383	19	9	3	185	177
16	12	2	216	233	10	20	2	317	313	2	30	2	337	342	13	3	3	342	356	1	11	3	545	515
18	12	2	309	293	12	20	2	98	105	4	30	2	198	194	15	3	3	142	136	3	11	3	538	530
20	12	2	265	262	14	20	2	154	143	8	30	2	139	144	17	3	3	257	252	5	11	3	366	340
0	14	2	278	297	16	20	2	202	182	10	30	2	262	262	19	3	3	198	195	7	11	3	309	294
2	14	2	740	734	18	20	2	240	235	12	30	2	231	230	1	5	3	204	208	9	11	3	430	400
4	14	2	220	225	0	22	2	595	586	2	32	2	230	257	3	5	3	621	647	11	11	3	216	220
6	14	2	146	139	2	22	2	381	363	4	32	2	77	106	5	5	3	178	162	15	11	3	285	320
8	14	2	162	153	4	22	2	366	351	6	32	2	391	381	7	5	3	277	308	17	11	3	176	183
10	14	2	455	451	8	22	2	151	154	8	32	2	86	86	9	5	3	453	473	19	11	3	190	200
12	14	2	254	249	10	22	2	225	225	10	32	2	190	195	11	5	3	194	209	1	13	3	657	613
14	14	2	366	364	12	22	2	350	343	0	34	2	57	59	13	5	3	213	219	3	13	3	226	217
16	14	2	173	182	14	22	2	239	232	2	34	2	352	345	15	5	3	324	350	5	13	3	593	594
18	14	2	69	75	16	22	2	229	225	10	34	2	265	279	17	5	3	154	155	7	13	3	500	473
2	16	2	447	430	2	24	2	173	171	4	36	2	137	131	19	5	3	209	208	9	13	3	124	127
4	16	2	132	121	4	24	2	489	484	6	36	2	277	280	1	7	3	637	610	11	13	3	367	365

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
13	13	3	332	327	5	21	3	203	186	13	29	3	179	173	2	4	4	684	652	10	10	4	309	311
15	13	3	69	68	7	21	3	221	222	1	31	3	186	162	4	4	4	182	194	14	10	4	154	159
17	13	3	227	225	9	21	3	426	407	3	31	3	302	318	6	4	4	58	32	16	10	4	112	139
19	13	3	184	194	11	21	3	148	147	5	31	3	172	160	8	4	4	392	423	18	10	4	349	381
1	15	3	456	436	13	21	3	242	234	7	31	3	143	158	10	4	4	340	344	0	12	4	694	701
3	15	3	562	517	15	21	3	331	321	9	31	3	230	228	12	4	4	502	565	2	12	4	609	581
5	15	3	266	258	1	23	3	358	345	11	31	3	128	132	14	4	4	237	228	4	12	4	320	310
7	15	3	298	285	3	23	3	124	129	1	33	3	155	168	16	4	4	272	277	6	12	4	69	82
9	15	3	396	387	5	23	3	344	338	3	33	3	198	192	18	4	4	83	57	8	12	4	212	215
11	15	3	280	269	7	23	3	402	401	5	33	3	185	190	20	4	4	63	43	10	12	4	406	400
13	15	3	220	227	9	23	3	205	189	7	33	3	167	175	2	6	4	47	66	12	12	4	225	235
15	15	3	308	305	11	23	3	360	349	9	33	3	131	150	4	6	4	241	230	14	12	4	262	260
17	15	3	133	144	13	23	3	222	205	1	35	3	193	207	6	6	4	846	846	16	12	4	128	134
19	15	3	148	154	15	23	3	132	121	3	35	3	156	176	8	6	4	255	266	2	14	4	237	231
1	17	3	363	334	1	25	3	190	192	5	35	3	198	201	10	6	4	309	333	4	14	4	525	497
3	17	3	386	362	3	25	3	320	337	7	35	3	151	166	12	6	4	51	45	6	14	4	400	415
5	17	3	386	358	5	25	3	297	293	1	37	3	137	139	14	6	4	115	128	8	14	4	494	504
7	17	3	242	247	7	25	3	314	323	3	37	3	221	232	16	6	4	189	178	10	14	4	137	137
9	17	3	452	445	9	25	3	286	267	0	0	4	595	627	18	6	4	405	414	14	14	4	132	140
11	17	3	182	186	11	25	3	232	217	8	0	4	494	510	20	6	4	105	110	16	14	4	283	286
13	17	3	326	322	13	25	3	202	190	12	0	4	608	644	0	8	4	301	246	18	14	4	164	168
15	17	3	216	226	15	25	3	182	171	16	0	4	225	236	2	8	4	665	648	0	16	4	811	773
17	17	3	202	214	1	27	3	216	216	20	0	4	88	95	4	8	4	310	299	2	16	4	194	189
1	19	3	257	243	3	27	3	380	362	2	2	4	140	144	6	8	4	236	228	4	16	4	350	347
3	19	3	226	221	5	27	3	209	214	4	2	4	800	842	8	8	4	184	194	6	16	4	122	105
5	19	3	316	289	7	27	3	233	239	6	2	4	353	378	10	8	4	423	436	8	16	4	240	242
7	19	3	464	455	9	27	3	314	311	8	2	4	664	719	12	8	4	147	147	10	16	4	51	64
9	19	3	113	110	11	27	3	182	182	10	2	4	131	129	14	8	4	409	437	12	16	4	486	515
11	19	3	361	365	13	27	3	156	154	12	2	4	185	204	16	8	4	76	84	14	16	4	97	102
13	19	3	264	271	1	29	3	327	309	14	2	4	54	40	18	8	4	97	92	16	16	4	231	244
15	19	3	158	160	3	29	3	66	62	16	2	4	239	255	2	10	4	229	213	2	18	4	57	72
17	19	3	288	280	5	29	3	338	340	18	2	4	145	122	4	10	4	336	305	4	18	4	481	475
1	21	3	143	160	7	29	3	354	347	20	2	4	273	269	6	10	4	726	739	6	18	4	206	195
3	21	3	425	420	11	29	3	241	247	0	4	4	542	561	8	10	4	94	88	8	18	4	554	546

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	18	4	97	82	2	28	4	393	392	9	3	5	146	140	17	9	5	215	234	9	17	5	307	291
12	18	4	117	105	4	28	4	176	178	11	3	5	358	355	19	9	5	173	170	11	17	5	219	212
16	18	4	325	317	6	28	4	89	84	13	3	5	357	375	1	11	5	325	307	13	17	5	272	272
18	18	4	89	85	8	28	4	112	97	15	3	5	194	195	3	11	5	409	401	15	17	5	178	177
0	20	4	349	348	10	28	4	296	282	17	3	5	286	278	5	11	5	114	104	17	17	5	143	151
2	20	4	398	389	12	28	4	174	171	19	3	5	189	170	7	11	5	209	210	1	19	5	354	334
4	20	4	147	148	2	30	4	171	163	1	5	5	572	553	9	11	5	393	392	3	19	5	135	137
6	20	4	52	47	4	30	4	301	282	3	5	5	690	700	11	11	5	197	185	5	19	5	306	285
8	20	4	113	121	6	30	4	257	253	5	5	5	520	547	13	11	5	173	162	7	19	5	306	304
10	20	4	272	268	8	30	4	305	311	7	5	5	336	360	15	11	5	321	325	9	19	5	84	90
12	20	4	445	438	10	30	4	106	96	9	5	5	468	488	17	11	5	167	168	11	19	5	334	336
14	20	4	232	244	0	32	4	436	433	11	5	5	110	106	19	11	5	146	157	13	19	5	304	299
16	20	4	187	193	2	32	4	138	145	13	5	5	293	307	1	13	5	502	489	15	19	5	98	99
2	22	4	118	117	4	32	4	259	268	15	5	5	291	290	3	13	5	61	65	17	19	5	207	213
4	22	4	313	305	8	32	4	86	88	17	5	5	94	109	5	13	5	450	455	1	21	5	248	246
6	22	4	443	426	4	34	4	266	280	19	5	5	179	183	7	13	5	409	393	3	21	5	399	385
8	22	4	307	296	8	34	4	268	279	1	7	5	487	493	9	13	5	100	83	5	21	5	247	244
10	22	4	227	207	0	36	4	357	365	3	7	5	274	275	11	13	5	257	273	7	21	5	242	209
12	22	4	69	77	2	36	4	89	106	5	7	5	354	362	13	13	5	189	192	9	21	5	287	273
14	22	4	176	172	4	36	4	171	170	7	7	5	348	369	15	13	5	65	39	11	21	5	148	149
16	22	4	119	125	1	1	5	286	314	9	7	5	158	159	17	13	5	202	204	13	21	5	158	165
0	24	4	177	161	3	1	5	406	472	11	7	5	326	326	1	15	5	207	201	15	21	5	220	222
2	24	4	401	414	5	1	5	264	266	13	7	5	270	298	3	15	5	523	506	1	23	5	268	260
4	24	4	59	55	7	1	5	332	332	15	7	5	191	190	5	15	5	112	117	3	23	5	153	154
10	24	4	366	373	9	1	5	370	400	17	7	5	264	280	7	15	5	274	267	5	23	5	219	201
12	24	4	149	154	11	1	5	281	308	19	7	5	169	179	9	15	5	418	407	7	23	5	280	278
14	24	4	302	300	13	1	5	250	248	1	9	5	436	425	11	15	5	156	165	9	23	5	102	110
2	26	4	277	291	15	1	5	305	301	3	9	5	310	294	13	15	5	230	232	11	23	5	321	326
6	26	4	536	539	17	1	5	207	199	5	9	5	578	585	15	15	5	300	304	13	23	5	211	213
8	26	4	77	78	19	1	5	169	175	7	9	5	297	301	17	15	5	124	137	15	23	5	81	88
10	26	4	302	283	1	3	5	320	345	9	9	5	191	187	1	17	5	438	440	1	25	5	189	192
12	26	4	74	71	3	3	5	203	205	11	9	5	266	282	3	17	5	383	369	3	25	5	266	270
14	26	4	124	125	5	3	5	446	476	13	9	5	167	182	5	17	5	373	378	5	25	5	204	199
0	28	4	333	333	7	3	5	504	534	15	9	5	158	161	7	17	5	228	216	7	25	5	250	248

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
9	25	5	256	253	6	2	6	46	36	4	10	6	337	358	8	18	6	121	122	0	30	6	230	217
11	25	5	156	161	8	2	6	102	90	6	10	6	106	112	10	18	6	362	367	2	30	6	342	323
13	25	5	204	190	10	2	6	257	305	8	10	6	231	223	12	18	6	138	133	4	30	6	131	130
1	27	5	147	140	12	2	6	209	206	10	10	6	124	125	14	18	6	332	362	8	30	6	137	124
3	27	5	334	329	14	2	6	430	444	12	10	6	347	363	2	20	6	229	240	2	32	6	200	193
5	27	5	156	151	16	2	6	84	75	14	10	6	231	237	4	20	6	309	311	4	32	6	65	68
7	27	5	178	184	18	2	6	77	50	16	10	6	190	209	6	20	6	371	357	6	32	6	339	329
9	27	5	273	277	2	4	6	282	279	2	12	6	204	207	8	20	6	245	243	2	34	6	253	268
11	27	5	154	143	4	4	6	396	421	4	12	6	425	421	10	20	6	197	185	1	1	7	350	351
13	27	5	150	150	6	4	6	475	482	6	12	6	322	316	12	20	6	122	106	3	1	7	464	488
1	29	5	327	335	8	4	6	326	330	8	12	6	371	368	14	20	6	89	100	5	1	7	252	260
5	29	5	292	280	10	4	6	308	311	10	12	6	231	240	0	22	6	319	318	7	1	7	182	201
7	29	5	246	263	14	4	6	182	171	12	12	6	60	79	2	22	6	218	230	9	1	7	241	245
11	29	5	219	222	16	4	6	261	264	14	12	6	155	146	4	22	6	189	218	11	1	7	247	239
1	31	5	172	157	18	4	6	254	266	16	12	6	209	221	8	22	6	190	179	13	1	7	219	224
3	31	5	309	302	0	6	6	830	807	18	12	6	159	168	10	22	6	249	246	15	1	7	261	268
5	31	5	89	104	2	6	6	301	328	0	14	6	403	385	12	22	6	313	311	17	1	7	134	124
7	31	5	199	194	4	6	6	417	446	2	14	6	419	411	14	22	6	171	173	1	3	7	475	474
9	31	5	215	208	6	6	6	92	90	4	14	6	326	325	2	24	6	117	114	3	3	7	208	227
1	33	5	226	233	8	6	6	204	216	6	14	6	132	115	4	24	6	380	372	5	3	7	359	365
3	33	5	150	153	10	6	6	168	168	8	14	6	154	141	6	24	6	127	108	7	3	7	330	369
5	33	5	181	175	12	6	6	461	494	10	14	6	367	367	8	24	6	316	322	9	3	7	113	106
7	33	5	173	186	14	6	6	157	167	12	14	6	189	181	12	24	6	58	57	11	3	7	321	353
1	35	5	215	219	16	6	6	228	250	14	14	6	367	365	14	24	6	58	57	13	3	7	261	250
3	35	5	147	149	18	6	6	61	34	16	14	6	120	129	0	26	6	440	427	15	3	7	66	73
5	35	5	176	176	2	8	6	120	113	2	16	6	382	372	4	26	6	239	241	17	3	7	253	240
2	0	6	342	339	4	8	6	515	516	4	16	6	111	113	6	26	6	54	43	1	5	7	154	167
6	0	6	539	561	6	8	6	53	37	6	16	6	612	575	8	26	6	214	218	3	5	7	433	431
10	0	6	452	486	8	8	6	523	542	10	16	6	323	332	12	26	6	332	341	5	5	7	313	323
14	0	6	311	298	10	8	6	126	144	12	16	6	70	55	2	28	6	136	133	7	5	7	217	225
18	0	6	330	328	12	8	6	115	137	14	16	6	135	130	4	28	6	320	309	9	5	7	409	432
0	2	6	425	450	16	8	6	372	370	0	18	6	182	183	6	28	6	206	209	13	5	7	277	285
2	2	6	734	753	0	10	6	583	603	2	18	6	403	405	8	28	6	342	333	15	5	7	302	303
4	2	6	183	197	2	10	6	147	158	6	18	6	59	38	10	28	6	80	67	17	5	7	127	119

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	7	7	257	243	17	13	7	173	175	5	23	7	282	276	16	2	8	288	303	4	12	8	224	213
3	7	7	155	159	1	15	7	280	266	7	23	7	217	205	0	4	8	483	484	8	12	8	149	147
5	7	7	296	309	3	15	7	400	383	9	23	7	85	81	2	4	8	331	330	10	12	8	352	357
7	7	7	359	356	5	15	7	306	305	11	23	7	204	192	4	4	8	266	266	12	12	8	219	228
9	7	7	190	184	7	15	7	98	104	13	23	7	151	154	6	4	8	141	134	14	12	8	292	307
11	7	7	231	230	9	15	7	380	381	1	25	7	259	255	8	4	8	139	146	16	12	8	138	146
13	7	7	253	261	11	15	7	134	131	3	25	7	280	277	10	4	8	266	261	2	14	8	118	111
15	7	7	195	208	13	15	7	174	184	5	25	7	180	180	12	4	8	281	278	4	14	8	403	406
17	7	7	213	235	15	15	7	218	223	7	25	7	194	185	14	4	8	253	259	6	14	8	247	254
1	9	7	243	250	1	17	7	249	240	9	25	7	210	212	16	4	8	147	142	8	14	8	329	331
3	9	7	190	181	3	17	7	298	286	11	25	7	195	199	2	6	8	193	196	10	14	8	121	130
5	9	7	350	369	5	17	7	232	242	1	27	7	211	208	4	6	8	188	190	14	14	8	71	76
7	9	7	379	384	7	17	7	215	224	3	27	7	343	327	6	6	8	494	500	0	16	8	550	554
9	9	7	268	285	9	17	7	186	181	5	27	7	179	186	8	6	8	215	223	2	16	8	90	90
11	9	7	274	283	11	17	7	235	238	7	27	7	157	159	10	6	8	221	223	4	16	8	254	252
13	9	7	252	251	13	17	7	207	227	9	27	7	241	228	14	6	8	109	101	8	16	8	182	179
15	9	7	165	167	15	17	7	203	200	1	29	7	257	248	16	6	8	132	138	10	16	8	111	98
17	9	7	150	154	1	19	7	371	373	5	29	7	249	245	0	8	8	161	167	12	16	8	409	396
1	11	7	163	159	3	19	7	124	114	7	29	7	180	191	2	8	8	486	495	14	16	8	74	78
3	11	7	469	445	5	19	7	316	316	1	31	7	141	138	4	8	8	61	96	4	18	8	383	382
5	11	7	215	220	7	19	7	220	208	3	31	7	223	222	8	8	8	76	76	6	18	8	85	81
7	11	7	197	207	9	19	7	165	143	5	31	7	124	115	10	8	8	386	378	8	18	8	393	397
9	11	7	404	403	11	19	7	249	243	1	33	7	154	160	12	8	8	68	67	10	18	8	55	29
11	11	7	181	182	13	19	7	224	199	0	0	8	652	708	14	8	8	367	386	12	18	8	72	64
13	11	7	149	157	15	19	7	88	61	4	0	8	371	382	2	10	8	231	230	14	18	8	82	72
15	11	7	304	308	1	21	7	148	158	8	0	8	231	255	4	10	8	184	168	0	20	8	469	474
1	13	7	461	442	3	21	7	307	301	12	0	8	361	385	6	10	8	527	514	2	20	8	253	235
3	13	7	98	96	5	21	7	130	129	16	0	8	199	196	8	10	8	122	120	4	20	8	219	217
5	13	7	383	358	7	21	7	197	206	2	2	8	112	130	10	10	8	215	226	8	20	8	61	48
7	13	7	342	338	9	21	7	235	247	4	2	8	450	470	12	10	8	116	104	10	20	8	142	145
9	13	7	78	59	11	21	7	122	108	6	2	8	198	196	14	10	8	148	132	12	20	8	300	310
11	13	7	312	321	13	21	7	159	159	8	2	8	342	334	16	10	8	88	67	2	22	8	177	173
13	13	7	210	222	1	23	7	329	330	10	2	8	58	63	0	12	8	332	319	4	22	8	204	195
15	13	7	60	25	3	23	7	151	149	14	2	8	78	79	2	12	8	364	362	6	22	8	339	348

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
8	22	8	238	222	5	5	9	163	159	1	15	9	276	293	7	25	9	198	191	10	8	10	63	61
10	22	8	206	206	7	5	9	203	199	3	15	9	234	244	1	27	9	136	136	0	10	10	431	421
12	22	8	63	25	9	5	9	282	283	5	15	9	182	186	3	27	9	139	148	4	10	10	286	274
0	24	8	196	187	11	5	9	146	153	7	15	9	246	241	5	27	9	199	188	6	10	10	72	78
2	24	8	430	402	13	5	9	159	167	9	15	9	244	236	2	0	10	287	312	8	10	10	203	213
4	24	8	71	92	15	5	9	180	174	11	15	9	140	149	6	0	10	525	542	10	10	10	121	119
6	24	8	83	70	1	7	9	311	301	13	15	9	181	177	10	0	10	266	269	12	10	10	337	354
10	24	8	280	278	3	7	9	210	215	1	17	9	212	212	14	0	10	136	118	2	12	10	114	121
2	26	8	182	178	5	7	9	296	306	3	17	9	232	228	0	2	10	133	128	4	12	10	314	315
4	26	8	67	68	7	7	9	202	205	5	17	9	236	228	2	2	10	329	340	6	12	10	266	273
6	26	8	373	368	9	7	9	208	210	7	17	9	200	204	4	2	10	138	137	8	12	10	303	295
8	26	8	84	70	11	7	9	229	243	9	17	9	198	193	6	2	10	79	65	10	12	10	147	151
0	28	8	180	175	13	7	9	222	201	11	17	9	187	191	8	2	10	108	103	0	14	10	253	217
2	28	8	285	281	15	7	9	110	86	13	17	9	112	122	10	2	10	370	364	2	14	10	403	372
6	28	8	72	55	1	9	9	199	187	1	19	9	295	290	12	2	10	141	136	6	14	10	89	89
2	30	8	84	97	3	9	9	362	365	3	19	9	94	81	14	2	10	279	281	8	14	10	99	88
4	30	8	219	231	5	9	9	213	220	5	19	9	268	282	2	4	10	153	159	10	14	10	259	251
1	1	9	284	297	7	9	9	301	308	7	19	9	234	227	4	4	10	256	263	12	14	10	135	143
3	1	9	312	321	9	9	9	175	180	9	19	9	122	123	6	4	10	266	286	2	16	10	180	192
5	1	9	209	205	11	9	9	254	254	11	19	9	211	195	8	4	10	329	329	6	16	10	386	374
7	1	9	223	246	13	9	9	193	188	1	21	9	161	164	10	4	10	155	184	10	16	10	182	178
9	1	9	232	234	15	9	9	100	103	3	21	9	320	317	14	4	10	95	90	0	18	10	92	95
11	1	9	196	209	1	11	9	194	223	5	21	9	118	131	0	6	10	230	227	2	18	10	386	360
13	1	9	123	118	3	11	9	282	267	7	21	9	165	162	2	6	10	124	112	4	18	10	142	142
15	1	9	235	226	5	11	9	214	199	9	21	9	261	255	4	6	10	234	239	6	18	10	64	31
1	3	9	390	384	7	11	9	239	238	11	21	9	72	93	6	6	10	64	45	10	18	10	229	229
3	3	9	50	43	9	11	9	295	305	1	23	9	222	221	8	6	10	215	214	2	20	10	165	167
5	3	9	352	365	11	11	9	104	114	3	23	9	64	73	10	6	10	110	119	4	20	10	134	136
7	3	9	198	226	13	11	9	174	186	5	23	9	246	246	12	6	10	323	321	6	20	10	302	294
11	3	9	225	227	1	13	9	263	258	7	23	9	233	218	14	6	10	147	137	8	20	10	170	171
13	3	9	210	222	5	13	9	300	300	9	23	9	113	128	2	8	10	74	74	0	22	10	336	337
15	3	9	112	114	7	13	9	271	262	1	25	9	190	179	4	8	10	325	347	2	22	10	174	164
1	5	9	129	133	11	13	9	258	259	3	25	9	163	161	6	8	10	59	61	4	22	10	186	186
3	5	9	368	356	13	13	9	214	212	5	25	9	240	229	8	8	10	352	356	6	22	10	62	35

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC
2	24	10	71	57
4	24	10	274	283
0	26	10	359	360
1	1	11	179	184
3	1	11	291	312
5	1	11	222	219
7	1	11	187	194
9	1	11	255	265
11	1	11	156	166
1	3	11	317	292
3	3	11	77	69
5	3	11	269	283
7	3	11	188	202
11	3	11	196	203
1	5	11	66	80
3	5	11	276	277
5	5	11	95	69
7	5	11	175	181
9	5	11	260	263
11	5	11	93	103
1	7	11	251	247
3	7	11	204	207
5	7	11	202	192
7	7	11	243	250
9	7	11	97	127
11	7	11	151	158
1	9	11	178	176
3	9	11	188	182
5	9	11	190	191
7	9	11	193	186
9	9	11	165	159
11	9	11	182	184
1	11	11	170	166
3	11	11	359	356
5	11	11	122	117
7	11	11	198	199
9	11	11	207	218
1	13	11	222	197
5	13	11	243	246
7	13	11	192	188
1	15	11	211	214
3	15	11	241	234
5	15	11	148	145
7	15	11	145	145
9	15	11	163	163
1	17	11	138	146
3	17	11	194	192
5	17	11	154	148
7	17	11	140	128
1	19	11	215	196
3	19	11	114	114
7	19	11	174	182
9	19	11	77	73
11	19	11	136	136
5	21	11	74	71
7	21	11	122	128
9	21	11	220	214
11	21	11	72	74
1	23	11	185	182
3	23	11	65	59
5	23	11	163	164
7	23	11	174	184
9	23	11	97	86
1	25	11	139	141
3	25	11	168	155
5	25	11	173	162
7	25	11	131	128
9	25	11	126	124
1	27	11	122	114
3	27	11	142	152
5	27	11	131	140
7	27	11	119	110
1	29	11	159	157
0	0	12	423	441
4	0	12	151	149
8	0	12	139	147
12	0	12	290	293
2	2	12	113	119
4	2	12	300	301
6	2	12	121	133
8	2	12	286	286
10	2	12	71	58
12	2	12	71	51
0	4	12	299	277
2	4	12	251	264
4	4	12	139	127
10	4	12	152	153
12	4	12	207	215
14	4	12	151	160
2	6	12	224	221
4	6	12	153	141
6	6	12	279	269
8	6	12	145	136
10	6	12	153	158
14	6	12	110	96
2	8	12	377	367
10	8	12	216	217
2	10	12	180	175
4	10	12	85	84
6	10	12	332	330
8	10	12	85	83
10	10	12	163	164
0	12	12	221	221
2	12	12	228	221
4	12	12	76	89
8	12	12	71	68
10	12	12	174	177
12	12	12	182	182
4	14	12	268	277
6	14	12	172	161
8	14	12	223	230
10	14	12	63	48
0	16	12	273	256
2	16	12	75	67
4	16	12	97	109
6	16	12	91	80
8	16	12	152	153
2	18	12	82	83
4	18	12	240	237
8	18	12	237	235
0	20	12	234	229
2	20	12	102	92
4	20	12	125	118
8	20	12	113	119
2	22	12	126	115
4	22	12	129	133
6	22	12	234	223
8	22	12	152	148
2	24	12	215	202
2	26	12	113	87
1	1	13	143	130
3	1	13	161	154
5	1	13	140	149
7	1	13	119	123
9	1	13	148	153
11	1	13	173	160
1	3	13	217	212
5	3	13	154	164
7	3	13	181	178
9	3	13	68	60
11	3	13	173	166
1	5	13	104	110
3	5	13	203	206
5	5	13	116	123
7	5	13	86	95
9	5	13	225	210
11	5	13	110	94
1	7	13	189	183
3	7	13	136	131
5	7	13	183	181
7	7	13	175	165
9	7	13	76	68
11	7	13	155	166
1	9	13	172	172
3	9	13	146	145
5	9	13	185	170
7	9	13	85	97
9	9	13	125	125
11	9	13	144	133
1	11	13	139	139
3	11	13	207	199
5	11	13	136	139
7	11	13	144	145
9	11	13	178	169
1	13	13	207	202
5	13	13	212	202
7	13	13	156	142
1	15	13	122	124
3	15	13	166	161
5	15	13	95	102

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR HO-EDTA STRUCTURE

H	K	L	FO	FC
7	15	13	139	146
9	15	13	131	142
1	17	13	128	150
3	17	13	189	185
5	17	13	133	132
7	17	13	154	134
1	19	13	177	163
5	19	13	155	148
1	21	13	115	104
3	21	13	204	189
2	0	14	135	151
6	0	14	249	238
0	2	14	82	88
2	2	14	205	209
4	2	14	73	67
8	2	14	66	43
2	4	14	110	123
4	4	14	136	144
6	4	14	190	184
8	4	14	139	135
0	6	14	215	225
2	6	14	111	112
4	6	14	159	144
8	6	14	87	79
4	8	14	222	213
0	10	14	273	265
4	10	14	150	147
2	12	14	113	104
4	12	14	199	189
6	12	14	142	139
0	14	14	201	206
2	14	14	213	203
4	14	14	105	95

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