SOLUTION EQUILIBRIA OF THE METHYLDOPA-COPPER(II) SYSTEM AND THE CRYSTAL AND MOLECULAR STRUCTURES OF SELECTED COMPOUNDS

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by

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SUMMARY

The contents of this thesis are essentially in two parts. The first deals with solution studies relating to the methyldopa-copper(II) system and its relevance to medicinal chemistry, a full abstract of which is given on page 1 of the main text. The second part describes five single crystal x-ray investigations into some interesting compounds isolated at this university. The abstracts to these topics may be found preceding the relevant sections as they appear in the text on pages 94, 118 and 146, respectively.

CONTENTS

PART I

SOLUTION EQUILIBRIA OF THE METHYLDOPA-COPPER(II) SYSTEM

ABSTRACT

The system copper(II) ions in aqueous solution in the presence of L-3-(3',4'-dihydroxyphenyl)-2-methylalanine (methyldopa), at 25°C and $I = 0{,}150$ mol dm^{-3} $Na^+ClO_4^-$ has been characterised using glass electrode potentiometry. Both mononuclear and oligonuclear complexes were found to occur, the former including a series of successively deprotonated species in the higher ligand to metal ratio titrations, the latter including a cyclic dimer in the 1:1 ligand to metal solutions. Interpretation of the results was facilitated by (i) ultraviolet/visible spectrophotometry of solutions containing copper(II), methyldopa or alanine or catechol at various pH's, (ii) ^1H NMR measurements of methyldopa in ^2H_2O solutions, (iii) glass electrode potentiometric measurements on alanine and catechol in the presence of copper(II) ions. Formation constants are given for 3 proton - and 11 copper(II) - complexes of methyldopa, 2 proton and 2 copper(II) complexes of alanine and 1 proton and 2 copper(II) complexes of catechol.

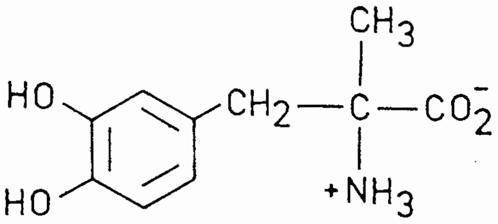
1. INTRODUCTION

1.1 Importance of methyldopa as an anti-hypertensive agent in vivo and its proposed mode of action.

Essential hypertension i.e. that condition of high blood pressure where the specific causes cannot be identified, can be classified into two types. Firstly, early or labile hypertension, where the haemodynamic pattern is characterised by increased cardiac output with the total peripheral resistance not significantly different from that of controls and generally diagnosed in relatively young hypertensive patients; and secondly, established hypertension, in which the haemodynamic pattern is a normal cardiac output but an increased total peripheral resistance. The mechanisms by which the transition from labile to established hypertension are brought about, as well as the fraction of patients that undergo it, as yet remains unknown[1].

The importance of L-3-(3',4'-dihydroxyphenyl)-2-methylalanine (methyldopa - see Fig 1.1.1) as a potential antihypertensive agent in remedying this condition was first reported in 1960 by Oates *et al.*[2] Since then, numerous experiments have confirmed its usefulness in this area[3,4] and today its clinical applications in man are becoming increasingly common. Of the two enantiomorphs of methyldopa, it has been shown that it is only the L-(-) isomer which has hypotensive activity[5]. Fig 1.1.2 depicts the Fischer projection representation of the active form. The absolute con-

Fig 1.1.1



figuration was determined by chemical methods[6] and optical rotatory dispersion data[7].

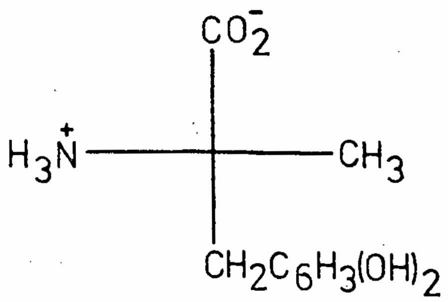


Fig 1.1.2

Various modes of action have been postulated to explain the drug's effect in vivo, the most important of which will now be briefly discussed.

(i) Decarboxylase inhibitor.

Methyldopa was initially thought to inhibit the decarboxylation of the related compound 3-(3',4'-dihydroxyphenyl)-2-alanine (dopa) to dopamine, and hence the subsequent formation of noradrenaline. The decreased rate of formation of noradrenaline (in hypertension there is a tendency for excessive noradrenaline to be released at the sympathetic nerve endings of arteriolar smooth muscle[8]) would then result in a fall in arterial blood pressure. This explanation was considered incomplete as:

(a) the antihypertensive effect persists longer than the enzymatic inhibition i.e. there is no causal relationship between the administration of methyldopa as a decarboxylase inhibitor and the expected fall in blood pressure;[9]

(b) several decarboxylase inhibitors which are more

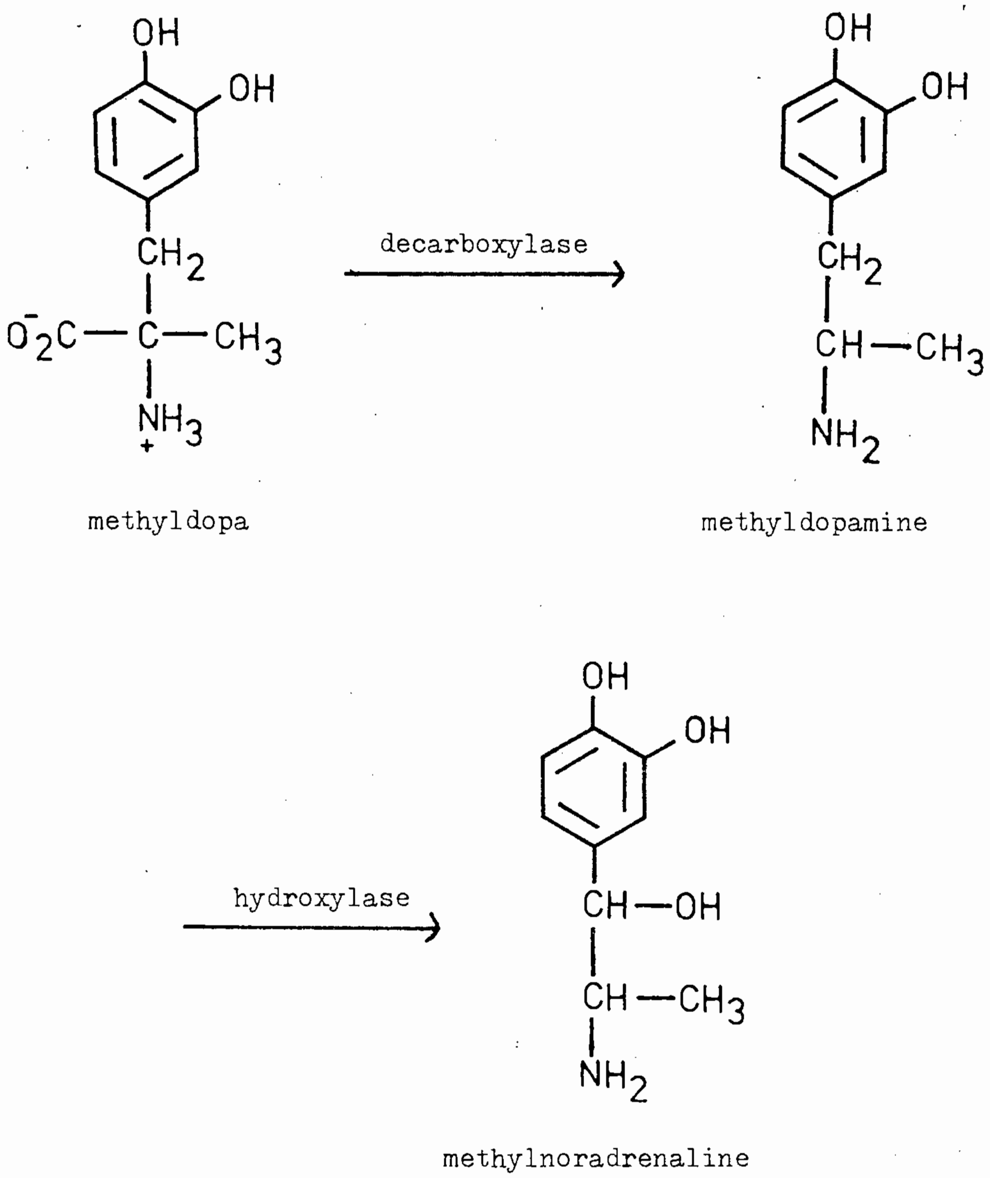


Fig 1.1.3

potent than methyldopa (methyldopa hydrazine, 4-bromo-3-hydroxybenzyloxyamine) do not lower the blood pressure of hypertensive patients;[10]

(ii) False-transmitter theory:[11]

Methyldopa is metabolised in the body via the enzymes dopa decarboxylase and dopamine-β-hydroxylase into methyldopamine and methylnoradrenaline (Fig 1.1.3), analogous to the biotransformation of dopa into dopamine and noradrenaline.

A mixture of stored methylnoradrenaline and noradrenaline is released from nerve endings as a result of peripheral adrenergic activity. If it is assumed that both transmitters compete for receptors in the target organ (in this case mainly the blood vessels), and that methylnoradrenaline is a less effective receptor stimulant than noradrenaline, this might explain the observed decrease in blood pressure. However, this false transmitter theory has also been proved to be unsatisfactory. Besides the unconvincing causal relationships detected, it is generally thought that the adrenergic properties of methylnoradrenaline and noradrenaline, although different in some species, is probably not different in all in which methyldopa is effective e.g. in man.[12]

(iii) Central Hypotensive Action.

There is increasing evidence that replacement of noradrenaline in sympathetic neurons by the less potent false-transmitter methylnoradrenaline does not completely account for the hypotensive action of methyldopa.[13,14] Experiments have confirmed that the hypotensive response due to methyldopa administered into the central nervous system, e.g. the cerebrospinal fluid, is significantly larger than systemic administration and that it is methylnoradrenaline which is the active metabolite. The medullary region of the lower brainstem contains α-adrenergic receptors which activate inhibitory neurons that diminish peripheral adrenergic activity.[15,16] The antihypertensive effect of methyldopa may thus be explained in terms of methylnoradrenaline coming into contact with these sites and being a more potent stimulant than noradrenaline, also present in this region. Adequate amounts of dopa decarboxylase and dopamine-β-hydroxylase are present in this region for the biotransformation of methyldopa into the active species to take place.

(iv) Suppression of Renin Release.

The ability of methyldopa to suppress renin release from the kidneys of patients whose hypertensive state is brought about by this condition has also been demonstrated.[17] Whether this property is due solely to a false-transmitter type effect of the drug on the post ganglionic renal adrenergic nerve, or whether a centrally mediated renin-suppressing action is also involved, awaits final demonstration.[18]

As a summary, it seems that the mode of action of methyldopa in relieving hypertension has not yet been established with certainty. The relative predominance of the possible modes depends to a large extent on the method of administration and the type of species being studied. However it is generally accepted that the centrally mediated action is the most important.

The use of methyldopa has its accompanying side effects. Amongst those detected are autoimmune haemolytic anaemia,[19] reversible abnormalities of liver function tests and low grade lactation.[20] The potency of tricyclic anti-depressant drugs (e.g. desipramine) administered concurrently with methyldopa has also been found to be reduced.[21]

1.2. Metal ion interactions in vivo:

It has been well established that metal ions, although contributing negligibly to total body weight, nevertheless play an important role in the healthy functioning of the living organism. Their importance is becoming increasingly apparent as a result of research into fields such as enzymology and neurology, where it has been found that deviation of total metal ion concentrations outside comparatively narrow limits can lead to a rapid deterioration in essential bodily functions.[22] Wilson's disease (a nervous disorder due to an excessive concentration of copper in the liver, brain and tissues[23]) and anaemia (caused by iron deficiency[24]) are but two of numerous examples in which the imbalance of metal ions in vivo is directly implicated in the breakdown of physiological processes. In most cases it is not known whether imbalances are the cause or the effect of the disease and the interplay of metal ion concentrations resulting from such imbalances is not well understood.

Nature has selected metal ions, and in particular those of the transition series, for the special role they play in life processes because of their ability to exist as stable ions, their capacity to form stereochemical bonds having low reaction energies and the comparative ease with which they are incorporated into redox systems. Pearson[25] in the early sixties developed the HSAB principle which classified acids and bases as hard or soft depending on their electronegativity, oxidisability and polarisability. Hard acids prefer hard bases and soft prefer soft. Given the vast range of species present in living systems, the HSAB principle applied to metal ion equilibria in vivo goes a long way in qualitatively explaining the bond strengths and sites of co-ordination of complexes that have been observed. In addition, the specificity of most of the reactions occurring can be understood on this basis.

The ions of sodium, potassium, calcium, magnesium, manganese, iron, cobalt, copper and zinc are generally accepted as part of the list of 25 elements essential for healthy life. Table 1.2.1. shows briefly some of the more important biological processes in which they participate.

Table 1.2.1.

The Important Role of Metal ions in the healthy organism.[22]

Na^+,K^+	Maintaining osmotic pressure on either side of the cell wall, muscle tone.
Ca^{2+},Mg^{2+}	Nerve impulse transmission, formation of bones and teeth, blood clotting.
Mn^{2+}/Mn^{3+}	Enzyme activation.
Fe^{2+}/Fe^{3+}	Protein formation, redox reactions, oxygen transport.
Co^{2+}/Co^{3+}	Manufacture of vitamin B_{12}, enzyme activation.
Cu^+/Cu^{2+}	Production of haemoglobin, oxygen storage and transport.
Zn^{2+}	Enzyme activation.

As can be seen from the table, metal ions figure predominantly in enzyme reactions. Enzymes promote physiological reactions by providing alternative pathways with lower activation energies and hence faster reaction rates. They have the ability of positioning the substrate adjacent to an active centre, where the three dimensional geometry and the energetics of the system bring about an enhanced biological reaction. Carboxy peptidase A is an enzyme which hydrolyses the c-terminal amino acid residue from a protein or peptide chain. Consisting of a polypeptide chain of 307 amino acid residues, it contains one Zn(II) ion per molecule, which if removed, renders the enzyme inactive. Some transition metal ions (Fe(II), Mn(II), Co(II), Ni(II)),by occupying the site formerly held by Zn(II), are able to regenerate peptidase activity in the apoenzyme.[26] Carbonic anhydrase oxaloacetate decarboxylase and alkaline phosphatase are other examples of enzymes which depend on bound metal ions for their activity.[27-29] Haemoglobin, an important oxygen transporter in the blood, binds its metal ion more tightly. In this case, iron is covalently bonded within a protected cavity formed by the surrounding molecule and is therefore well sheltered from outside attack. In fact, metal ions in blood plasma can conviently be subdivided into four fractions depending on the type of chelation with co-existing ligands.

(i) Tightly bound by proteins and therefore not exchangeable under mild chemical conditions. Examples are haemoglobin and the cobaltic complex of vitamin B_{12}.

(ii) Loosely bound by proteins and therefore in labile equilibrium. Included here are most of the enzymes and the metal ion carriers e.g. iron in transferrin and copper in serum albumen.

(iii) Complexed to numerous low molecular weight ligands such as amino acids, carboxylates, phosphates, nucleosides and nucleotides.

(iv) Non-chelated and existing in its free or aquated form.

For a given metal, the great proportion exists in the first two fractions, and it has been tentatively theorised that the second fraction can act as a so-called metal ion buffer. This idea has been shown to be useful in the calculation of the distribution of metal ions in physiological solutions by computer simulation.[30]

The importance of metal ions in transport systems across cell membranes also warrants mention. For example, the concentration difference of Na^+ ions on either side of certain cell membranes has been shown to be intimately involved in the active transport of amino acids and sugars into cells.[31] The concentration gradient is believed to be brought about by a so-called ion pump using ATP as the energy source. Chelates of dopa with metal ions, in particular Cu(II) and Zn(II), are transported across the blood/brain barrier at a faster rate than the uncomplexed ligand.[32] The metal ion, by being complexed to the amine group of dopa is thought to inhibit the decarboxylation of dopa to dopamine by enzymes present in the precerebral areas.

Despite the mammoth amount of work which has been done on metal ion interactions in vivo, quantitative knowledge concerning the selective preferences of these metal ions for the many varied ligand species present in the body is still lacking. A comprehensive understanding of the role of metal ions in life processes, with its resultant implications as far as nutrition, therapeutics and pollution are concerned, must of necessity await further progress.

1.3. Previous work on dopa-metal ion interactions and related systems.

Mention should be made of the more important factors influencing the magnitude of formation constants of metal ion-ligand interactions in general. Under a given set of conditions these depend on:

(i) The nature of the metal ion. For the transition series, the well established Irving-Williams order is often followed i.e. Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II).[33] Their position is a function of the electronic configuration of the outermost electrons, and is a manifestation of the crystal field stabilisation energy (CFSE) which the metal ion undergoes on complex formation.[34]

(ii) The number of metal ion-ligand bonds per ligand. The so-called chelate effect, predicting the normal order of increasing stability (monodentate < bidentate < terdentate) can be explained using thermodynamic and statistical arguments.

For example, in the system,

$$Cu(NH_3)_4^{2} + tren \rightleftarrows Cu(tren)^{2+} + 4NH_3 ,$$

the equilibrium lies well over to the right for all but extremely low tren concentrations (tren ≡ triethylenetetramine).[35]

(iii) The acidity of the donor atoms. A ligand which binds protons strongly will have a high affinity for other cations.[36] A contributing factor here is the nature of any adjacent functional groups. Electron withdrawing groups will depress the pKa of a potential donor atom, making it a less potent complexing agent, whereas an electron donating group will have the opposite effect.

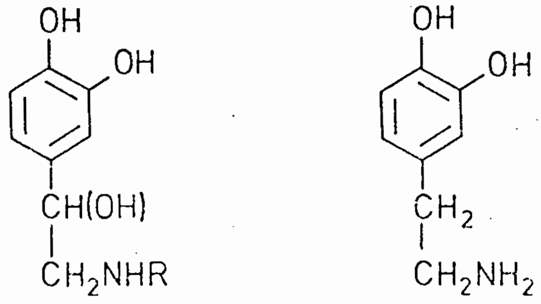
(iv) Steric factors. Metal ion-amino acid chelates tend to form 5-membered planar ring structures. A distortion with accompanying bond strain brought about by bulky substituents on a participating atom will tend to have a destabilising influence.[37]

(v) Neutralisation of charge. When two oppositely charged species complex to form a neutral species, solvent molecules are released from the inner co-ordination spheres of the reactants. The resultant increased freedom of translational motion of these solvent molecules generally results in a positive entropy change for the reaction, and hence an enhanced stability for the complex. Clearly exothermic reactions favour complex formation and endothermic do not.

(vi) The type of bond formed. An amine nitrogen is able to form a σ type bond with a transition metal ion, whereas a pyridyl or imadazole group has additional π-acceptor qualities. Electron density on the metal ion is reduced through the back donation of d electrons into vacant π orbitals of appropriate ligands, leading to a higher formation constant for the species involved than one would normally expect.[38]

(vii) The nature of the donor atoms. In a review, Sigel has noted that $Cu(bipyridyl)^{2+}$ binds ligands with oxygen donors more firmly than those with nitrogen donors. Mixed N,O ligands have constants with intermediate values.[39]

Exploratory work on dopa related catecholamines such as adrenaline, noradrenaline and dopamine (Fig 1.3.1) with metal ions has aided the understanding of the metal binding characteristics of dopa itself.



R = CH_3 : adrenaline
R = H : noradrenaline

dopamine

Fig 1 3.1

Weber *et al*[40] found in such systems that with zinc (II), cadium(II) and lead(II) as the metal ion, only 1:1 catechol type complexes were present, and these were much less stable than the corresponding complexes of copper(II) and nickel(II). These last two metal ions were able to form species with two ligands per metal ion. Below a ligand:copper(II) ratio of 2:1, Jameson and Neillie[41] working with adrenaline and noradrenaline reported the formation of tetramers (Fig 1.3.2) with not only the phenolic groups but also the side chain participating in complexation. In the case of catechol, this side chain participation is not possible, and the formation of the 2:1 complex on further addition of base is postulated, with the eventual precipitation of copper hydroxide. The formation of 1:1 and 2:1 catechol-copper(II) chelates has also

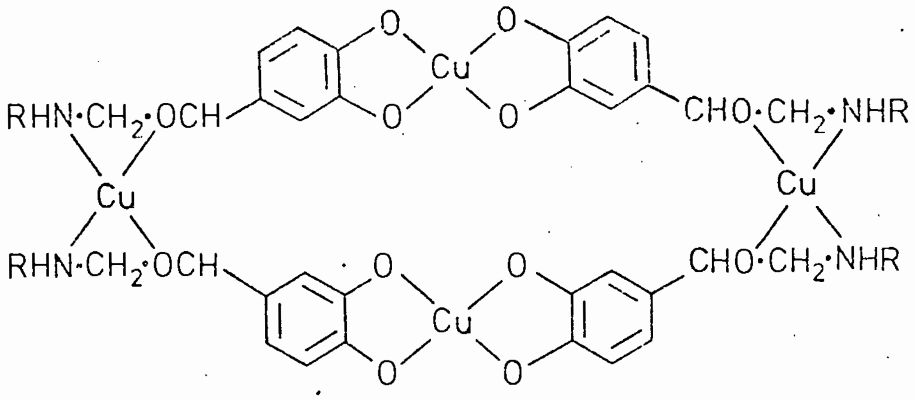


Fig 1.3.2

been reported by other workers.[42,43]

Interest in dopa as a complexing ligand stems from the fact that, in addition to the terminal carboxylic acid-amine structure common to all amino acids, it possesses potential metal ion binding sites at its opposite end in the form of the two hydroxyl groups. Of all the dopa-metal ion systems that have been investigated, those involving copper(II) as the metal ion have received the most attention. This is likely due to this metal ion's kinetic lability and the high stability in aqueous media of many of its complexes.[44] In addition, copper(II) has been shown to play an important role in the in vivo reactions of catecholamines.[45]

Although there is general agreement on the mode of complexation predominant at high and low pH values in the dopa-copper(II) system, inconsistencies as to the structures and stoichiometries of the species involved still remain. Experimental data obtained from potentiometry, ESR, UV/visible spectrophotometry and cyclic voltametry indicate that the bonding site of copper(II) to dopa is strongly pH dependent.[40,32,46-52]

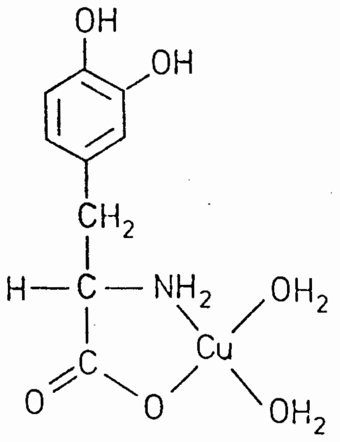
Gorton and Jameson[46] found that in a 1:1 dopa-copper(II) mixture a monomeric complex with the metal ion bound at the aminocarboxylate end of the ligand at a pH below 4 was replaced by a cyclic dimer involving catechol type bonding as the pH was increased to 6. (Fig 1.3.3)

In a subsequent paper,[47] the model was extended by introducing polymers. In studies with higher ligand to copper(II) ratios, Gergely and Kiss[51] have determined the stability constants of complexes containing one and two ligands per metal ion, the bonds being of the amino acid type at low pH (<5) and of the catechol type at high pH (>9). A mixed complex with N,O and O,O bonds, as well as cyclic and open chain species in which dopa behaves as a bridging ligand, were evident in the intermediate pH range. Polymers of higher order were also postulated, but were not included in the final model due in part to their very low concentration. Further evidence of the ability of dopa to act as a simple amino acid at lower pH values and as catechol at higher pH values has been provided by the isolation and characterisation of a bluish-purple solid at pH 5 and an olive-green solid at pH 9,5 showing respectively these types of bonding.[50]

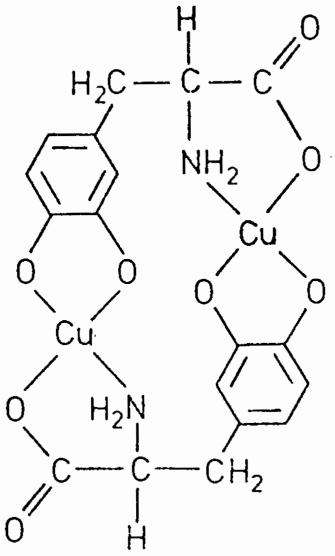
Copper(II) is known to bind simple amino acids strongly in the ratio of one or two ligands per metal ion at pH values between 3 and 5.[37,53] In addition, the preference of copper(II) for ligands containing conjugated π ring systems for d electron back donation has already been mentioned.[38] Studies of catechol-copper(II) systems have shown that complexation with copper(II) occurs on the deprotonation of the catecholic hydroxyls at pH values only above 5, due to the high pKa's of these groups.[43] Thus it is reasonable to expect the pH

Fig 1.3.3

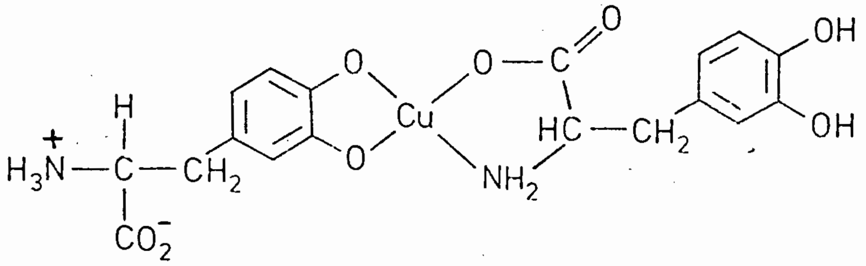
Modes of complexations in the dopa-copper(II) system



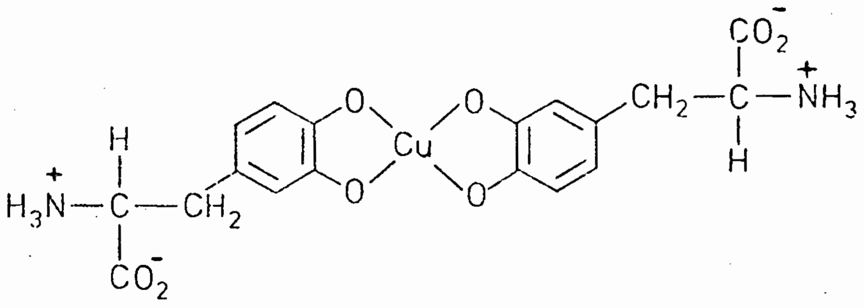
Monomeric amino acid type



Cyclic dimer



Mixed O,O and N,O type



Dimeric catechol type

dependent mode of complexation of copper(II) to dopa to be mainly amino acid type chelation at low pH values and catechol type at high pH values.

Dopa complexations with metal ions other than copper(II) have not been as widely studied. Evidence at the present time suggests that nickel(II) forms amino acid type complexes with dopa, whereas magnesium(II) and zinc(II) prefer catechol type.[54]

1.4. Ligand-metal ion equilibria in solution.

The theory of the study of ligand-metal ion equilibria in solution is comprehensively covered in many texts,[55-57] and so only a brief account will be given here.

The relative amounts of complexes which exist in an aqueous solution can be calculated from their thermodynamic formation or stability constants, which relate the activity of the complex under investigation to the activities of the free components comprising the system. Thus for a system of 3 components, represented by A (ligand), B (metal ion) and H (proton), in which the following equilibrium is established,

$$pA + qB + rH \rightleftharpoons A_p B_q H_r$$

$$\beta^T_{pqr} = \frac{\{A_p B_q H_r\}}{\{A\}^p \{B\}^q \{H\}^r} \qquad \ldots\ldots 1.4.1$$

β^T_{pqr} as defined above is the overall or cumulative thermodynamic formation constant. The concentration of water is generally unaffected by the participating equilibria within the system due to its large excess, and hence is omitted in the calculations. When $r = -1$ this refers to a proton removed to a water molecule or a hydroxide ligand added.

The system can also be expressed in terms of stepwise thermodynamic formation constants, K^T_{pqr}, which can be related to the β^T_{pqr}'S. Hence, in the absence of metal ions, with just one ligand,

$$K^T_{101} = \frac{\{AH\}}{\{A\}\{H\}} = \beta^T_{101}$$

$$K^T_{102} = \frac{\{AH_2\}}{\{AH\}\{H\}} = \frac{\beta^T_{102}}{K^T_{101}}$$

$$\vdots$$

$$K^T_{10n} = \frac{\{AH_n\}}{\{AH_{n-1}\}\{H\}} = \frac{\beta^T_{10n}}{\prod_{i=1}^{n-1} K^T_{10i}}$$

Clearly analogous relationships can be derived in extended systems.

In practice, because of the difficulty in measuring activities, complex equilibria are usually expressed in terms of the concentrations of species. This technique entails using a non-complexing background electrolyte of sufficiently high molarity to maintain the activity coefficients of the reacting species effectively constant during the measurements. Hence for a given electrolyte, the activities of the components partaking in the equilibria are determined primarily by the total ionic strength of the medium, and are largely unaffected by a small change which may be caused through a slight perturbation of the equilibria. A limitation to this method is that the stability constants are only applicable to the ionic strength and the medium in which they are measured and their value in others can only be estimated. Nevertheless the stability constants can be measured over a wide range of ionic strengths, and thus extrapolated to zero ionic strength where the activities are represented by the concentrations.

1.5. Objectives.

The importance of metal ions in biological processes involving catecholamines has been made apparent in a number of cases. For example, copper containing enzymes have been shown to be intimately involved in the metabolism of biogenic amines such as adrenaline and noradrenaline.[58,59] Dopa, a member of this class, has for a number of years been administered in the treatment of Parkinson's disease, a disorder of the central nervous system. When chelated to certain metal ions, the drug shows an increased rate of transport across the blood/brain barrier in comparison to unchelated dopa.[32] Methyldopa in turn has found wide application in the lowering of high blood pressure in man.

This work was undertaken in order to advance investigations concerning the stoichiometry, identity and distribution of methyldopa-copper(II) complexes co-existing in solution in the hope that it might throw further light on the understanding of the drug's clinical usefulness.

The techniques employed were:

(i) Potentiometry and computer analysis, primarily in stability constant determination and identification of the complex species co-existing in equilibrium under various conditions e.g. concentration of the components and pH.

(ii) Ultraviolet/visible spectrophotometry and nuclear magnetic resonance (NMR) with the aim of identifying the coordination and protonation sites of the methyldopa molecule.

(iii) The computer program ECCLES[30] was used as an aid in estimating the relative metal ion populations at the two predominant sites of methyldopa.

The major part of the effort went into (i) whilst (ii) and (iii) were used to facilitate the selection of feasible models in (i).

2. TECHNIQUES USED

2.1. Computer programs used in model fitting.

2.1.1. MINIQUAD.

A solution containing components which are potentially capable of forming complexes will consist at equilibrium of a series of species, the stoichiometry and amounts of which will depend on the physical conditions prevalent, the chemical nature of the components and the magnitude of their attraction. In a study to determine their nature, the procedure is to make use of chemical knowledge gained from similar systems, or alternative experimental techniques, in choosing a model which will within reasonable error match the observed experimental data. The method of testing a postulated model on a set of potentiometric titration data as followed by the program MINIQUAD[60] for a system of 3 components (if need be up to five can be handled) will now be briefly described.

In a mixture containing several species of various types (mononuclear binary, protonated, hydroxo, oligonuclear), the total concentrations of the components can be expressed in terms of the free concentrations of the components and the various stability constants of the N complexes. Thus

$$[A]_T = [A] + \sum_{r=-R}^{R} \sum_{q=0}^{Q} \sum_{p=1}^{P} p\beta_{pqr} \; [A]^p [B]^q [H]^r \qquad \ldots \; 2.1.1.1.$$

$$[B]_T = [B] + \sum_{r=-R}^{R} \sum_{q=1}^{Q} \sum_{p=1}^{P} q\,\beta_{pqr} \; [A]^p [B]^q [H]^r \qquad \ldots \; 2.1.1.2.$$

$$[H]_T = [H] + \sum_{r=-R}^{R} \sum_{q=0}^{Q} \sum_{p=1}^{P} r\,\beta_{pqr} \; [A]^p [B]^q [H]^r \qquad \ldots \; 2.1.1.3.$$

A model with estimated formation constants is postulated. In a set of n titration points a total of 3n equations is set up. If only a glass or other $[H^+]$ sensitive electrode is used in the potentiometric measurements, it follows that the free hydrogen ion concentration for each point is known, and so the number of unknowns is (2n + m), where m is the number of formation constants to be determined. The number of degrees of freedom is (n - m). By an iterative process, using the Gauss-Newton least squares method, the parameters [A] and [B] for each titration point, and the β_{pqr}'s common to all, are adjusted so as to minimize the error square sum

$$U = \sum_{i=1}^{3n} (f_i^{calc} - f_i^{obs})^2$$

where f_i^{calc} are the total component concentrations as calculated according to equations 2.1.1.1. to 2.1.1.3, and f_i^{obs} the corresponding experimental values. The model is said to be a possible representation of the true chemical state if the parameters are refined such that the function U is less than a pre-specified value. An important feature of MINIQUAD is the optimisation of the parameter shifts, and successful refinement occurs when the shift changes after each cycle become sufficiently small.

Useful statistical outputs of the program include the following functions:

(i) R-factor:

$$R = \sum_{i=1}^{3n} (f_i^{calc} - f_i^{obs})^2 / \sum_{i=1}^{3n} (f_i^{obs})^2 \qquad \ldots \quad 2.1.1.4.$$

Generally the higher R is, the less good is the fit. A limiting value of R can be calculated using conservative estimates of the errors in the experimental measurements and following the method of propagation of errors (see Appendix A), and if the R as calculated in 2.1.1.4 is less than this R_{LIM}, the model can be said to be within the maximum allowed experimental error. It may so happen that two models give values R_1 and R_2 which are both less than this R_{LIM}. Vacca *et al*[61] have applied a method developed by Hamilton involving the ratio R_1/R_2 whereby one can decide whether they are significantly different at the α confidence level. If it is found that they are not, the simplest of the models matching the experimental data should be taken.

(ii) X^2 - chi squared

This function as it appears in the program allows one to decide how closely the $(f_i^{calc} - f_i^{obs})$ values follow a normal Gaussian distribution about its zero mean, an indication as to the distribution of residuals on either side of the mean.

(iii) The residuals:

A scan of the residuals $(f_i^{calc} - f_i^{obs})$ on the mass balance equations may aid the user in postulating alternative models in subsequent runs, or perhaps to detect erroneous experimental points.

2.1.2. ZPLOT.

This program calculates the formation curve parameters $\bar{Z}$ and P[A], assuming only mononuclear binary complexes are formed, where

$\bar{Z}$ = average no. of ligand molecules bound to metal per metal ion

$$= \frac{[\text{A bound to B}]}{[\text{B}]_T} \qquad \text{.... 2.1.2.1}$$

and

$$\text{P[A]} = -\log[\text{fully deprotonated ligand}] \qquad \text{.... 2.1.2.2}$$

The protonation formation curve parameter $\bar{Z}_H$, analogous to $\bar{Z}$, is calculated as

$$\bar{Z}_H = \frac{[\text{bound H}]}{[\text{A not bound to B}]} \qquad \text{.... 2.1.2.3}$$

$$= \frac{\sum_{j=0}^{J} j[H]^j \beta_{10j}}{\sum_{j=0}^{J} [H]^j \beta_{10j}}$$

From equation 2.1.2.1

$$\bar{Z} = \frac{[A]_T - [A \text{ not bound to } B]}{[B]_T} \qquad \ldots\ldots\ 2.1.2.4$$

Substituting from equation 2.1.2.3, we obtain

$$\bar{Z} = \frac{[A]_T - [\text{bound } H]/\bar{Z}_H}{[B]_T}$$

$$= \frac{[A]_T - ([H]_T - [H] + Kw[H]^{-1})/\bar{Z}_H}{[B]_T} \qquad \ldots\ldots\ 2.1.2.5$$

To calculate the value of [A] at this point, use is made of equation 2.1.2.4 expressed in an equivalent form, i.e.

$$\bar{Z} = \frac{[A]_T - [A]\sum_{j=0}^{J} [H]^j \beta_{10j}}{[B]_T}$$

Solving for [A],

$$[A] = \frac{[A]_T - \bar{Z}[B]_T}{\sum_{j=0}^{J} [H]^j \beta_{10j}} \qquad \ldots\ldots\ 2.1.2.6$$

The program thus presumes no knowledge of the ligand-metal ion species in solution or their stability constants, and computes $\bar{Z}$ and P[A] (equations 2.1.2.5 and 2.1.2.6) solely from a knowledge of the protonation constants of the ligand, the free hydrogen ion concentration from potentiometric data, and the total concentrations of the components.

The equivalent theoretical expression for $\bar{Z}$ is

$$\bar{Z} = \frac{\sum_{j=0}^{N} j[A]^j \beta j_{10}}{\sum_{j=0}^{N} [A]^j \beta j_{10}}$$

This shows $\bar{Z}$ to be a function of [A] only. If it is found that for a number of titrations at varying concentrations and ratios that non-overlapping of the formation curves occurs, then one or more of other types of complexes e.g. protonated, hydroxo, oligonuclear etc. are present in the mixture as well.[62]

2.1.3. PSEUDOPLOT:

This program is essentially a marriage between the programs HALTAFALL and ZPLOT, an idea proposed by D.R. Williams of UWIST, Cardiff University.[63] The former computes the equilibrium concentrations of the various constituents in solution, including the free hydrogen ion concentration, by an iterative process using equations 2.1.1.1 to 2.1.1.3. The information required comprises the total concentration of each component, the composition of all possible complexes postulated in a given model to describe the system, and their various stability constants. The refined free hydrogen ion concentrations for each point are then used to calculate $\bar{Z}$ and P[A] using the ZPLOT part of the program, which outputs the 'theoretical' formation curve. A comparison between this and the analogous experimental formation curve serves as a further check as to the validity of a postulated model.

2.1.4. ECCLES:

This program, developed at the University of Cape Town by P.M. May,[30] can compute the equilibrium concentrations of metal-ligand complexes in aqueous equilibrium systems at various free hydrogen ion concentrations and, like HALTAFALL, requires the formation constants for all the complexes and the total or free concentrations of the components present in the mixture.

In a system containing more than two components in addition to hydrogen e.g. two ligands and a metal ion, there is a strong possibility of the formation of ternary complexes. This possibility is enhanced statistically when the probability of such complexes being formed is considered. An additional factor is the influence which energetically favourable (or unfavourable) effects might have on the magnitude of these ternary formation constants as compared to the binary formation constants. ECCLES contains a subroutine whereby these considerations are utilised in the estimation of ternary formation constants, based on values for the binary complexes and on stabilisation factors. The presence of these ternary complexes are then taken into account in the computation of species present at equilibrium.

2.1.5. GEPOLYC.

GEPOLYC[47] is a program, developed at the University of Dundee, for treating a 1:1 ligand to metal equilibrium mixture, where the ligand has two possible bidentate coordination sites, one at each end of the molecule, and where the allowable species consist of an infinite series of closed chain polymers, the formation constant K of each in the series being defined such that they are equal and independent of the number of units n, and an infinite set of open chain polymers of formation constant Kc defined analogously. The ligand must have four dissociable protons, two at each bidentate site. A unit is considered as one ligand bound to a metal ion at one end. Units are added to the chain one at a time; thus the possible infinite set of all straight open chain polymers is treated as a subset of the simplest set, the dimer, with one associated chain forming constant. The invariance of the formation constants with n is a reasonable assumption if the concentration of polymers of large n is small and the addition of a moiety at one end is considered to be negligibly affected by what is complexed at the other end due to it being far from the site in question.

It is to be appreciated that polymers become a necessity for the 1:1 methyldopa-copper(II) system in which the four dissociable protons are neutralised at a pH well below the pKa of the most basic, if hydroxo or six coordinate complexes are to be excluded.

The GEPOLYC treatment was applied successfully by Gorton and Jameson to the dopa-copper(II) system,[47], and hence its adaptability to the structurally related methyldopa-copper(II) system was tested.

In the calculations, the parameters $\bar{Z}'$ and $[L']$ are introduced as the formation curve parameters. They are experimentally defined as:

$$\bar{Z}' = \frac{[OH]_T - 2[B]_T}{2[B]_T} \qquad \ldots\ldots 2.1.5.1$$

and

$$[L'] = \frac{2[B]_T - [OH]_T/2}{\beta'_{102}[H]^2} \qquad \ldots\ldots 2.1.5.2$$

$[OH]_T$ is the total concentration of proton removed from the ligand, calculated from a defined point in the titration and obtained from the amount of hydroxide added and the initial mineral acid concentration. $[B]_T$ is again the total metal ion concentration. $\bar{Z}'$ hence represents the fraction of proton pairs replaced by copper(II) from the catechol end of the molecule.

β'_{102} is the second overall formation constant for methyldopa when the fully deprotonated ligand is regarded as being the trianon. [H] is the free hydrogen ion concentration. L' thus has no definite structure, but is related to a series of open chain polymers in which one end is complexed to copper (alanine type), whilst the other is catechol type, deprotonated but uncomplexed (Fig 2.1.5)

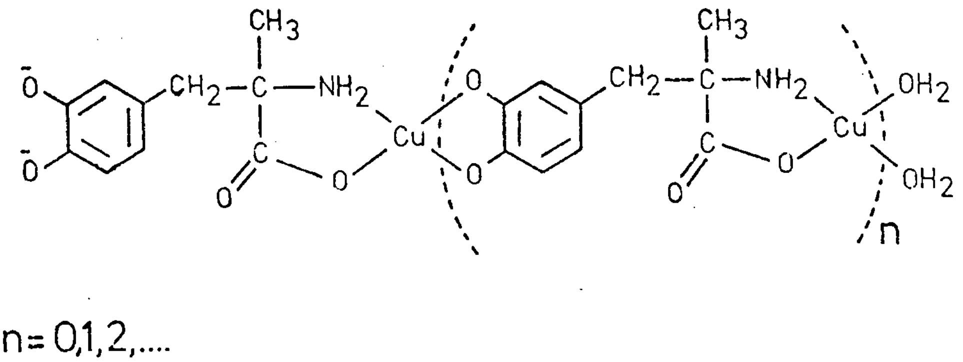


Fig 2.1.5

In the methyldopa system in the absence of copper(II), the second proton to be added to the fully ionised molecule is attached to the amine moiety and not at a hydroxy position as suggested by the expression above for [L']. However, since copper is already assumed to be complexed at the alanine end and [L'] is introduced merely to facilitate the calculation, this can be overlooked.

In summary, the functions $\bar{Z}'$ and [L'] can be visualised as the formation curve parameters for the system after the 1:1 alanine type complex formed initially begins to polymerise through interaction with its catechol end, i.e. at $\bar{Z}' = 0$, the ligand exists totally in the form ABH, but progressively begins to form long chain polymers as the titration proceeds and the catechol protons become neutralised.

Theoretical expressions for $\bar{Z}'$ and [L'] containing the constants K and Kc will now be derived. The total ligand concentration can be approximated as:

$$[A]_T = \sum_{n=1}^{\infty} n[A_nB_nH_{2-n}] + \sum_{n=2}^{\infty} n[A_nB_nH_{-n}] \qquad \ldots. \ 2.1.5.3.$$

The first term is the concentration of the open chain polymers, the second the closed. Towards the lower pH values, the total ligand effectively exists as ABH. Under these conditions the uncomplexed ligand is taken to be stoichiometrically negligible. As the pH is raised, so the different polymeric species become significant and contribute towards $\bar{Z}'$.

From these considerations, it follows that

$$\bar{Z}'[A]_T = \sum_{n=1}^{\infty} (n-1)[A_nB_nH_{2-n}] + \sum_{n=2}^{\infty} n[A_nB_nH_{-n}] \qquad \ldots. \ 2.1.5.4.$$

Let the formation of a closed chain polymer be represented by K, such that

$$K = \frac{[A_nB_nH_{-n}][ABH]}{[A_nB_nH_{2-n}][ABH^*_{-1}]}$$

ABH^*_{-1} is ABH deprotonated twice at the catechol end and its concentration is stoichiometrically zero as appreciable ionisation of the catechol group protons does not occur in the pH region studied.

Let the formation of an open chain polymer be represented by Kc, such that

$$Kc = \frac{[A_nB_nH_{2-n}]}{[A_{n-1}B_{n-1}H_{3-n}][ABH^*_{-1}]}$$

If both K and Kc are assumed to be independent of n, then in general

$$[A_nB_nH_{2-n}] = (Kc[ABH^*_{-1}])^{n-1}[ABH] \qquad \ldots. 2.1.5.5$$

and

$$[A_nB_nH_{-n}] = (K_c[ABH^*_{-1}])^{n-1}\ K[ABH^*_{-1}] \qquad \ldots.\ 2.1.5.6.$$

Continuing, letting

$X = K_c[ABH^*_{-1}]$ and substituting in 2.1.5.3.,

one obtains

$$[A]_T = \sum_{n=1}^{\infty} nX^{(n-1)}[ABH] + \sum_{n=2}^{\infty} nX^{(n-1)}\ K[ABH^*_{-1}] \qquad \ldots.\ 2.1.5.7.$$

Similar treatment of equation 2.1.5.4. yields

$$\bar{Z}'[A]_T = \sum_{n=1}^{\infty} (n-1)X^{(n-1)}[ABH] + \sum_{n=2}^{\infty} nX^{(n-1)}K[ABH^*_{-1}] \qquad \ldots.\ 2.1.5.8.$$

Solving for [ABH] in 2.1.5.7. and substitution in 2.1.5.8. yields

$$\bar{Z}'[A]_T = \frac{\sum_{n=1}^{\infty} (n-1)X^{(n-1)}\left[[L]_T - \sum_{n=2}^{\infty} nX^{(n-1)}K[ABH^*_{-1}]\right]}{\sum_{n=1}^{\infty} nX^{(n-1)}}$$

$$+ \sum_{n=2}^{\infty} nX^{(n-1)}K[ABH^*_{-1}] \qquad \ldots.\ 2.1.5.9.$$

The numerator of the expression for [L'](equation 2.1.5.2) refers to the concentration of that series of complexes which still has a proton pair bound at the catechol site. It must therefore be equal to the difference between the total ligand concentration and that fraction of the total ligand concentration which has been deprotonated, i.e.

$$[L'] = \frac{[A]_T(1-\bar{Z}')}{K'[H]^2} \qquad \ldots.\ 2.1.5.10.$$

where

$$K' = \frac{[ABH]}{[ABH^*_{-1}][H]^2} \qquad \ldots.\ 2.1.5.11.$$

β'_{102} and K' are equal if complexation at the alanine site does not affect the protonation constants at the catechol site.

Substituting for $K'[H]^2$, (equation 2.1.5.11), and $[A]_T(1-\bar{Z}')$, (equation 2.1.5.4 subtracted from equation 2.1.5.3), in equation 2.1.5.10, one obtains,

$$[L'] = \frac{([ABH] + [A_2B_2] + [A_3B_3H_{-1}] + \ldots)[ABH^*_{-1}]}{[ABH]}$$

$$= \frac{\sum_{n=1}^{\infty} X^{(n-1)} [ABH][ABH^*_{-1}]}{[ABH]}$$

$$= \sum_{n=1}^{\infty} X^{(n-1)} [ABH^*_{-1}] \qquad \ldots\ldots 2.1.5.12.$$

Experimental values of $\bar{Z}'$ and $-\log[L']$ using equations 2.1.5.1. and 2.1.5.2. are first calculated from potentiometric data. Estimated values of log K and log K_c are then submitted to the program GEPOLYC, which outputs the theoretical formation curve parameters (equations 2.1.5.9. and 2.1.5.12). These values are adjusted until the best fit with the experimental curve is achieved. The program allows the maximum size of the closed chain species to be predetermined, but this is not possible with the open chain species as the relevant summation expression is in an explicit form.

The concentration of any particular species can be calculated at any point in the titration.

From equation 2.1.5.12,

$$[L'] = \frac{[ABH^*_{-1}]}{1 - X} = \frac{[ABH^*_{-1}]}{1 - Kc[ABH^*_{-1}]}$$

$$\therefore [ABH^*_{-1}] = \frac{[L']}{1 + [L']K_c} \qquad \ldots\ldots 2.1.5.13.$$

From equations 2.1.5.7 and 2.1.5.8,

$$[A]_T(1 - \bar{Z}') = \sum_{n=1}^{\infty} X^{(n-1)} [ABH]$$

$$\therefore [ABH] = [A]_T(1 - \bar{Z}')(1 - X) \qquad \ldots\ldots 2.1.5.14.$$

$[ABH^*_{-1}]$ and $[ABH]$ may be calculated from equations 2.1.5.13 and 2.1.5.14 respectively. Hence $[A_nB_nH_{2-n}]$ and $[A_nB_nH_{-n}]$ may be calculated using equations 2.1.5.5. and 2.1.5.6.

2.1.6. MAGEC.

MAGEC is a program developed at this laboratory to calibrate the $[H^+]$ sensitive glass electrodes used in this work.[64] It uses as input data ml and mV readings obtained from the titration of a weak monoprotic acid with a strong base. Estimates of the seven parameters necessary to define the system are then used to solve for the value of base added at each point, V'_{calc}. The seven parameters are : β_H, the protonation constant of the acid; Fn and E°, the slope and intercept respectively of the Nernst equation (equation 2.4.1); Kw, the ionic product of water at the background ionic strength; $[AH]_o$, the initial concentration of the acid used; [NaOH], the concentration of the titrant; and $[V]_o$, the initial volume of titrate. Those parameters most likely to contain errors in their estimates are adjusted iteratively by the simplex routine in minimising the sum of the squares of the individual residuals, $\sum_{i=1}^{n}(V'_{calc} - V'_{obs})^2$. A scan of the sense of the residuals for systematic trends provides a check on the validity of the assumption that equation 2.4.1 is linear for the electrode used.

All the programs were run in FORTRAN V on the University of Cape Town Univac 1106.

2.2. Applications of ultraviolet/visible spectrophotometry.

In general, solution potentiometry can provide useful information as to the stoichiometry of the complexes formed and the strengths of the bonds formed in any ligand-metal ion interactions. However, structural information such as bonding sites must generally be obtained by other methods. The structure of methyldopa is such that if it could be cleaved at the position shown in Fig 2.2.1, the one half would be identical to catechol whilst the other would closely resemble alanine.

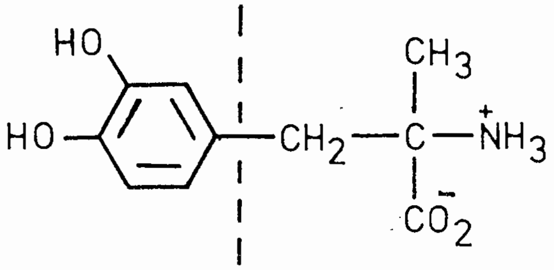


Fig 2.2.1

Hence given an absorption spectrum of a methyldopa-copper(II) solution which shows strong similarities to a spectrum obtained from an alanine-copper(II) solution under the same conditions, one could with some justification presume that the copper atom giving rise to the absorption maxima in the two solutions exists in similar chemical environments. An analogous deduction must follow for similarities in the spectra of a methyldopa-copper(II) solution and a catechol-copper(II) solution. An intermediate spectrum of a methyldopa-copper(II) solution which contained characteristics of both 'pure' spectra hence would indicate both types of bonding to be present. Clearly the more distinct and simple the spectra arising from the different chemical environments, the easier it would be to estimate copper(II) populations at the two complexing sites in question.

2.3. Application of nuclear magnetic resonance (NMR).

The pH dependence in the chemical shift of a proton in close proximity to a dissociable proton can in cases be used to give a rough estimate of the pKa of the dissociable proton. Hence that region where the observable rate of change of chemical shift with pH is a maximum can be taken to approximately equal the pKa of the nearest group with a dissociable proton, for at this point the chemical surroundings influencing the shielding of the proton nucleus being observed is changing most rapidly.

The technique described was attempted in the determination of the protonation sites of the methyldopa dianion (Fig 5(2)).

2.4. Potentiometric approach : apparatus and materials.

The apparatus as shown in Fig 2.4.1. was used to titrate solutions containing various concentrations of ligand, copper(II) perchlorate and perchloric acid or sodium hydroxide against either sodium hydroxide or perchloric acid, the ionic strength being maintained at 0,15 M ClO_4^- by added sodium perchlorate. The reaction was followed using a combination of a Russell pH Ltd. glass electrode (SF 75/C14) and a calomel electrode in which the KCl had been replaced by NaCl. The reference electrode and the titration vessel (Metrohm Cat. No. EA876-20) were thermostated at 25° ± 0,1°C using a Lauda (Type K4RD) thermostat. Burettes (Metrohm Cat.No. E274) and

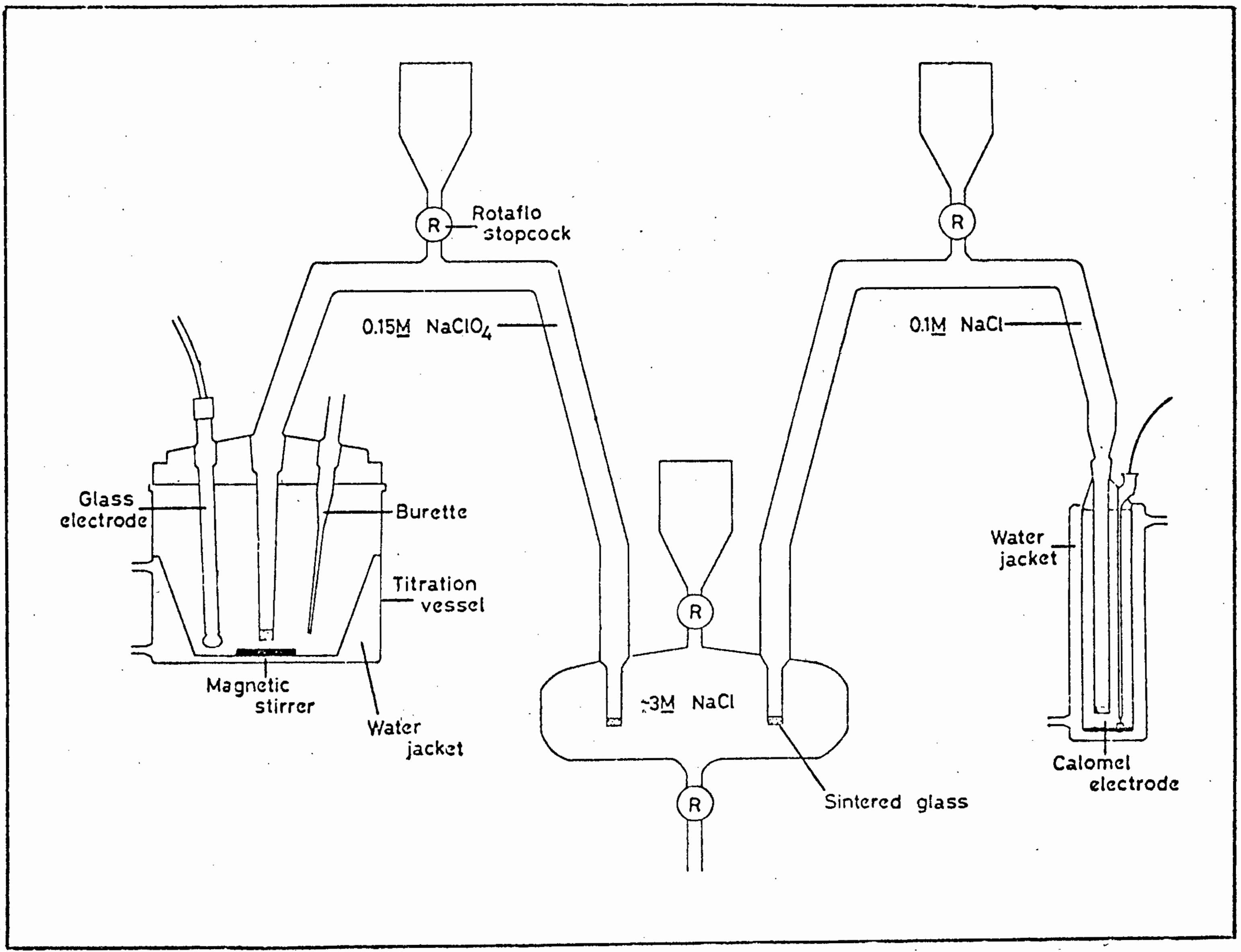


Diagram of apparatus used in the determination of formation constants.
The nitrogen bubbler, thermometer and potentiometer are not shown.

Fig 2.4.1

pipettes were calibrated before use. The e.m.f. readings were taken using a Radiometer PHM 64 digital pH-meter. The construction and composition of the salt bridge were such as to minimise diffusion effects yet facilitate the renewal of the liquid junction potentials between titrations. The high purity nitrogen (AFROX) under which the reactions were studied was further purified by bubbling through a sequence of gas wash bottles before being admitted to the titration vessel.

(i) 50% KOH to remove CO_2;

(ii) 15 g pyrogallol in 100 ml 50% NaOH to remove O_2;[65]

(iii) lead wool immersed in an alkaline (200 g dm^{-3} KOH) 1% sodium 1,2-naphthoquinone-4-sulphonate solution to remove O_2;[66]

(iv) an excess of zinc amalgam in contact with an acidic (50 ml dm^{-3} conc. H_2SO_4) chromous/chromic sulphate (300 g dm^{-3} $Cr_2(SO_4)_3 \cdot 15H_2O$) solution to remove O_2;[66]

(v) an empty wash bottle;

(vi) the support electrolyte (0,15 $\underline{M}$ $NaClO_4$) thermostated at 25°C.

Back diffusion after passing through the titration vessel was prevented by releasing the nitrogen to the atmosphere via an ionic backround solution trap.

Glass distilled CO_2-free water was used in the preparation of all solutions. $NaClO_4$ (Merck) was further purified by filtering through a 8,0 μ PVC membrane (Sartorius). The pH was adjusted to 12 and left for 3 days to precipitate any metal impurities present, and then refiltered through a 0,45 μ membrane. Acidification and boiling to remove CO_2 then followed. After cooling, the solution was finally adjusted to pH 7. The $NaClO_4$ concentration was determined gravimetrically by evaporating a pipetted volume to dryness under vacuum. The

$Cu(ClO_4)_2$ (K and K Laboratories) stock solution was standardised by EDTA titration.[67] The NaOH was prepared from ampoules (Merck) and standardised with potassium hydrogen phthalate. $HClO_4$ (Merck) concentration was determined by titration with the NaOH and checked using borax which had been recrystallised and stored over a sugar/salt solution. Methyldopa (Fluka, Puriss) was used as supplied (Found : C, 50,3; H, 6,8; N, 6,0. $C_{10}H_{13}O_4N\cdot 1\frac{1}{2}H_2O$ requires C, 50,4; H, 6,7; N, 5,9%). Catechol (Fluka, Puriss) after being triply sublimed and alanine (Sigma Chemical Co.) were found to be >99% pure. The ligand was weighed directly into the titrating vessel containing 20 ml of pipetted acidified $Cu(ClO_4)_2$ solution at the required concentration before each titration. The mixture was allowed to equilibrate for ½ hour before titrating was commenced. Reproducibility in titrations was improved if the glass electrodes were allowed to 'recover' after a titration by soaking them in an acidified (0,1 M $HClO_4$) solution at the ionic backround concentration before being used again. Hence two electrodes were used in rotation in the experiments.

The $[H^+]$ value at 25°C was calculated according to the equation,

$$E = E° + 59{,}16 \log [H^+] \qquad \ldots\ 2.4.1.$$

E is a function of the potential difference in mV between the glass and reference electrodes as read by the potentiometer, and varies according to the difference in the concentration of hydrogen ions on either side of the glass electrode. E° is a constant dependent on the apparatus design. Before each titration the value of E° was evaluated using a solution of known $[H^+]$ (section 3.3), and the linear relationship (equation 2.4.1) was assumed to hold over the complete pH range studied. Hence mV readings versus known additions of titrant were obtained and used with the E° value as input data to the computer programs employed in the model fitting.

3. CALIBRATION AND ASSESSMENT OF POTENTIOMETRIC TECHNIQUE.

Before investigating an unknown system using untested apparatus, it is necessary to analyse known systems and compare the results obtained with those from the literature. Agreement allows one to place confidence in any readings one might obtain from future experiments. With this in mind, potentiometric titrations using our apparatus were carried out on solutions of acetic acid, glycine-copper(II) and perchloric acid at 0,15 M $NaClO_4$ and 25°C, the purpose being to:

(i) test the linearity of the glass electrodes used in the pH range to be studied;

(ii) assess the reproducibility of the apparatus;

(iii) obtain formation constants for the relevant systems, literature values for which are well established, and in so doing to calibrate the apparatus.

3.1. Acetic acid protonation constant.

Solutions of acetic acid (Merck) varying in concentration from 0,005 M to 0,05 M were titrated potentiometrically with NaOH to a pH of 5.5. The results were processed using the program MAGEC (see section 2.1.6).

A FIX label required that the value given be held constant throughout the calculation. FIND means that the variable is refined. FREE means the value is initially fixed but is permitted later to vary along with the FIND variables.

The optimised $[HOAc]_0$ values (Table 3.1.1) agreed favourably with those obtained by a Gran plot[68], these being 0,00592 M, 0,00999 M and 0,0503 M respectively. The protonation constant of acetic acid at 25°C in 0,2 M KNO_3 has been reported by Feldman and Koval[69]. An estimation of its value at 0,15 M ionic strength was calculated using the Davies relationship (equation 4.6.1) and found to be $4{,}22\text{x}10^4$. From the study, the linearity of the electrodes and the reproducibility of the apparatus were found to be satisfactory.

Table 3.1.1.

Optimised parameter values for acetic acid titration ($0{,}15$ M $NaClO_4$, 25°C)

E°	317,6	316,4	315,4	FIND
β^H	$3{,}3807\text{x}10^4$	$3{,}3947\text{x}10^4$	$3{,}2825\text{x}10^4$	FREE
Slope	59,16	59,16	59,16	FIX
Kw	$1{,}73\text{x}10^{-14}$	$1{,}73\text{x}10^{-14}$	$1{,}73\text{x}10^{-14}$	FIX
$[HOAc]_0$	$5{,}9204\text{x}10^{-3}$	$9{,}9416\text{x}10^{-3}$	$5{,}0172\text{x}10^{-2}$	FIND
[NaOH]	$1{,}988\text{x}10^{-2}$	$1{,}988\text{x}10^{-2}$	$3{,}009\text{x}10^{-1}$	FIX
$[V]_0$	20,0	20,0	20,0	FIX

3.2. Glycine-proton and glycine-copper(II) formation constants.

Formation constants of glycine (BDH) were determined by titrating 0,05 M ligand solutions in 0,05 M $HClO_4$ with 0,03 M NaOH in the absence of metal ions up to a pH of 10. The refined values (MINIQUAD) appear in Table 3.2.1. The first protonation constant is assigned to the amine nitrogen of glycine, the second to the carboxyl group.

The glycine-copper(II) stability constants were determined by titrating 0,05 M glycine, 0,05 M $HClO_4$ and 0,005 M $Cu(ClO_4)_2$ with 0,03 M NaOH. The protonation constants included in the refinement (MINIQUAD) were those in Table 3.2.1, and were not permitted to vary. The results appear in Table 3.2.2.

Table 3.2.1.

Logarithms of protonation constants for glycine
(0,15 M NaClO$_4$, 25 °C)
No. of titration points = 129 R = 0,0018

Complex	log β_{por}	log K_{por}	std.dev.in log β_{por}	log β_{por} (lit)[70]
AH	9,536	9,536	0,007	9,62
AH$_2$	11,912	2,376	0,011	12,06

The small value of log K_{310} as compared to log K_{110} and log K_{210}, corresponding to a third ligand molecule complexing to the metal, is consistent with the prediction that copper(II) accepts a third bidentate ligand relatively unwillingly in rearranging itself from a square planar coordination geometry into a distorted octahedral environment (Jahn-Teller effect).

Table 3.2.2.

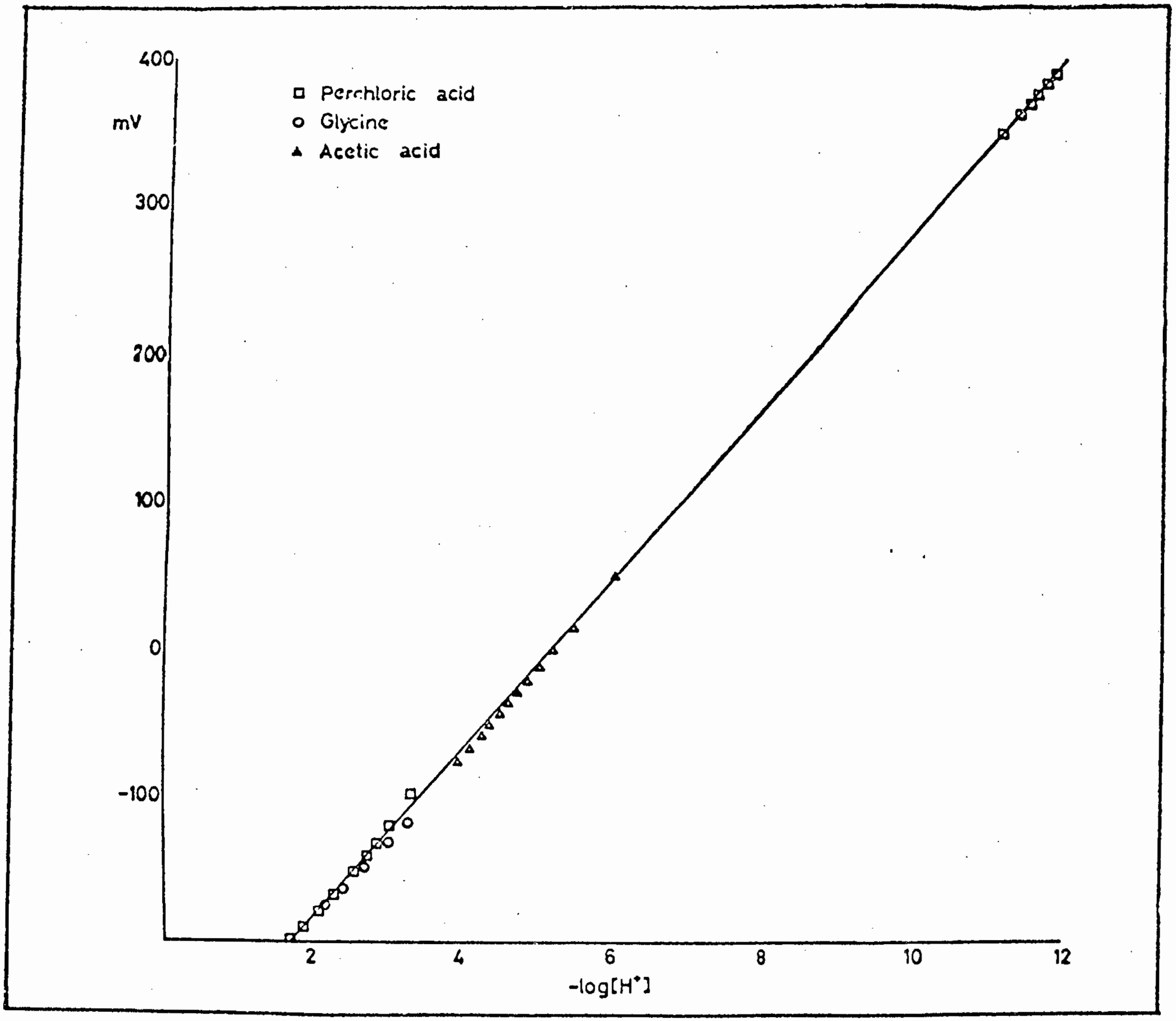
Logarithms of formation constants for the glycine-copper(II) system (0,15 M NaClO$_4$, 25°C)
No. of titration points = 109 R = 0,0033

Complex	log β_{pqo}	log K_{pqo}	std.dev.in log β_{pqo}	log β_{pqo} (lit)[70]
AB	8,250	8,250	0,021	8,18
A$_2$B	15,072	6,822	0,055	15,02
A$_3$B	16,300	1,228	0,107	-

3.3. Calibration of the apparatus.

From mass balance and electrical neutrality considerations, $[H^+]$ can be calculated at any point in the titration of a weak acid by a strong base, provided the dissociation constant of the weak acid is known under the conditions of the titration. $-\log[H^+]$ can then be plotted against the potentiometer readings obtained and the result checked to see whether equation 2.4.1 is obeyed. An example of such calculations on readings obtained from titrations of glycine, acetic acid and perchloric acid with NaOH using one electrode can be seen in Fig 3.3.1. The acids were chosen so as to incorporate as wide a range as possible in $-\log[H^+]$. The linearity of the electrode used is evident.

The method for determining E° in a titration in which $[H^+]$ was unknown is now described. A buffer solution of known $[H^+]$ made up of acetic acid and NaOH in 0,15 M $NaClO_4$ was placed in the titration vessel and the potentiometer reading noted using a glass electrode whose linearity over the range to be studied had been established employing the methods described above. Equation 2.4.1. was solved for E°, a value that was then used in the titration to follow in the calculation of $[H^+]$ at each point. The procedure was repeated before each subsequent titration with the electrode, since E° can be expected to vary slightly due to the renewal of the liquid junction carried out between titrations and changes in the potential of the glass electrode membrane.



Electrode calibration

Fig 3.3.1

4. STUDY OF METHYLDOPA-PROTON AND METHYLDOPA-COPPER(II) EQUILIBRIA: RESULTS

4.1. Ultraviolet/visible spectrophotometric results.

All spectra were recorded in 10mm cuvettes at 25°C and $I = 0{,}150$ mol dm^{-3} $Na^{+}ClO_{4}^{-}$ against water as a reference using a Beckman DK2A recording spectrophotometer. Spectra (1000nm - 350nm) at progressively increasing pH values were obtained from solutions in which the total ligand concentration ranged from 0,088 M to 0,010 M, the ligand:copper(II) ratio varying from 6:1 to 1:1. With the stated aim in mind (section 2.2), the analysis was initially directed more at positional maxima in the spectra than their absolute absorbance.

(i) Alanine-copper(II):

Spectra of a solution at various pH values in which the total concentration of alanine was 0,010 M and that of copper(II) was 0,004 M are shown in Fig 4.1.1. The absorption maximum at pH4 shows a hypsochromic shift with an increase in intensity as the pH is brought up to 6. Above this value the band remains essentially constant at ≃ 610 nm, the variation in absorbance being non-uniform. An asymmetric absorption maximum in the range 600 to 700 nm is typical of the d-d transitions found in copper(II) complexes.[34,71,72]

(ii) Catechol-copper(II):

Fig 4.1.2 shows the spectra obtained at various pH values from a solution containing initially 0,010 M catechol and 0,004 M copper(II) respectively. Towards the high pH region, the spectra consist of two broad bands. One band centred at about 700 nm at pH 6, first increases and then decreases slightly in intensity with a hypsochromic shift as the pH is raised, and is probably of the type mentioned above involving the d-d transitions of copper(II). The other band at approximately 415 nm increases in intensity in undergoing the same pH change, the position of the absorption maximum remaining essentially constant. Charge transfer bands in this latter region are evidently characteristic of copper(II) - O,O bonds[73].

(iii) Methyldopa-copper(II):

The spectra at different pH values for a solution in which both the methyldopa and copper(II) concentrations were 0,010 M is shown in Fig 4.1.3. The spectra appear to be an approximate overlap of those described above. The conclusion hence is that below pH4, copper(II) is predominantly bound to the alanine-type moiety of methyldopa, with complexation at the catechol-type site being minimal. As the pH increases, binding to both the alanine and catechol ends becomes evident. Due to the complicated pH dependence of the absorbances, however, a detailed estimate of the relative coordination distribution appears to be not feasible.

An interesting observation detected during the methyldopa-copper(II) spectra measurements was the increased competitiveness for the catechol site of the ligand by copper(II) as the concentration of the components was increased, an effect paralleled for decreasing values of the ligand:metal ion ratio at constant ligand concentration. This was made apparent by the lower pH at which the band at 415 nm first showed itself in these solutions.

Spectra of alanine-copper(II) complexes. Concentrations (10^{-3} mol dm^{-3}) of A and B are 10,0 and 4,0. Reference, water.

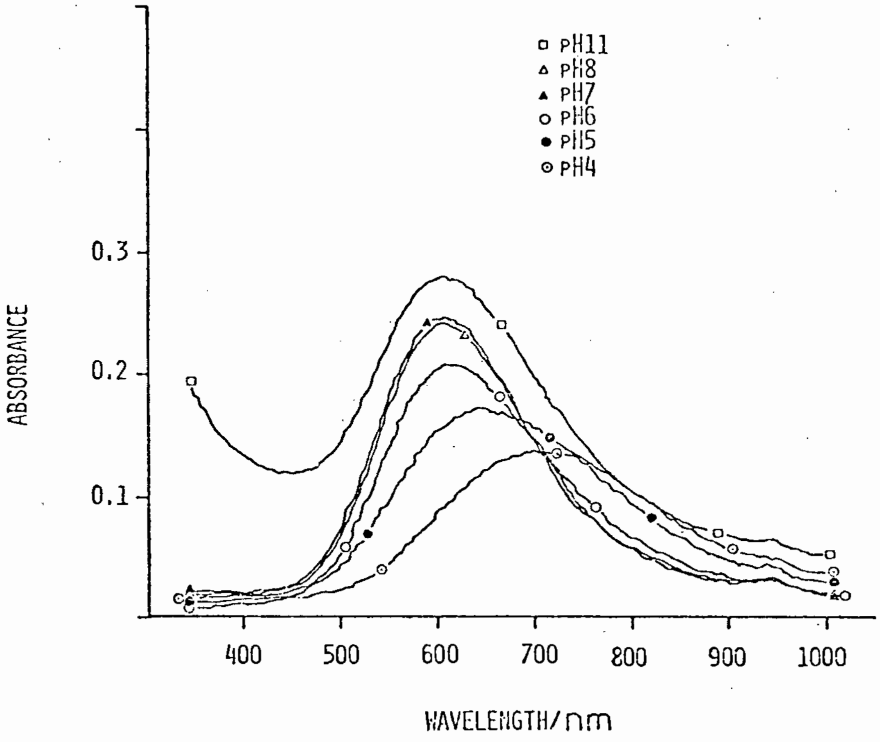


Fig 4.1.1

Spectra of catechol-copper(II) complexes. Concentrations $(10^{-3}$ mol dm$^{-3})$ of A and B are 10,0 and 4,0. Reference, water.

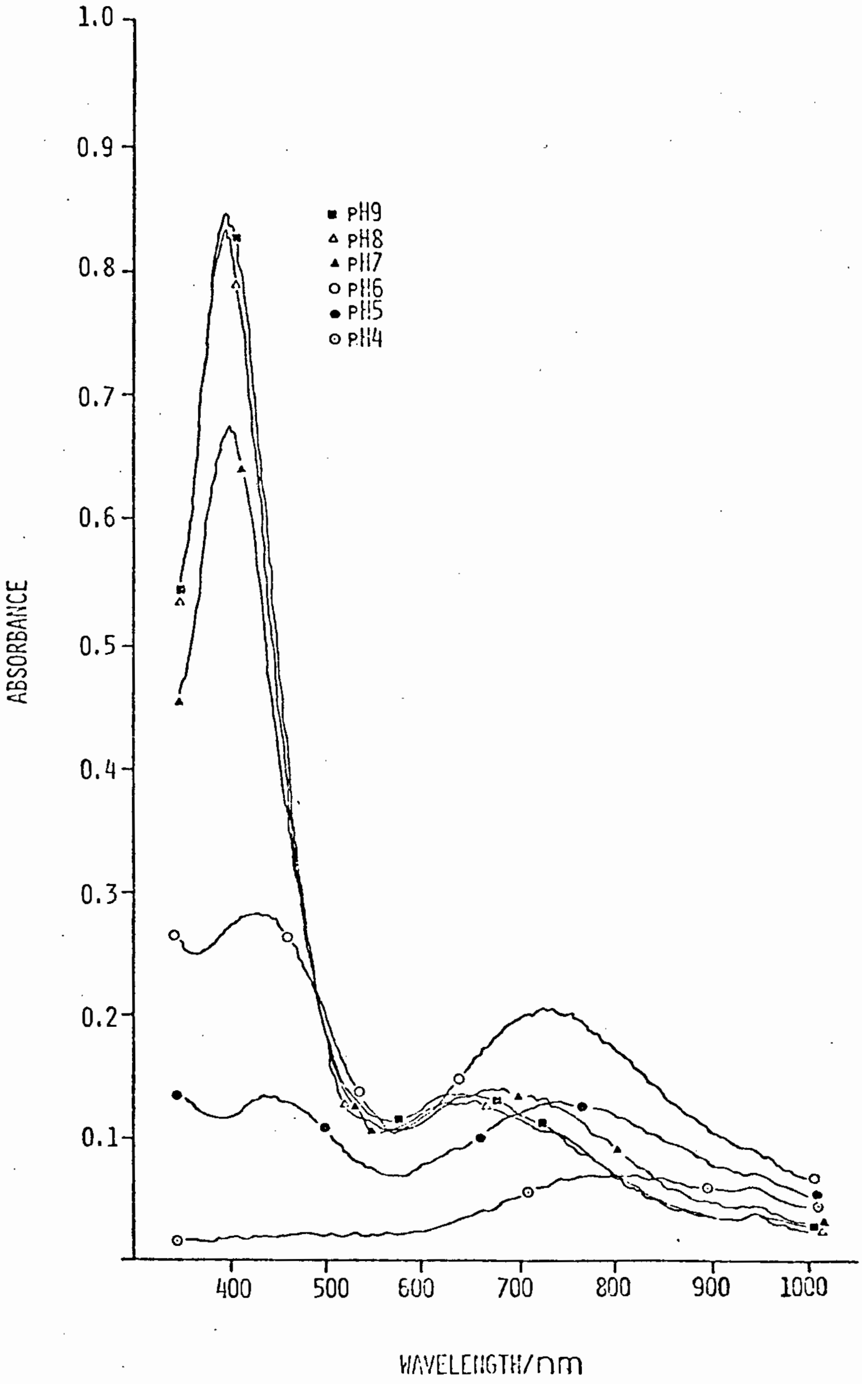


Fig 4.1.2

Spectra of methyldopa-copper(II) complexes. Concentrations (10^{-3} mol dm^{-3}) of A and B are 10,0 and 10,0. Reference, water.

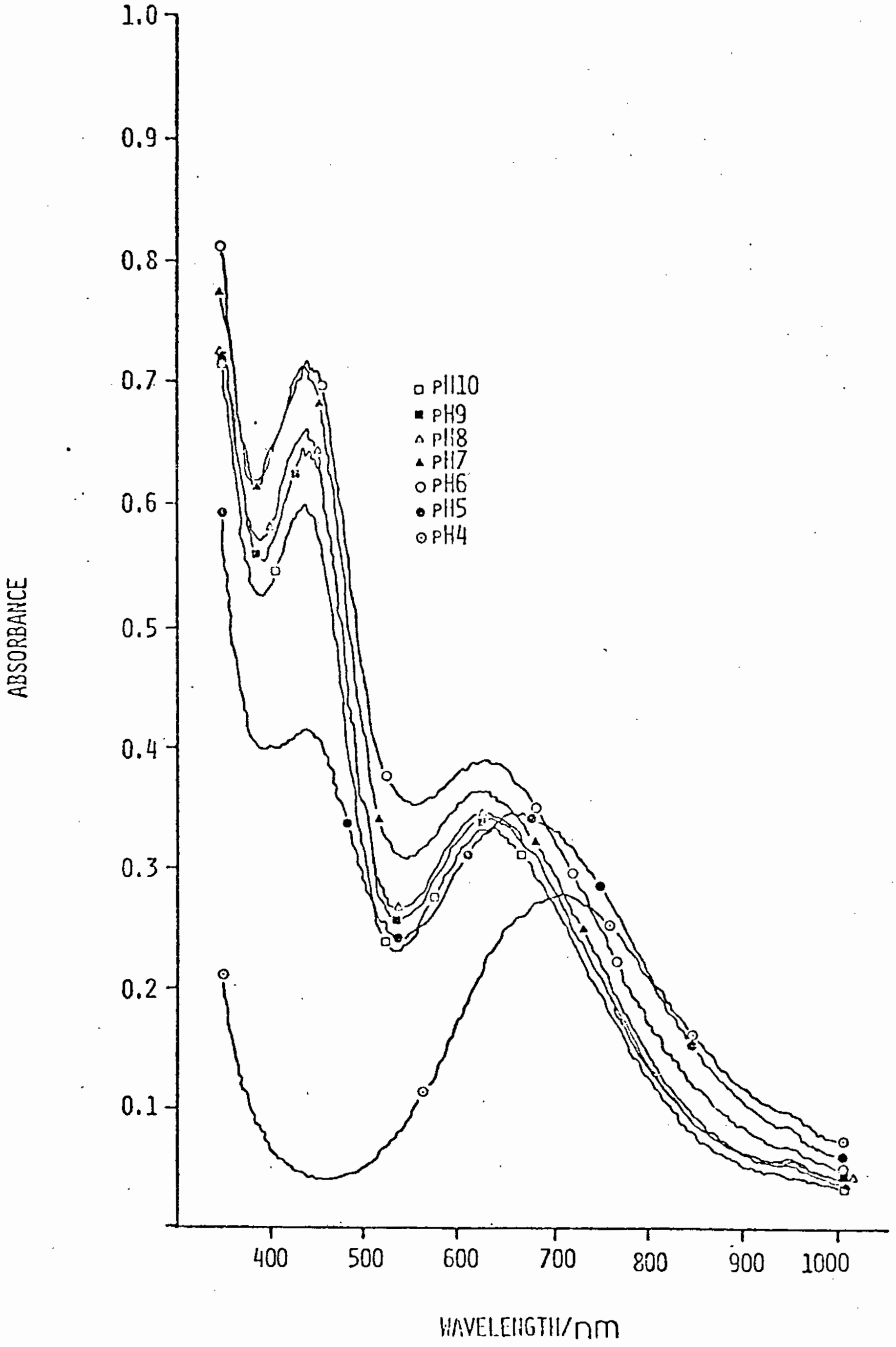


Fig 4.1.3

4.2. NMR results.

Spectra were recorded at 90 MHz on a Bruker WH-90DS spectrometer operating in the Fourier transform mode. Ligand solutions (0,05 mol dm^{-3}) in ^2H_2O were adjusted to the required pH with NaO^2H and ^2HCl. The pH of the solutions were calculated from pD = pH + 0,4. The sodium salt of 3-trimethylsilyl propane sulphonic acid was used as internal reference.

The chemical shifts for the protons on C(3), C(2)-CH_3, C(2'), C(5') and C(6') were measured as a function of pH in the methyldopa molecule (Fig 5(1)). The pH corresponding to the maximum rate of change of chemical shift for C(3) and C(2)-CH_3 was observed in the range 9,80-9,96, and corresponds to the approximate pKa of the protonated amino group. For the aromatic protons the apparent pKa was in the range 9,1-9,2.

It has been found that in the phenol/phenoxide and substituted phenol systems in which there is a unique site of deprotonation, the protons in the ortho and para positions show much larger upfield shifts than the meta protons.[74,75] In the methyldopa molecule however, the aromatic proton shifts are: C(2') 20 Hz, C(5') 24 Hz and C(6') 26 Hz. As an explanation it appears that the remaining proton on the catechol mono-anion moiety either is in rapid exchange between two sites or is held in a 'symmetric' hydrogen bonded bridged structure.

A NMR study consisting of T_1 experiments[76] at pH 4 and pH 8,5 with ligand:metal ion ratios in the vicinity of 100:1 failed to provide further information as regards the pH dependence of copper(II) bonding at the two coordination sites of methyldopa. This arose due to the fact that the changes in

T_2 were very much faster than those in T_1. The consequent overlapping of the aromatic resonances made quantitative measurement impossible.

4.3. ECCLES results.

In order to determine the feasibility of 'mixed bonding' occurring in the methyldopa-copper(II) system involving both N,O and O,O bonds, a model consisting of copper(II) in solution with molecules in which the potential donor groups of methyldopa occur in different ligands was inputted to the program ECCLES. The ligands used were alanine and catechol. The treatment necessitated a knowledge of the protonation and copper(II) stability constants of the ligands concerned. These were determined potentiometrically by the same method used for methyldopa. Titration data were in each case submitted to the program MINIQUAD for refinement of the β's, the final values for which appear in Tables 4.3.1 and 4.3.2 respectively.

In the ECCLES calculations, total alanine concentration was initially equal to total catechol concentration at 0,02 M. Total copper(II) initial concentration was 0,004 M. Employing a stabilisation factor of 0,40[30], the stability constant of the ternary alanine-copper(II)-catechol complex as computed by ECCLES was 19,65. The distribution with pH of complexes as calculated by ECCLES is shown in Fig 4.3.1. The designation Ala-Cu(II) on the graph includes both the 1:1 and 2:1 alanine-copper(II) complexes, as does Cat-Cu(II) in the case of the catechol-copper(II) complexes. The significant contribution of the ternary complex towards the total bound copper(II) at pH 7,5 substantiates the proposal that a 'mixed' mode of complexation is present in the methyldopa-copper(II) system in the same region. Also noteworthy is the obvious preference of copper(II) for N,O type bonding at low pH values and O,O type bonding at high pH values, given equal concentrations of both options.

Table 4.3.1.

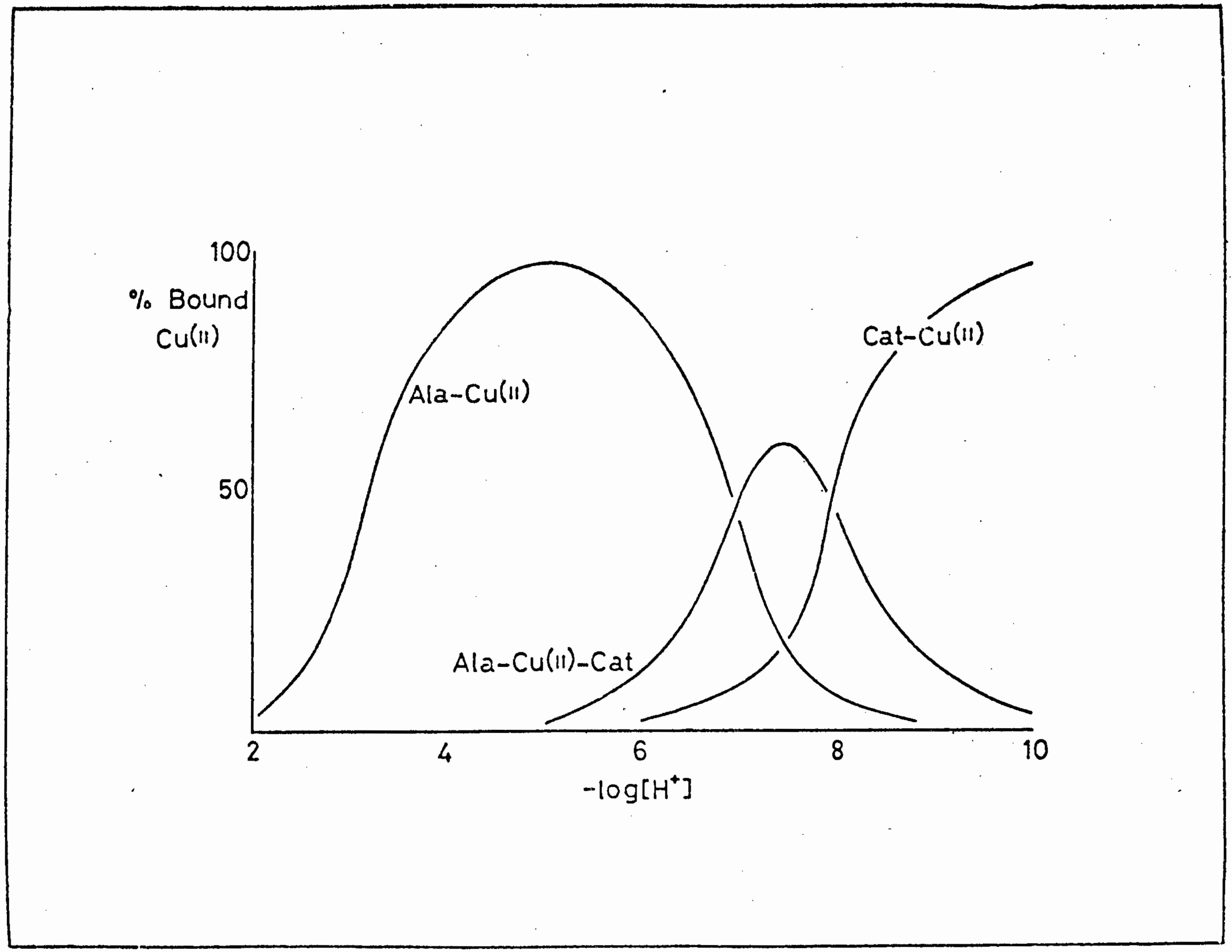
Logarithms of protonation and formation constants for the alanine-copper(II) system (0,15 $\underline{M}$ $NaClO_4$, 25°C)
No. of titration points = 78 R = 0,0062

Complex	$\log \beta_{pqr}$	std. dev. in $\log \beta_{pqr}$	$\log \beta_{pqr}$ [77] $I = 0{,}1\ \underline{M}\ NaClO_4$
AH	9,659	0,007	9,83
AH	11,970	0,032	12,09
AB	8,128	0,072	8,25
A_2B	14,956	0,062	15,30

Table 4.3.2.

Logarithms of protonation and formation constants for the catechol-copper(II) system (0,15 $\underline{M}$ $NaClO_4$, 25°C)
No. of titration points = 61 R = 0,0145

Complex	$\log \beta_{pqr}$	std. dev. in $\log \beta_{pqr}$	$\log \beta_{pqr}$ [77] $I = 0{,}10\ \underline{M}\ NaClO_4$
AH	9,091	0,055	9,32
ABH_{-1}	0,835	0,076	0,96
A_2BH_{-2}	-1,041	0,159	-0,97



Distribution of complexes in alanine-copper(II)-catechol system calculated by ECCLES.

Fig 4.3.1

4.4. Methyldopa protonation constants.

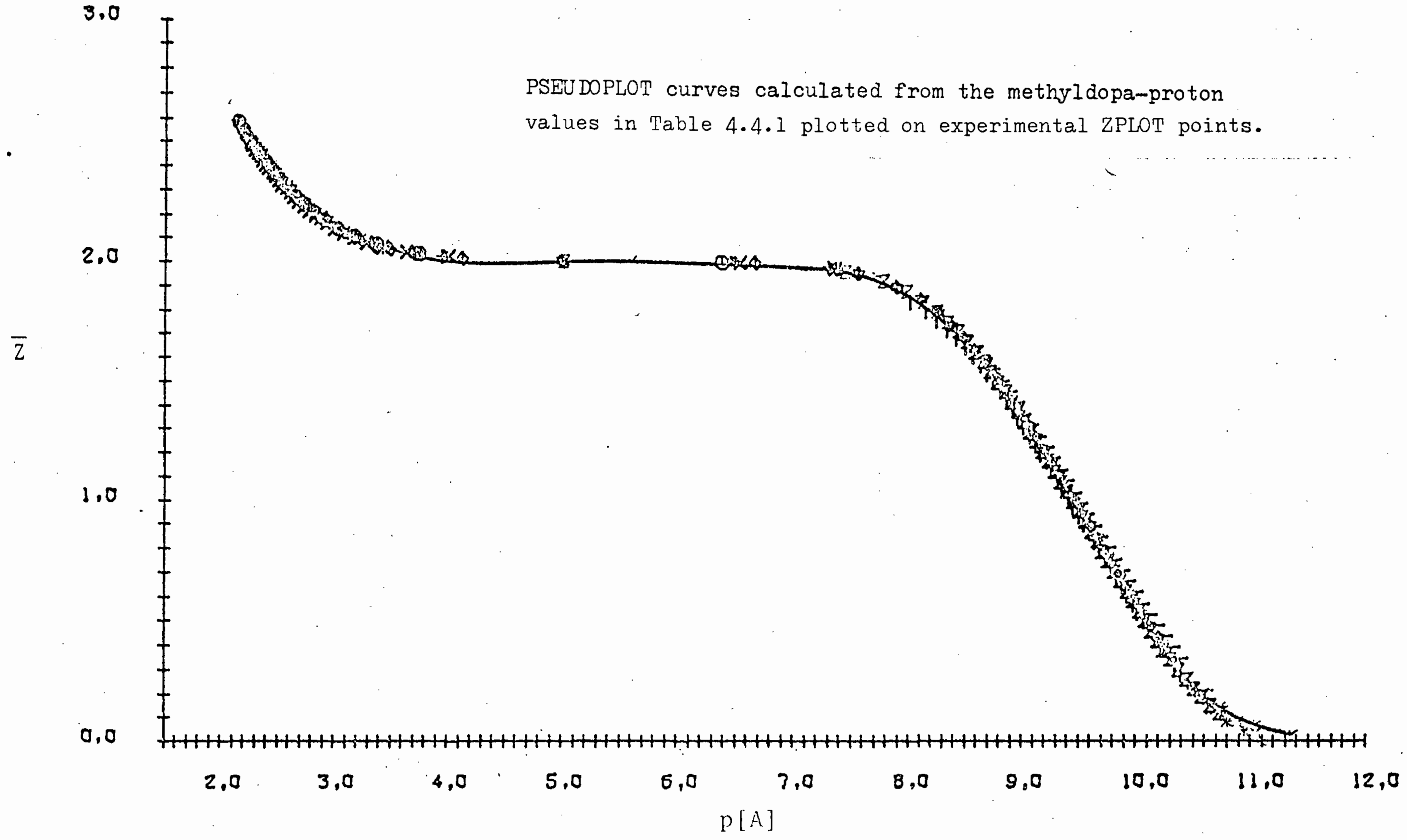
The logarithms of the overall protonation constants of methyldopa as determined by MINIQUAD appear in Table 4.4.1. The experimental (ZPLOT) and theoretical (PSEUDOPLOT) formation curves appear in Fig 4.4.1.

Table 4.4.1.

Logarithms of the overall protonation constants of methyldopa (0,15 M $NaClO_4$, 25°C)
R = 0,0123

Complex	Site	log β_{por}	std.deviation in log β_{por}	No. of exp. observations
AH	NH_2	9,982	0,005	289
AH_2	O^-	18,886	0,006	439
AH_3	CO_2^-	21,104	0,014	288

The refinement was carried out on data points obtained from forward and backward titrations varying in initial ligand concentration from 0,008 M to 0,037 M, up to a pH of approximately 11,6. Slight oxidation effects, made evident by the discolouration of the titration mixture in the high pH range, proved to be insignificant in that the formation curves for both forward and backward titrations overlapped almost exactly. It was found impractical, considering the comparatively low background electrolyte ionic strength used in this work, to determine potentiometrically the protonation constant of the trianion of methyldopa due to its expected value lying close to the ionic product of water. (However, see Section 4.6). It has been suggested that the very strong



PSEUDOPLOT curves calculated from the methyldopa-proton values in Table 4.4.1 plotted on experimental ZPLOT points.

Fig 4.4.1

basic nature of one of the catechol oxygen atoms is caused by hydrogen bonding between the hydroxyl and phenoxide groups.[78] The ligand A unless otherwise stated hence refers to the doubly charged methyldopa anion resulting from the ionisations of the carboxylate group, one phenolic group and the amino group (Fig 5(2)). The assignments of the formation constants to their respective protonation sites by NMR measurements is described in Section 4.2.

4.5. Methyldopa-copper(II) formation constants (MINIQUAD):

Table 4.5.1 shows the most consistent set of complexes found, together with the respective logarithms of the formation constants, as refined by MINIQUAD. The validity of the model is illustrated by the excellent matching of the experimental $\bar{Z}$obs/p[A] points in Fig 4.5.1 to the corresponding theoretical formation curves computed by PSEUDOPLOT, using the formation constants in Table 4.5.1. Fig 4.5.2(a)-(f) are the HALTAFALL plots of the concentrations of complexes as a function of pH for the 10:1, 2½:1 and 1:1 ligand: metal ion ratios studied. The 5:1 distributions are similar to the 10:1 and are not shown.

The MINIQUAD computations were carried out on a series of forward and backward titrations varying in total reactant concentration from 0,004 to 0,037 mol dm^{-3}. In all refinements the protonation formation constants of the ligand were fixed and not allowed to vary, and the hydrolysis reactions,[85]

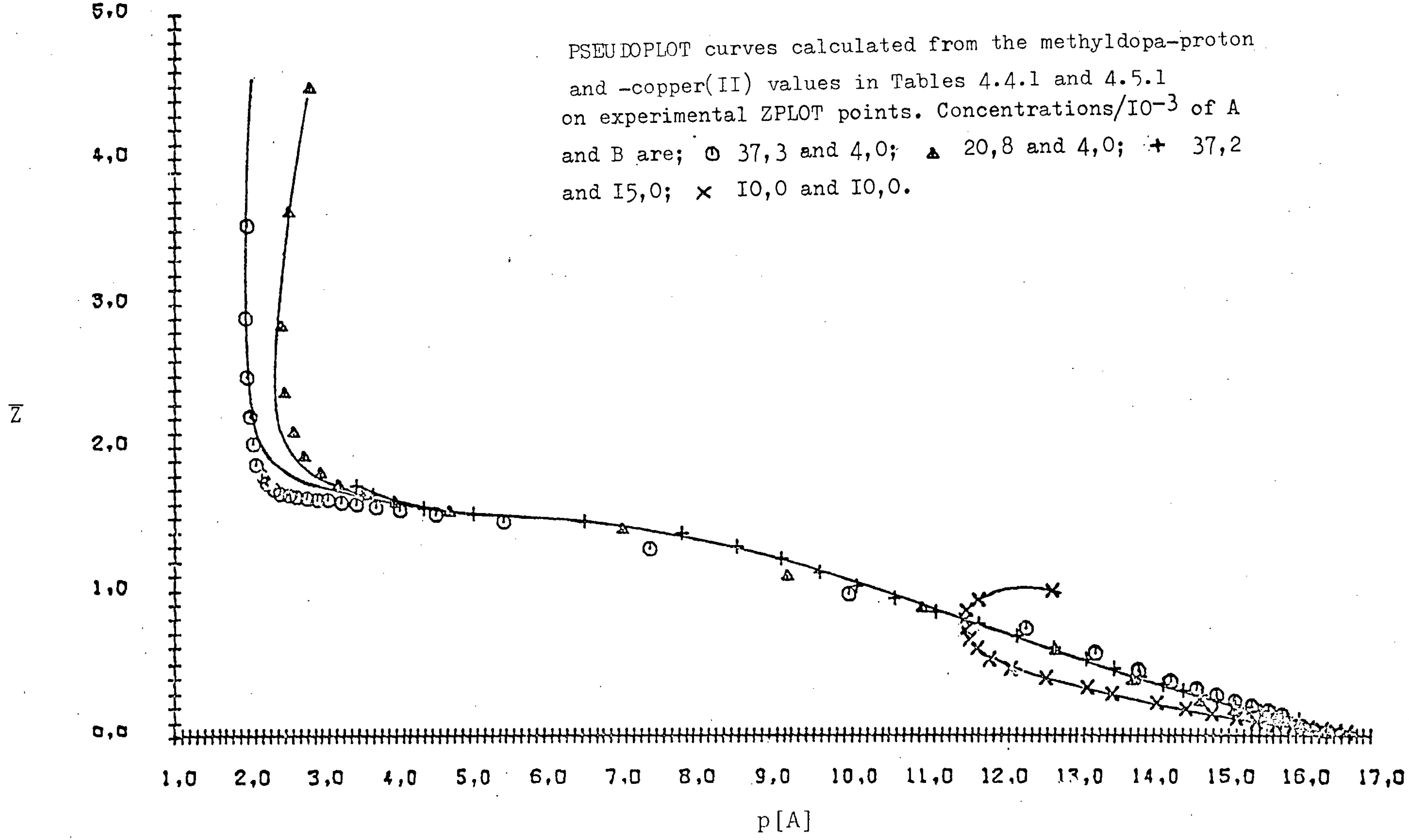
$$Cu^{2+} + H_2O \rightleftharpoons CuOH^{+} + H^{+}, \qquad \log K = -8{,}0;$$

$$2Cu^{2+} + 2H_2O \rightleftharpoons (Cu)_2(OH_2)^{2+} + 2H^{+}, \qquad \log K = -10{,}6,$$

were incorporated into every trial. The high degree of non-overlapping together with the fanning back pattern observed in the experimental formation curves for the various total concentrations of ligand and metal (Fig 4.5.1) indicate that not only mononuclear binary but also other types of complex, e.g. protonated, hydroxo and polynuclear, are formed. Attempts to refine all ratios together failed (see chapter 5), and this necessitated successive division and grouping of the titration data in various ways according to the ligand:metal ratios and the range of pH in order to obtain a consistent chemical model to explain the entire set of potentiometric data. Thus the final formation constants of the species ABH, A_2BH_2 and ABH_2 were obtained through refinement using titration data points from all ratios, but restricted to those corresponding to a pH less than 3,5. In subsequent refinements at higher pH values when additional complexes were included in the model, β_{111}, β_{212} and β_{112} were fixed together with the ligand protonation and hydrolysis constants and not varied in the refinement process.

Referring to Fig.4.5.2(a), the 10:1 (and 5:1) ratio solutions in particular are characterised by complexes corresponding to successive deprotonations of the species A_2BH_2, with no polynuclear species present.

The presence of a series of open chain polymers and a cyclic dimer in the 1:1 ligand:metal solutions was indicated using results obtained from the program GEPOLYC (see Section 4.6) and substantiated through successful refinement of this model with the program MINIQUAD. Based on the GEPOLYC results, the concentration of the open chain polymers $A_nB_nH_{2-n}$ becomes negligible for $n \geq 5$. In agreement with this is the finding from MINIQUAD calculations that the linear dimer, the trimer and the tetramer are the only significant representatives of these polymers in the 1:1 ratio solutions.



PSEUDOPLOT curves calculated from the methyldopa-proton and -copper(II) values in Tables 4.4.1 and 4.5.1 on experimental ZPLOT points. Concentrations/IO^{-3} of A and B are; ʘ 37,3 and 4,0; ▲ 20,8 and 4,0; + 37,2 and I5,0; × I0,0 and I0,0.

Fig 4.5.1

Table 4.5.1

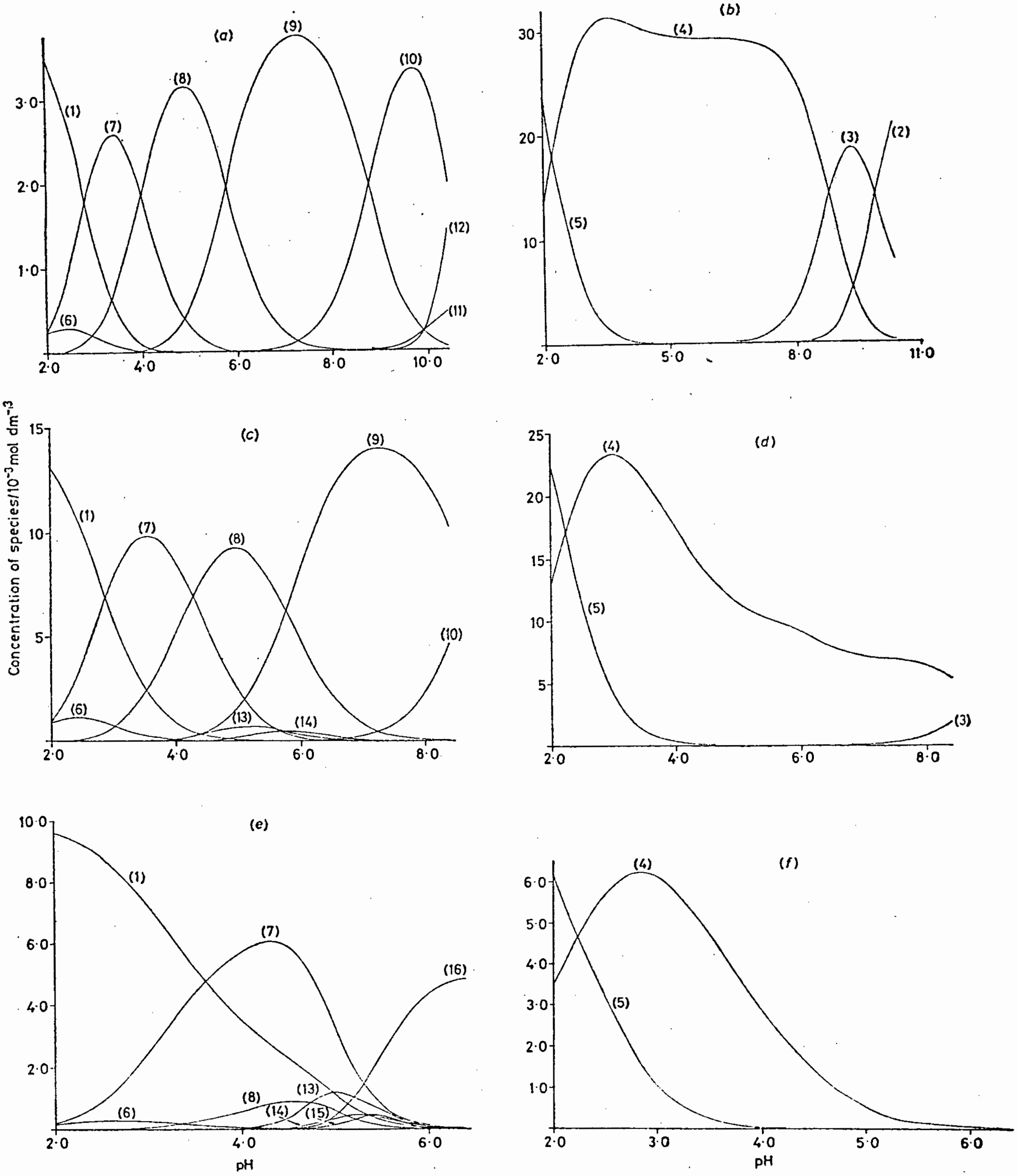
Logarithms of the formation constants for the copper(II) complexes of methyldopa (0,15 M $NaClO_4$, 25°C)

Complex	$\log\beta_{pqr}$	Std.deviation in $\log\beta_{pqr}$	No.of experimental observations
ABH	17,613	0,005	167
A_2BH_2	34,004	0,031	75
ABH_2	19,568	0,085	167
A_2BH	28,234	0,011	66
A_2B	19,487	0,018	105
A_2BH_{-1}	8,447	0,264	48
A_2BH_{-2}	-1,454	0,094	44
A_2B_2	27,290	0,035	107
$A_3B_3H_{-1}$	36,850	0,136	89
$A_4B_4H_{-2}$	46,625	0,129	82
$A_2B_2H_{-2}$	16,894	0,012	87

R = 0,0030 for the 10:1, 5:1 and 2½:1 ratio solutions and 0,0044 for the 1:1 solutions.

The observation that the formation curve of the 1:1 solution resides in a very different region to that of the other ratios is probably indicative of the higher fraction of oligonuclear species which are apparent in these solutions and is likely due to the relatively large proportion of metal ion present. The concentration of these oligonuclear species is seen to be particularly high between pH 5 and 6, a region in which the ligand and protonated ligand concentrations are extremely small (Fig 4.5.2(f)).

The 2½:1 ratio solutions were found to be of intermediate character between the 10:1 and 5:1 ratios on the one hand and the 1:1 ratio on the other. Thus the species A_2BH and A_2B are important in the 10:1, 5:1 and 2½:1 solutions but not in the 1:1, whilst the species A_2B_2 and $A_3B_3H_{-1}$ are significant only in the 2½:1 and 1:1 solutions but not in the others. In fact, the distributions of complexes in the 1:1 solutions are seen to be distincly different from those with A:B ratios of 10:1 and 5:1.



HALTAFALL plots of the concentrations of complexes present as a function of pH for the methyldopa–copper(II) system when the total concentrations (10^{-3} mol dm^{-3}) of A and B(Cu^{2+}) are: 37.3 and 4.00 [(*a*), (*b*)]; 37.2 and 15.0 [(*c*), (*d*)]; and **10.0 and** 10.0 [(*e*), (*f*)]. Species: Cu^{2+} (1), A^{2-} (2), HA^- (3), H_2A (4), H_3A^+ (5), $[Cu(H_2A)]^{2+}$ (6), $[Cu(HA)]^+$ (7), $[Cu(AH)_2]$ (8), $CuA(HA)]^-$ (9), $[CuA_2]^{2-}$ (10), $[CuA(H_{-1}A)]^{3-}$ (11), $[Cu(AH_{-1})_2]^{4-}$ (12), $[Cu_2A_2]$ (13), $[Cu_3A_3H_{-1}]^-$ (14), $[Cu_4A_4H_{-2}]^{2-}$ (15), $[Cu_2A_2H_{-2}]^{2-}$ **(16)**

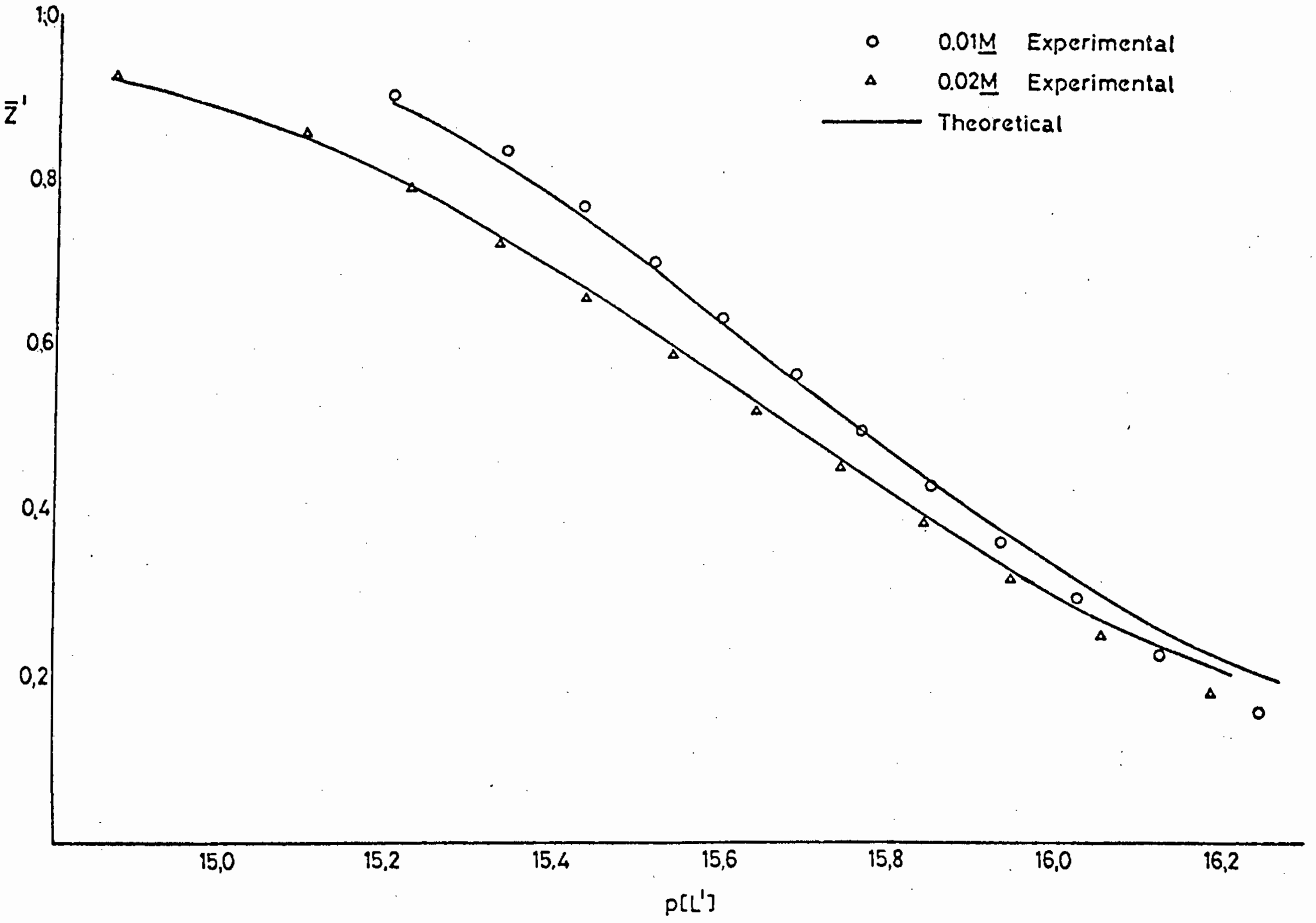
Fig 4.5.2

4.6. Methyldopa-copper(II) formation constants (GEPOLYC).

Application of the program GEPOLYC to the 1:1 ligand: metal ion solutions studied necessitated a knowledge of the protonation constant of the trianion of methyldopa (eqn. 2.1.5.2), a value found too high to determine experimentally in the present study owing to the low background electrolyte used. An attempt was made to find a good estimate of this first protonation constant at 0,15 M ionic strength using the Davies equation,[79]

$$-\log f = AZ^2\left(\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - CI\right) \qquad \ldots\ldots 4.6.1$$

based on the value for dopa measured at I = 1,00 by Gorton and Jameson.[46] An average value of C was estimated by comparing K'_{102} and K'_{103} for dopa and methyldopa at the two respective ionic strengths, and this was then used to estimate the first protonation constant at 0,15 M ionic strength for methyldopa. K'_{102} and K'_{103} refer to the second and third stepwise protonation constants of the ligand respectively when the fully deprotonated ligand is the trianion. The value for K'_{101} obtained is $10^{13,84}$. The GEPOLYC approach was applied on two 1:1 mixtures of 0,02 M and 0,01 M initial concentration. The best fit was a model which included the series of open chain polymers ($A_nB_nH_{2-n}$) but only the cyclic dimer ($A_2B_2H_{-2}$) representing the closed chain species, with values of 13,30 for log K and 15,55 for log Kc. The formation curves for both concentrations appear in Fig 4.6.1. The computed concentrations of the various species present at selected pH values are shown in Table 4.6.1.



Formation curves for methyldopa-copper(II) 1:1 solutions (GEPOLYC).

Fig 4.6.1

Table 4.6.1

Distribution of complexes (% of total ligand) in 0,02 M 1:1 solution as a function of pH (GEPOLYC)

Complex	pH 4,9	pH 5,1	pH 5,5
ABH	51,24	28,53	8,14
A_2B_2	13,63	12,24	5,32
$A_3B_3H_{-1}$	3,62	5,20	3,48
$A_4B_4H_{-2}$	0,96	2,21	2,27
$A_5B_5H_{-3}$	0,26	0,94	1,49
$A_6B_6H_{-4}$	0,07	0,40	0,97
$A_2B_2H_{-2}$	2,44	6,45	16,01

5. GENERAL DISCUSSION OF RESULTS.

This work has indicated that the complexing characteristics of copper(II) with methyldopa are very similar to those reported for the closely related dopa-copper(II) system.[40,32,46-52] Below pH 5 predominantly amino acid type chelation exists, changing progressively (to some extent via mixed catechol and amino acid type complexes) to catechol type as the pH is increased. As regards the applicability of this to medicinal chemistry, one can say with some assurance that copper(II) is capable of bonding at both sites at physiological pH, an important structural consideration when the role played by copper(II) in the in vivo metabolism of methyldopa is discussed. The distribution of complexes in a solution containing methyldopa as the only ligand and copper(II) as the only metal ion at concentrations found in the blood of a patient undergoing treatment (typically 0,5 to 1,9 x 10^{-5} mol dm^{-3} for methyldopa[80] and 10^{-11} to 10^{-19} mol dm^{-3} for free copper(II) ions[81]) would probably closely resemble that in Fig 4.5.2(a). Considering the charged nature of $[CuA(AH)]^-$ which predominates at the physiological pH of 7.4 in this figure, it is unlikely that this species facilitates the passive transport of methyldopa across biological membranes.

It is realised however that neutral ternary species involving other low molecular weight ligand are likely to be present in human blood plasma and future computations simulating these conditions using the program ECCLES[81] might help to clarify the picture.

Before arriving at the results as presented in section

4.5, an enormous amount of computing was done. This was because it was frequently found that a model that had been successfully refined from titration data grouped in a particular way gave unsuccessful refinement of a solution which was mathematically satisfactory but chemically unsound when applied to the full set of titration data points. That this is a result of unreliability in experimental data is unlikely as reproducibility was fully checked in all cases. The complex nature of the ligand is an important factor as is the wide range of pH and ligand:metal ion ratios over which the titrations were carried out. Clearly for this system, the type of complex species is strongly pH dependent, and even at a given pH the solution composition can be expected to change from one concentration ratio to another. Thus polymer formation seems to be important in the 1:1 ligand:metal ion solutions, but less so in other ratios. As regards refining the complete set together, the observed phenomenon may be explained by proposing that some species important in a minority of concentration ratios tend to be rejected whilst those significant in the majority tend to be retained. Thus the 'weight' of the more predominant species appear to overwhelm the contribution of the less so in the optimisation process. Division and grouping of the titration data according to these considerations hence became necessary. In summary it can be said that the model as reported in section 4,5 is the result of exhaustive efforts at resolving this difficulty, and likely represents the best solution consistent with the available data.

Tables 5.1 and 5.2 contain protonation constants for dopa and complexation constants for the copa-copper(II) system respectively as obtained by other workers. Although determined under different conditions, the constants where applicable compare favourably with the values found for the methyldopa-copper(II) system during the work presented here.

Important in the evaluation of a model is the assignment of structures to the species refined. The hypothesis that ABH and A_2BH_2 refer to the 1:1 and 2:1 ligand: metal ion complexes respectively, with co-ordination through the aminocarboxylate end of methyldopa, can be inferred from the following.

The stepwise stability constant for the formation of ABH can be defined as:

$$K_{111} = \frac{[ABH]}{[AH][B]}$$

$$= \frac{[ABH]}{[A][B][H]} \quad \frac{[A][H]}{[AH]}$$

i.e. $\log K_{111} = \log \beta_{111} - \log \beta_{101}$

Similarly, K_{212} for the binary complex A_2BH_2 can be defined as:

$$K_{212} = \frac{[A_2B\,H_2]}{[AH][ABH]}$$

$$= \frac{[A_2BH_2]}{[A]^2[B][H]^2} \quad \frac{[AH][B]}{[ABH]} \quad \frac{[A]^2[H]^2}{[AH]^2}$$

Table 5.1

Logarithms of protonation constants of methyldopa and dopa

Ligand	Ionic strength/ medium	Temp. (^oC)	log β_{101}	log β_{102}	log β_{103}	Ref.
Methyldopa	0,15 M NaClo$_4$	25	9,982	18,866	21,104	this work
Dopa	1,0 M KNO	25	9,74	18,45	20,76	46
Dopa	1,0 M KNO	25	9,78	18,58	20,98	32
Dopa	0,37 M NaNO	20	9,87	18,68	20,72	40
Dopa	0(KCl)	25	10,629	19,786	22,004	82
Dopa	0,2 M KCl	25	9,83	18,63	20,85	51

Table 5.2.

Logarithms of formation constants for the copper(II) complexes of methyldopa and dopa

Methyldopa		Dopa	Ref.
Complex	log β_{pqr}	0/°C, I/mol dm^{-3}, log β_{pqr}	
ABH	17,613	25, 1,0(KNO$_3$), log β_{111} = 16,86, log β_{212} = 32,89, log β_{11-1} = -0,41, log β_{21-2} = -1,86, log β_{22-2} = 14,59	46
A_2BH_2	34,004		
ABH_2	19,568	25, 1,0 (KNO$_3$), log β_{111} = 17,38, log β_{11-1} = 3,08	32
A_2BH	28,234	20, 0,37 (NaNO$_3$), log β_{111} = 17,47, log β_{212} = 34,25	40
A_2B	19,487	25, 0,2 (KCl), log β_{111} = 17,35, log β_{212} = 33,81, log β_{211} = 27,01, log β_{210} = 18,53, log β_{21-1} = 9,03, log β_{21-2} = -1,33, log β_{220} = 26,55, log β_{22-2} = 15,10	51
A_2BH_{-1}	8,447		
A_2BH_{-2}	-1,454		
A_2B_2	27,290		
$A_3B_3H_{-1}$	36,850		
$A_4B_4H_{-2}$	46,625		
$A_2B_2H_{-2}$	16,894		

i.e. $\log K_{212} = \log \beta_{212} - \log K_{111} - 2 \log \beta_{101}$

According to Sigel,[39] discussing mono-and bis-complexes, since more coordination positions are available for bonding of the first ligand to a metal ion than for the second ligand, one would expect $\log K_{212} < \log K_{111}$, and this difference should be between 1 and 2 log units for a bidentate ligand.

Hence, using the refined values from Table 4.5.1,

$\log K_{212} - \log K_{111} = \log \beta_{212} - 2 \log \beta_{111}$

$= -1{,}22$

In addition, potentiometric work carried out concurrently at this laboratory to determine the stability constants of the methyltyrosine-copper(II) system under similar conditions yielded complexes of the type ABH and A_2BH_2 with $\log \beta$ values of comparative magnitude to those obtained in the methyldopa-copper(II) system (18,05 and 35,01 respectively). Methyltyrosine differs from methyldopa in having only one hydroxy group on the phenyl ring, this in the 3' position. Since the only mode of binding likely with methyltyrosine is through its alanine end, complexes of the type ABH and A_2BH_2 obtained in the methyldopa-copper(II) system must represent similar modes of ligand-metal binding.

Based on the conclusion that in bis(glycinato)Cu(II), where the two planar rings are attached to copper(II) in a *cis* arrangement,[35] the geometrical structure of A_2BH_2 in the present system is assumed to be of a similar type.

The species A_2BH in the methyldopa-copper(II) system could be regarded as being formed from A_2BH_2 through the deprotonation of a hydroxy group of one of the ligands. This being the case, if it is assumed that the dissociation quotient $[A_2BH][H]/[A_2BH_2]$ can be approximated to $K_{102}^{-1} = [AH][H]/[AH_2]$

(K_{102} is the second stepwise protonation constant for the ligand), then

$$\beta_{211} = \frac{[A_2BH]}{[A]^2[B][H]}$$

$$= \frac{[A_2BH_2]}{[A]^2[B][H]^2} \quad \frac{[A_2BH][H]}{[A_2BH_2]}$$

$$\approx \frac{[A_2BH_2]}{[A]^2[B][H]^2} \quad \frac{[AH][H]}{[AH_2]}$$

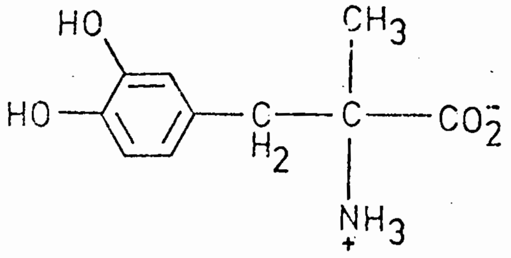
i.e. $\log \beta_{211} \approx \log \beta_{212} - \log K_{102}$

The value obtained is 25,12, which is markedly different from the experimental value of 28,234. Thus the structure assigned to A_2BH on this basis is probably incorrect. In accordance with the enhanced stability of A_2BH, the structure is more likely to be a complex involving copper(II) in a mixed mode of bonding, i.e. complexed to the alanine end of one ligand and the catechol end of the other as depicted in Fig 5(3). The implied proposal that neither phenoxide of the methyldopa ligand is protonated when this moiety is complexed to copper(II) is in agreement with results obtained from potentiometric titrations on the catechol-copper(II) system (section 4.3), where species in which this was not the case were not detectable. Hence it appears that the phenolic proton of the methyldopa dianion (Fig 5(2)) becomes displaced upon 0,0 coordination to copper(II).

The next in the series of successively deprotonated bis-complexes is A_2B. By similar reasoning as with A_2BH, this complex could be regarded as being derived from A_2BH through neutralisation of one of its uncomplexed catechol protons. In

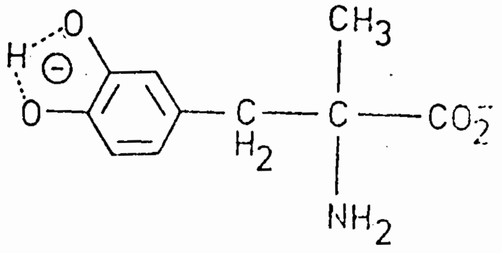
Fig 5

AH_2



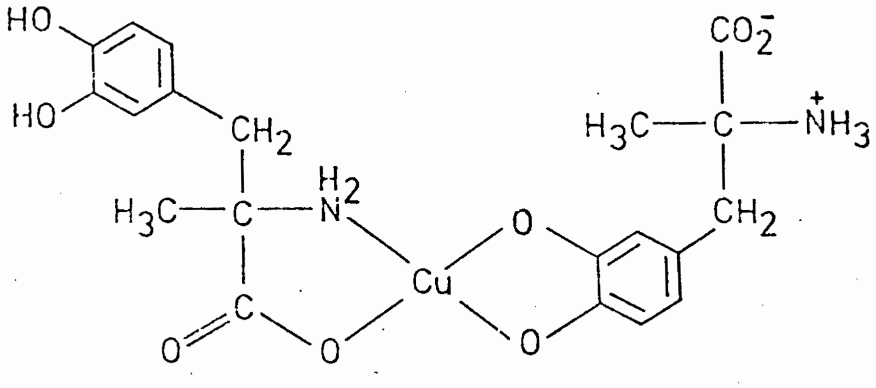
(1)

A



(2)

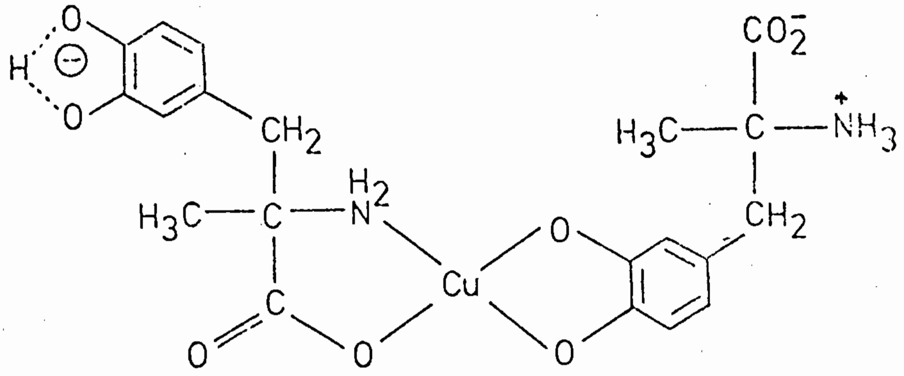
A_2BH



(3)

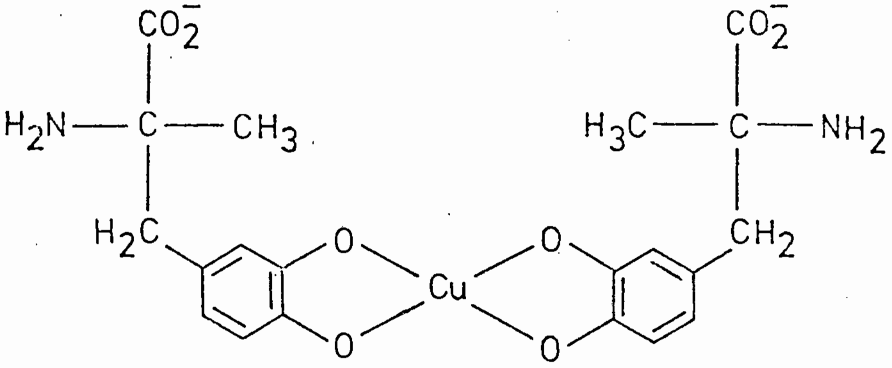
Fig 5 (contd.)

A_2B



(4)

A_2BH_{-2}

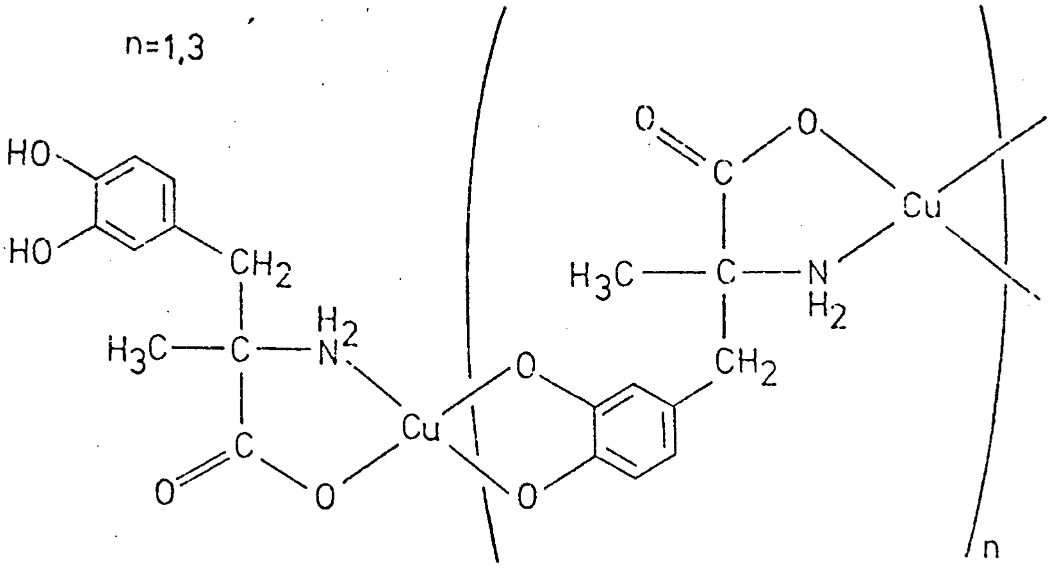


(5)

Fig 5 (contd.)

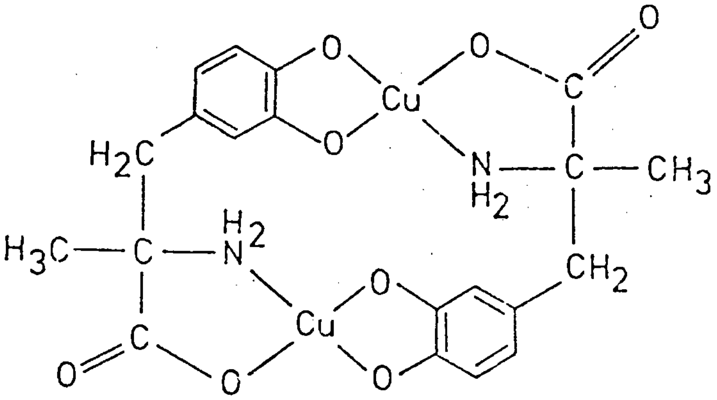
$A_nB_nH_{2-n}$

n=1,3



(6)

$A_2B_2H_{-2}$



(7)

this case if the quotient $[A_2B][H]/[A_2BH]$ can be approximated to by $[AH][H]/[AH_2]$, then $\log \beta_{210} \approx \log \beta_{211} - \log K_{102}$. The value obtained is 19,35, which is close to the observed value of 19,487. On this basis the structure assigned to the species is as depicted in Fig 5(4). This conclusion is in disagreement with the structure proposed by Gergely and Kiss[51] for the analogous A_2B species detected in the dopa-copper(II) system, in which the bis-complex discussed is assigned a structure in which the metal ion is involved in O,O binding with both ligands.

Considering the high pKa for the phenolic proton on the methyldopa dianion i.e. 13 to 14, and that A_2BH_{-2} begins to form at about pH 9, the only feasible structure for this complex is that shown in Fig 5(5). A_2BH_{-1} can hence be thought of as being formed either from the deprotonation of the uncomplexed amino group of (4) or the protonation of one of the uncomplexed amino groups of (5). In the former case, the estimated $\log \beta_{21-1}$ value is $\log \beta_{210} - \log \beta_{101} = 9{,}505$. In the latter $\log \beta_{21-1} \approx \log \beta_{21-2} + \log \beta_{101} = 8{,}528$. Since the observed value for $\log \beta_{21-1}$ is 8,447, the second implied structure is perhaps the more likely, though not definite.

The structures of the series of open chain polymers $A_nB_nH_{2-n}$ found in MINIQUAD calculations on the 1:1 ligand:metal ion ratio solutions are as shown in Fig 5(6), and involve copper(II) in a 'mixed' mode of bonding as required by the GEPOLYC approach. In support of this assignment was the failure to detect species of analogous stoichiometry in the methyltyrosine-copper(II) and catechol-copper(II) solutions studied, where such polymer formation is structurally impossible.

During model-fitting using MINIQUAD on the 1:1 solutions, it was found that equally successful refinement occurred when the species $A_2B_2H_{-2}$ was substituted for by ABH_{-1}. A complex of stoichiometry ABH_{-1} would by necessity require either the amino group or one of the phenolic protons to be neutralised, or have the copper ion in a hydrolysed form. However, its presence in significant amounts at a pH of 4,5 and the fact that a corresponding species could again not be detected in the methyltyrosine-copper(II) solutions indicated that ABH_{-1} in the methyldopa-copper(II) system was perhaps a fortuitous coincidence in the refinement. The preferred species is hence $A_2B_2H_{-2}$ (Fig. 5(7)), and represents the cyclic dimer suggested by the GEPOLYC calculations. Its formation can be thought to occur via the terminal copper(II) atom in A_2B_2 bending back onto the catechol end of the same molecule with accompanying release of two protons. The feasibility of this species was initially questioned as a Dreiding model showed the copper(II) to aromatic ring distance for the dimer to be only about 3 Å, with the necessary absence of an apical aquo ligand. This difficulty has however been partially resolved in that in the crystal structure of bis-(L-tyrosinato) copper(II),[83] a weak interaction of similar magnitude has been observed between the phenolic rings and a copper(II) ion.

A relationship can be derived between the GEPOLYC constants Kc and K and those as refined by MINIQUAD for the 1:1 ligand: metal ion ratio solutions.

From Section 2.1.5

$$\frac{Kc}{K} = \frac{[A_nB_nH_{2-n}]^2}{[A_{n-1}B_{n-1}H_{3-n}]\,[A_nB_nH_{-n}]\,[ABH]}$$

Putting n = 2 (K = 0 for n ≥ 3 in the final model and undefined for n = 1), one obtains

$$\frac{Kc}{K} = \frac{[A_2B_2]^2}{[ABH]^2\,[A_2B_2H_{-2}]}$$

$$= \frac{[A_2B_2]^2}{[A]^4\,[B]^4} \quad \frac{[A]^2\,[B]^2\,[H]^2}{[ABH]^2} \quad \frac{[A]^2\,[B]^2\,[H]^{-2}}{[A_2B_2H_{-2}]}$$

i.e. $\log Kc - \log K = 2 \log \beta_{220} - 2 \log \beta_{111} - \log \beta_{22-2}$.

Substituting for the relevant constants from Sections 4.5 and 4.6 one obtains the difference between the left hand side and right hand side of the above equation to be 0,21 log units, indicating the compatability of the two approaches.

APPENDIX

A. Calculation of R_{LIM} based on maximum experimental errors incurred in a typical titration.

A calculation of R_{LIM} based on propagation of error theory[84] using maximum tolerances of apparatus used both in the standardisation of solutions and in the titration itself appears below. The calculations are applied to a hypothetical titration involving the addition of 5 ml of 0,18 M sodium hydroxide to a solution comprising 0,02 M methyldopa, 0,019 M perchloric acid and 0,004 M copper perchlorate. The method will also illustrate the preparation of the solutions. The tolerances of the apparatus used appear in Table A.1.[65] The error in weighing was assumed to be negligible. In the preperation of some of the solutions, buretted volumes greater than 20 ml were required which necessitated the filling of the burette at least twice. This is accounted for in the calculations.

Table A.1

	Nominal capacity of apparatus (ml)			
Tolerance ± ml	10	20	250	500
Burette (Class A)	0,02	0,04		
Pipette (Class B)	0,04	0,05		
Vol. flask (Class B)			0,2	0,3

After addition of 5 ml of sodium hydroxide, the total hydrogen concentration is:

$$\begin{aligned} T_3 &= [\text{Total hydrogen}] \\ &= \frac{[HClO_4]_o\, V_o}{V_o + v} + \frac{2[AH_2]_o\, V_o}{V_o + v} - \frac{[NaOH]_o\, v}{V_o + v} \\ &= \frac{(0{,}019)(20{,}0)}{25{,}0} + \frac{(2)(0{,}02)(20{,}0)}{25{,}0} - \frac{(0{,}18)(5{,}0)}{25{,}0} \\ &= 0{,}0112\ \underline{M} \end{aligned}$$

The perchloric acid in the titration vessel is made up of contributions from an acidified copper perchlorate stock solution and from a perchloric acid stock solution.

$$[HClO_4] = \frac{[HClO_4]'V'}{250} + \frac{[HClO_4]''V''}{250}$$

The molarity of the perchloric acid stock solution was determined using borax.

$$\begin{aligned} [HClO_4]'' &= \frac{10^3(\text{mass of borax})/(\text{equiv. wt. of borax})}{(\text{standardisation vol. of perchloric acid})} \\ &\approx \frac{(10^3)(0{,}2500)/190{,}72}{9{,}0} \approx 0{,}15\ \underline{M} \end{aligned}$$

$$\begin{aligned} \delta[HClO_4]'' &= \left[\left(-\frac{(10^3)(0{,}2500)/190{,}72}{(9{,}0)^2}\right)^2 (0{,}02)^2\right]^{\frac{1}{2}} \\ &= 3{,}2 \times 10^{-4} \end{aligned}$$

The molarity of the sodium hydroxide titrating solution was determined using potassium hydrogen phthalate.

$$\begin{aligned} [NaOH]_o &= \frac{(10^3)(\text{mass of KHPHTH})/(\text{mol. wt. of KHPHTH})}{(\text{standardisation vol. of sodium hydroxide})} \\ &\approx \frac{(10^3)(0{,}2600)/204{,}22}{7{,}0} \approx 0{,}18\ \underline{M} \end{aligned}$$

$$\delta[\mathrm{NaOH}]_o = \left[\left(-\frac{(10^3)(0{,}2600)/204{,}22}{(7{,}0)^2}\right)^2 (0{,}02)^2\right]^{\frac{1}{2}}$$

$$= 5{,}2 \times 10^{-4}$$

The molarity of the perchloric acid in the copper perchlorate stock solution was determined using the above sodium hydroxide solution.

$$[\mathrm{HClO_4}]' = \frac{[\mathrm{NaOH}]_o(\text{vol. of sodium hydroxide need to neutralise})}{(\text{volume of copper perchlorate stock solution taken})}$$

$$\simeq \frac{(0{,}18)(1{,}0)}{10{,}0} \simeq 0{,}02\ \underline{M}$$

$$\delta[\mathrm{HClO_4}]' = \left[\left(\frac{1{,}0}{10{,}0}\right)^2 (5{,}2 \times 10^{-4})^2 + \left(\frac{0{,}18}{10{,}0}\right)^2 (0{,}02)^2 + \left(-\frac{(0{,}18)(1{,}0)}{(10{,}0)^2}\right)^2 (0{,}04)^2\right]^{\frac{1}{2}}$$

$$= 3{,}7 \times 10^{-4}$$

$$\text{Let } X = \frac{[\mathrm{HClO_4}]'V'}{250} \simeq \frac{(0{,}02)(42{,}0)}{250} \simeq 0{,}003\ \underline{M}$$

$$\delta X = \left[\left(\frac{0{,}02}{250}\right)^2 (0{,}06)^2 + \left(\frac{42{,}0}{250}\right)^2 (3{,}7 \times 10^{-4})^2 + \left(-\frac{(0{,}02)(42{,}0)}{(250)^2}\right)^2 (0{,}2)^2\right]^{\frac{1}{2}}$$

$$= 6{,}23 \times 10^{-5}$$

$$\text{Let } Y = \frac{[\mathrm{HClO_4}]''V''}{250} \simeq \frac{(0{,}15)(26{,}0)}{250} \simeq 0{,}016\ M$$

<u>Note</u>: $[\mathrm{HClO_4}]_o = X + Y = 0{,}019\ \underline{M}$

$$\delta Y = \left[\left(\frac{0{,}15}{250}\right)^2 (0{,}06)^2 + \left(\frac{26{,}0}{250}\right)^2 (3{,}2 \times 10^{-4})^2 + \left(-\frac{(0{,}15)(26{,}0)}{(250)^2}\right)^2 (0{,}2)^2\right]^{\frac{1}{2}}$$

$$= 5{,}06 \times 10^{-5}$$

$$V_o + v = 25{,}0 \text{ ml}$$

$$\delta(V_o + v) = \{(0{,}05)^2 + (0{,}02)^2\}$$

$$= 5{,}4 \times 10^{-2}$$

$$[AH_2]_o = \frac{(10^3)(\text{mass of methyldopa})/(\text{mol. wt. of methyldopa})}{V_o}$$

$$= \frac{(10^3)(0{,}1000)/238{,}0}{20{,}0} \approx 0{,}02\ \underline{M}$$

$$\delta[AH_2]_o = \left[\left(-\frac{(10^3)(0{,}1000)/238{,}0}{(20{,}0)^2}\right)^2 (0{,}05)^2\right]^{\frac{1}{2}}$$

$$= 5{,}25 \text{ x } 10^{-5}$$

At this stage it is convenient to write T_3 as:

$$T_3 = \frac{V_oX}{V_o+v} + \frac{V_oY}{V_o+v} + \frac{2[AH_2]_oV_o}{V_o+v} - \frac{[NaOH]_o\ V_o}{V_o+v}$$

$$\text{Let } A = \frac{V_oX}{V_o+v}$$

$$\delta A = \left[\left(\frac{20{,}0}{25{,}0}\right)^2 (6{,}23 \text{ x } 10^{-5})^2 + \left(\frac{0{,}003}{25{,}0}\right)^2 (0{,}05)^2 + \left(-\frac{(20{,}0)(0{,}003)}{(25{,}0)^2}\right)^2 (5{,}4 \text{ x } 10^{-2})^2\right]^{\frac{1}{2}}$$

$$= 5{,}04 \text{ x } 10^{-5}$$

$$\text{Let } B = \frac{V_oY}{V_o+v}$$

$$\delta B = \left[\left(\frac{20{,}0}{25{,}0}\right)^2 (5{,}06 \text{ x } 10^{-5})^2 + \left(\frac{0{,}016}{25{,}0}\right)^2 (0{,}05)^2 + \left(-\frac{(20{,}0)(0{,}016)}{(25{,}0)^2}\right)^2 (5{,}4 \text{ x } 10^{-2}\ {}^2\right]^{\frac{1}{2}}$$

$$= 5{,}85 \text{ x } 10^{-5}$$

$$\text{Let } C = \frac{2[AH_2]_o\ V_o}{V_o + v}$$

$$\delta C = \left[\left(\frac{(2)(20{,}0)}{25{,}0}\right)^2 (5{,}25 \text{ x } 10^{-5})^2 + \left(\frac{(2)(0{,}02)}{25{,}0}\right)^2 (0{,}05)^2 + \left(-\frac{(2)(20{,}0)(0{,}02)}{(25{,}0)^2}\right)^2 (5{,}4 \text{ x } 10^{-2})^2\right]^{\frac{1}{2}}$$

$$= 1{,}35 \text{ x } 10^{-4}$$

Let $D = \dfrac{[\mathrm{NaOH}]_o\, v}{V_o + v}$

$$\delta D = \left[\left(\frac{0{,}18}{25{,}0}\right)^2 (0{,}02)^2 + \left(\frac{5{,}0}{25{,}0}\right)^2 (5{,}2 \times 10^{-4})^2 + \left(-\frac{(0{,}18)(5{,}0)}{(25{,}0)^2}\right)^2 (5{,}4 \times 10^{-2})^2\right]^{\frac{1}{2}}$$

$$= 1{,}94 \times 10^{-4}$$

Thus $\delta T_3 = \left((\delta A)^2 + (\delta B)^2 + (\delta C)^2 + (\delta D)^2\right)^{\frac{1}{2}}$

$$= 2{,}49 \times 10^{-4}$$

The error in the total copper molarity of the titration vessel solution, δT_2, is now calculated.

$$[\mathrm{EDTA}] = \frac{(10^3)(\text{mass of EDTA})/(\text{mol. wt. of EDTA})}{(\text{total vol. of solution})}$$

$$\simeq \frac{(10^3)(1{,}9700)/372{,}24}{500} \simeq 0{,}01\ \underline{M}$$

$$\delta[\mathrm{EDTA}] = \left[\left(-\frac{(10^3)(1{,}9700)/372{,}24}{(500)^2}\right)^2 (0{,}3)^2\right]^{\frac{1}{2}}$$

$$= 6{,}35 \times 10^{-6}$$

$$[\mathrm{Cu(ClO_4)_2}]' = \frac{[\mathrm{EDTA}](\text{titration vol. of EDTA})}{(\text{Vol. of copper perchlorate stock solution taken})}$$

$$\simeq \frac{(0{,}01)(24{,}0)}{10{,}0} \simeq 0{,}24\ \underline{M}$$

$$\delta[\mathrm{Cu(ClO_4)_2}]' = \left[\left(\frac{0{,}01}{10{,}0}\right)^2 (0{,}06)^2 + \left(\frac{24{,}0}{10{,}0}\right)^2 (6{,}35 \times 10^{-6})^2 + \left(-\frac{(0{,}01)(24{,}0)}{(10{,}0)^2}\right)^2 (0{,}04)^2\right]^{\frac{1}{2}}$$

$$= 1{,}14 \times 10^{-4}$$

$$[\mathrm{Cu(ClO_4)_2}]_o = \frac{[\mathrm{Cu(ClO_4)_2}]'(V')}{250}$$

$$\simeq \frac{(0{,}024)(42{,}0)}{250} \simeq 0{,}004\ \underline{M}$$

$$\delta[\mathrm{Cu(ClO_4)_2}]_o = \left[\left(\frac{0{,}024}{250}\right)^2 (0{,}06)^2 + \left(\frac{42{,}0}{250}\right)^2 (1{,}14 \times 10^{-4})^2 + \left(-\frac{(0{,}024)(42{,}0)}{(250)^2}\right)^2 (0{,}2)^2\right]^{\frac{1}{2}}$$

$$= 2{,}03 \times 10^{-5}$$

$$T_2 = \frac{[\mathrm{Cu(ClO_4)_2}]_o(V_o)}{(V_o + v)}$$

$$= \frac{(0{,}004)(20{,}0)}{25{,}0} = 0{,}0032\ \underline{M}$$

$$\delta T_2 = \left[\left(\frac{0{,}004}{25{,}0}\right)^2 (0{,}05)^2 + \left(\frac{20{,}0}{25{,}0}\right)^2 (2{,}03 \times 10^{-5})^2 + \left(-\frac{(0{,}004)(20)}{(25{,}0)^2}\right)^2 (5{,}4 \times 10^{-2})^2\right]^{\frac{1}{2}}$$

$$= 1{,}94 \times 10^{-5}$$

The error in the total ligand molarity of the titration vessel solution, δT_1, is now calculated.

$$T_1 = \frac{[\mathrm{AH_2}]_o(V_o)}{(V_o + v)}$$

$$= \frac{(0{,}02)(20)}{25} = 0{,}016\ \underline{M}$$

$$\delta T_1 = \left[\left(\frac{0{,}02}{25{,}0}\right)^2 (0{,}05)^2 + \left(\frac{20{,}0}{25{,}0}\right)^2 (5{,}25 \times 10^{-5})^2 + \left(-\frac{(0{,}02)(20{,}0)}{(25{,}0)^2}\right)^2 (5{,}4 \times 10^{-2})^2\right]^{\frac{1}{2}}$$

$$= 6{,}75 \times 10^{-5}$$

$$\text{Hence } R_{LIM} = \left(\frac{(\delta T_1)^2 + (\delta T_2)^2 + (\delta T_3)^2}{(T_1)^2 + (T_2)^2 + (T_3)^2}\right)^{\frac{1}{2}}$$

$$= \left(\frac{(6{,}75 \times 10^{-5})^2 + (1{,}94 \times 10^{-5}\ {}^2 + (2{,}49 \times 10^{-4})^2}{(1{,}6 \times 10^{-2})^2 + (3{,}2 \times 10^{-3})^2 + (1{,}12 \times 10^{-2})^2}\right)^{\frac{1}{2}}$$

$$= 0{,}0131$$

This is of a somewhat higher order to the R-factor outputted by MINIQUAD in a successful refinement, as might be expected. It must be noted, however, that in this work the preferred criterion in judging a refined model was a comparison of the experimental ZPLOT formation curve with that of the theoretical PSEUDOPLOT. Nevertheless, a correlation in general exists between the value of the R-factor and the degree of overlap between the formation curves.

Symbols used in Appendix A

T_1 = [Total ligand] in titration vessel after addition of v ml of sodium hydroxide.

T_2 = [Total metal] in titration vessel after addition of v ml of sodium hydroxide.

T_3 = [Total hydrogen] in titration vessel after addition of v ml of sodium hydroxide.

V_o = initial volume of solution in titration vessel (20 ml).

v = volume of sodium hydroxide added (5 ml).

$[AH_2]_o$ = initial molarity of methyldopa in titration vessel (0,02 M).

$[Cu(ClO_4)_2]_o$ = initial molarity of copper perchlorate in titration vessel (0,004 M).

$[HClO_4]_o$ = initial molarity of perchloric acid in titration vessel (0,019 M).

$[NaOH]_o$ = molarity of sodium hydroxide titrating solution (0,18 M).

$[Cu(ClO_4)_2]'$ = molarity of copper perchlorate stock solution (0,24 M).

$[HClO_4]'$ = molarity of perchloric acid in copper perchlorate stock solution (0,02 M).

$[HClO_4]''$ = molarity of perchloric acid stock solution (0,15 M).

V' = volume of copper perchlorate stock solution needed to yield 250 ml of 0,004 M copper perchlorate.

V'' = volume of perchloric acid stock solution needed to bring the initial perchloric acid molarity of the titration vessel solution to 0,019 M.

[EDTA] = molarity of ethylenediaminetetra-acetic acid (disodium salt) used in standardisation of copper perchlorate stock solution. (0,01 M).

B. The effect of reactant concentration on formation constants.

For a given background electrolyte concentration, there appears to be a limit to the maximum concentration that participating charged reactants can have, if the stability constants derived therefrom are to be quoted at the electrolyte concentration used. For example, for a background medium of 3,00 M perchlorate ion, the sum of the equivalent concentrations of all positive and negative ions disappearing during a complex forming reaction should not exceed 0,15 M, if the activity coefficient are to be effectively held constant.[86]

Calculations were carried out using data from a 1:1 ligand: metal ion titration. The initial ligand concentration was 0,02 M (initial volume 20 ml) and the sodium hydroxide concentration was 0,142 M. Using the distribution plot of the refined model, the total concentrations of all singly and doubly charged species, anionic and cationic, were computed and two points in the titration, one before any base had been added (i = initial), and the other towards the completion of the titration after 6 ml of base had been added (f = final). Equation B.1.[55] then yielded the ionic strengths at the two respective points.

$$I = \tfrac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \qquad \text{.... B.1.}$$

The Davies relationship (equation 4.6.1) with A = 0,509 and C = 0,3 was then used to calculate the activity coefficient of the singly and doubly charged species at the different ionic strengths. For each species, using equation 1.4.1, the ratio $\frac{\beta_{pqr(i)}}{\beta_{pqr(f)}}$ was then calculated (see Table B.1). The deviation of this from unity indicates how the values of the stability constants are affected because of a change in the ionic strength of the solution due to dilution and shifts in solution composition. These calculations were repeated for a hypothetical titration in which the concentrations of the compounds were doubled, but the background electrolyte remained at 0,15 M. In this it was assumed that the distribution plot remained unchanged. Here the effect on the stability constants of changing the conditions is even more pronounced, as is expected.

Table B.1.

Concentration effect on formation constants during typical 1:1 methyldopa-copper(II) titrations. (i = initial, f = final).

Species	$\frac{\beta_{pqr(i)}}{\beta_{pqr(f)}}$ when $[A]_T$ = 0,01 M at start	$\frac{\beta_{pqr(i)}}{\beta_{(pqr)f}}$ when $[A]_T$ = 0,02 M at start
AH	.990	.978
AH_2	.985	.972
AH_3	.985	.972
ABH	.981	.956
A_2BH_2	.966	.924
ABH_2	.985	.972
A_2B_2	.962	.914
$A_3B_3H_{-1}$	.948	.883
$A_4B_4H_{-2}$	.938	.863
$A_2B_2H_{-2}$	.976	.945

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PART II

CRYSTAL AND MOLECULAR STRUCTURES OF SELECTED COMPOUNDS

CHAPTER 1

GENERAL EXPERIMENTAL AND COMPUTATIONAL PROCEDURES USED IN CRYSTALLOGRAPHIC ANALYSIS

1.1 General experimental and computational procedures used in crystallographic analysis.

In the case of all the compounds presented in this work, the procedure followed as regards the preliminary space group determination of the crystals and their data collections was essentially the same, and as outlined below. The stoichiometric composition of each compound was determined by microanalytical estimates of their carbon, hydrogen and nitrogen content, and their density by flotation in suitable solvents. X-radiation (nickel-filtered CuKα, λ = 1.5418 Å) for the photographic work was generated either by the Philips PW 1120 or the PW 1008 models operating at 20 mA and 40 kV, and used in conjunction with Stoe (Heidelberg) Weissenberg and precession goniometers. Preliminary crystallographic information was obtained from single crystal oscillation, Weissenberg and precession photographs taken about the principal axes in order to establish the space group symmetry. The x-ray films used were supplied by Kodak (3M) and the developer and fixer solutions by Medex.

Suitable selected single crystal specimens of each compound were mounted onto glass fibres and sent along with unmounted spares to Dr. G. Gafner at the National Physical Research Laboratory, C.S.I.R. (Pretoria), who very kindly carried out the data collections onto magnetic tapes using a Philips PW 1100 computer controlled four-circle diffractometer. In cases where absorption effects were expected to be especially significant, these were minimised by cutting the crystals into cubes or grinding them into spheres where possible. The x-radiation (graphite monochromated MoKα, λ = 0.7107 Å) used in the intensity measurements was supplied by a Philips 1130 3 kW x-ray generator operating at 20 mA and 50 kV. Lattice constants were obtained at room temperature by a least squares fit of the χ, ϕ and 2θ angles of 25 reflections accurately centred on the diffractometer. In all cases, crystal and instrumental stability were monitored by measuring the intensities of three suitable reference reflections approximately every hour. The criterion as to whether a particular reflection was to be considered 'observed' or not in the refinement of a particular structure involved calculation of the standard error $\sigma\underline{I}_{(rel)}$ in the relative integrated intensity $\underline{I}_{(rel)}$ of the reflection, and given by:

$$\sigma\underline{I}_{(rel)} = [(0{,}02\ N_o)^2 + K^2\ N_b + N_o]^{\frac{1}{2}}$$

N_o is the gross peak count for the reflection, N_b the background count (measured on each side at the peak), and K the ratio of scan to background times. Lorentz-polarization corrections were applied to all reflection data in Pretoria immediately after data collection but absorption effects were not accounted for.

All calculations were carried out on a UNIVAC 1106 computer at the University of Cape Town. The program SHELX[1.1] was employed for data reduction and in the solution and refinement of the structures. Solutions were effected by Patterson and Fourier techniques, and by use of centrosymmetric direct methods. All structures were refined by full-matrix least-squares, where the function minimized was $w(F_o-F_c)^2$. The functions $\underline{R} = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $\underline{R}w = \Sigma w^{\frac{1}{2}}||F_o|-|F_c||/\Sigma w^{\frac{1}{2}}|F_o|$, were used as indicators of the accuracy of each structure determination. The program XANADU[1.2] supplied bond distances, angles, torsion angles and least square planes from final atomic coordinates where needed, whilst PLUTO[1.3] gave the molecular illustration. The subroutine BONDLA, part of the XRAY 72[1.4] program system, was used to obtain estimated standard deviations in the close contacts reported.

CHAPTER 2

PACKING PATTERNS IN LANTHANIDE-EDTA COMPLEXES: CRYSTAL AND MOLECULAR STRUCTURES OF SODIUM TRIAQUOETHYLENEDIAMINETETRAACETATODYSPROSIUM(III) PENTAHYDRATE AND CAESIUM DIAQUOETHYLENEDIAMINETETRAACETATOYTTERBIUM(III) TRIHYDRATE

ABSTRACT

$Na^+[DyEDTA(3H_2O)]^-.5H_2O$ crystallises in the space group $\underline{F}dd2$ with $\underline{a}$ = 19,34(1), $\underline{b}$ = 35,40(2), $\underline{c}$ = 12,116(6) Å, $\underline{z}$ = 16. $Cs^+[YbEDTA(2H_2O)]^-.3H_2O$ crystallises in the space group $\underline{P}2_1/c$ with $\underline{a}$ = 12,935(6), $\underline{b}$ = 8,997(5), $\underline{c}$ = 17,22(1) Å, β = 106,7(2)°, $\underline{z}$ = 4. The structures were determined by Patterson and Fourier methods and refined by full-matrix least-squares to a final R of 0,045 and 0,050 respectively. The decrease in ionic radius from Dy^{3+} to Yb^{3+} results in a change in coordination number of the Ln^{3+} ion from 9 to 8 with concomitant loss of a water molecule. The changed geometry of the lanthanide complex gives rise to a different space group.

2.1 Introduction

During the 1940's, the development of methods for the ion exchange seperation of lanthanide fission products instigated intensive research on their complexation properties, and since that time the number of papers concerning this and other aspects of these 4f elements has mushroomed.[2.1] Having said this, it is nevertheless true to say that the total number of lanthanide species possible is limited when compared to the transition metal ions because of the following factors: the 4f orbitals are significantly hidden beneath the $4d^{10}5s^{2}5p^{6}$ noble gas atom type of outermost electronic configuration and hence are largely unavailable for ligand formation (the ligand field stabilisation energies are of the order of only 4 kJ mol^{-1}); although the most common oxidation state for the lanthanide ions is 3+, electrostatic attractions are minimised due to the large size of the ion; ligand exchange reactions involving the lanthanide species in solution have been shown to be extremely rapid, limiting the number of isolatable species; there is strong competition by water for coordination sites which precludes coordination by any but the strongest donors and restricts isolatable complexes very largely to those of chelating ligands; and finally the 'hard' nature of the lanthanide ions largely limits the donor atoms to those of similar character, e.g. oxygen and nitrogen.

Although the definite composition of isolated lanthanide complexes in the solid form can be determined, ligand lability precludes any guarantee that these same species will exist in solution. The formation constants of those complexes that have been evaluated in aqueous systems by the standard techniques have shown that there is a more or less regular increase in stability as one progresses across the series, with the chelates being essentially entropy stabilised.

The reasonably large size of the lanthanide ion (1,02 Å for La^{3+} and 0,85 Å for Lu^{3+}) results in generally high coordination numbers being observed. The spatial positions of the donor atoms with respect to the central atom in a given complex are in turn primarily determined by the coordination number and the nature of the ligand. Hence x-ray studies have established Er^{3+} to be six-coordinated in an octahedral geometry[2.2] in the complex $[Er(NCS)_6]^{3-}$, yet nine-coordinated in a tricapped trigonal prismatic geometry in the tris(dimethyl sulphoxide) adduct of erbium nitrate.[2.3]

Since 1956, when a lanthanum-cyclopentadienyl complex was first synthesised, investigations into the organo-metallic chemistry of the lanthanide elements have become possible. These investigations have provided information on the nature of the metal-carbon bond and the possibility of the participation of *f* electrons in the metal-ligand bond in these structures. X-ray investigations have shown that the tricyclopentadienyl complexes $M(C_5H_5)_3$, with M = Pr, Pm, Gd and Tb, crystallise in the same space group, *Pbcm*, and have the same structure as when M is Sm. The arrangement around the central atom is a distorted tetrahedron, with one of the π-bonded cyclopentadienyl rings being effectively shared by two lanthanide ions, the infinite zig-zag $M(C_5H_5)_3$ chains so formed running along the c axis and parallel to (100).[2.4] Single crystal diffraction studies of $Tm(C_5H_5)_3$ however show that this compound crystallises in the space group *Pnam* or *Pna2₁*, indicating a change in structure type.[2.5] It is thought that this change probably occurs earlier in the lanthanide series, but it is not certain at which element this first becomes apparent.

A similar observation has been reported for the EDTA salts of the lanthanides (EDTA = ethylenediaminetetraacetate). Studies on complexes having the general formula $MLnEDTA.8H_2O$ show that potassium salts with Ln = La, Nd or Gd, sodium salts with Ln = Nd, Tb, or Er, and ammonium salts with Ln = Nd or Gd all crystallise in the space group Fdd2 with z = 16. Consideration of the relative atomic sizes of the central atom has suggested that in the sequence La^{3+} to Lu^{3+} there should be a transition from nine-coordinate $[LnEDTA(3H_2O)]^-$ to eight coordinate $[LnEDTA(2H_2O)]^-$, with a prediction that Tb would be eight-coordinate.[2.6] However the structure of $NaTbEDTA.8H_2O$ has shown Tb to be nine co-ordinate.[2.7] . It was therefore thought interesting to investigate structures of both the Dy and Yb complexes to determine their coordination and packing patterns.

2.2 Crystal preparation and data collection

Crystals of the dysprosium complex $Na^+[DyEDTA(3H_2O)]^-.5H_2O$ were prepared by refluxing 10 mmole of dysprosium oxide and 25 mmole of EDTA in 50 ml water for 15 hours, periodically adding sodium hydroxide pellets until the oxide had dissolved and the pH had reached 5.5. Cooling and evaporation yielded the desired crystals. The ytterbium complex $Cs^+[YbEDTA(2H_2O)]^-.3H_2O$ was prepared in an analogous manner.

Weissenberg photographs of the dysprosium complex (I) showed the conditions limiting possible reflections to be:

hkl : h+k, k+1, (1+h) = 2n
okl : k+1 = 4n (k,1 = 2n)
hol : 1+h = 4n (1,h = 2n)
hko : (h,k = 2n)
hoo : (h = 4n)
oko : (k = 4n)
ool : (1 = 4n)

These conditions uniquely determine the space group as *Fdd2*.[2.8]

In the case of the ytterbium complex(II), the conditions limiting possible reflections were:

hkl : No conditions
hol : 1 = 2n
oko : k = 2n

These conditions uniquely determine the space group as $P2_1/c$.

Crystal data of the specimens used in the intensity measurements and details of the data collection are listed in Table 2.1.

2.3 Solution and refinement of the structures.

The expected Patterson map for complex (I) with z = 16 yielded 48 non-origin vector positions each of weight 4. However, because the lattice is face-centred the observed Patterson map can be interpreted by using the 12 non-origin vectors which arise from the general positions of the space group without taking centering into account. The expected positions of such vectors are given in Table 2.2.

The position of the Dy^{3+} atom thus deduced was 0,080; 0,155; 0,000 (the two-fold axis parallel to the Z-axis allows

Table 2.1

Crystal data and experimental and refinement parameters for the crystal structures of the dysprosium-EDTA complex (I) and the ytterbium-EDTA complex (II).

Crystal data	(I)	(II)
Molecular formula	$Na^{+}[DyEDTA(3H_2O)]^{-}.5H_2O$	$Cs^{+}[YbEDTA(2H_2O)]^{-}.3H_2O$
Mr	617,8	684,2
Space Group	Fdd2	$P2_1/c$
a	19,34(1) Å	12,935(6) Å
b	35,40(2)	8,997(5)
c	12,116(6)	17,22(1)
β		106,7(2)°
Dm	1,96 Mg m^{-3}	2,35 Mg m^{-3}
Dc	1,98 for z = 16	2,37 for z = 4
μ(MoKα)	3,51 mm^{-1}	6,47 mm^{-1}
F(000)	4912	1300
Data collection		
Crystal dimensions	0,20x0,30x0,50 mm	0,25x0,20x0,20 mm
Scan mode	ω - 2θ	ω - 2θ
Scan width	1,2° θ	1,2° θ
Scan speed	0,03° θ s^{-1}	0,04° θ s^{-1}
Range scanned (2θ)	6 - 44°	6 - 50°
Stability of standard reflections	1,7%	0,65%
Number of reflections collected	1423	3614
Number of 'observed' reflections	1192 with $I_{(rel)} > 3\sigma I_{(rel)}$	3354 with $I_{(rel)} > 2\sigma I_{(rel)}$
Final refinement		
Number of variables	125	120
$R=\Sigma\|\|Fo\|-\|Fc\|\|/\Sigma\|Fo\|$	0,045	0,050
$Rw=\Sigma w^{\frac{1}{2}}\|\|Fo\|-\|Fc\|\|/\Sigma w^{\frac{1}{2}}\|Fo\|$	0,043	0,058
Weighting scheme w	$(\sigma^2 F)^{-1}$	$(\sigma^2 F+2x10^{-3}F^2)^{-1}$
U (methylene H)		0,018 Å^2

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

Table 2.2

the Z-coordinate to be arbitrarily fixed at 0,000). Three cycles of least squares refinement with the dysprosium atom treated as Dy^{O} gave an R value of 0,202. Subsequent weighted difference Fourier synthesis yielded the positions of all the remaining non-hydrogen atoms. The final full-matrix least squares refinement was carried out with the dysprosium atom anisotropic and the remaining non-hydrogen atoms isotropic. At no stage of the refinement could hydrogen atoms be located in difference maps and they were therefore omitted from the final model.

A comparison of the expected Patterson map assuming two heavy atoms per asymmetric unit (Table 2.3) with the computed Patterson map yielded possible positions for the Yb^{3+} atom and

	x_1, y_1, z_1	$-x_1$, $-y_1$, $-z_1$	$-x_1$, $\frac{1}{2}+y_1$, $\frac{1}{2}-z_1$	x_1, $\frac{1}{2}-y_1$, $\frac{1}{2}+z_1$	x_2, y_2, z_2	$-x_2$, $-y_2$, $-z_2$	$-x_2$, $\frac{1}{2}+y_2$, $\frac{1}{2}-z_2$	x_2, $\frac{1}{2}-y_2$, $\frac{1}{2}+z_2$
x_1, y_1, z_1	0, 0, 0	$-2x_1$, $-2y_1$, $-2z_1$	$-2x_1$, $\frac{1}{2}$, $\frac{1}{2}-2z_1$	0, $\frac{1}{2}-2y_1$, $\frac{1}{2}$	$-x_1+x_2$, $-y_1+y_2$, $-z_1+z_2$	$-x_1-x_2$, $-y_1-y_2$, $-z_1-z_2$	$-x_1-x_2$, $\frac{1}{2}-y_1+y_2$, $\frac{1}{2}-z_1-z_2$	$-x_1+x_2$, $\frac{1}{2}-y_1-y_2$, $\frac{1}{2}-z_1+z_2$
$-x_1$, $-y_1$, $-z_1$	$2x_1$, $2y_1$, $2z_1$	0, 0, 0	0, $\frac{1}{2}+2y_1$, $\frac{1}{2}$	$2x_1$, $\frac{1}{2}$, $\frac{1}{2}+2z_1$	x_1+x_2, y_1+y_2, z_1+z_2	x_1-x_2, y_1-y_2, z_1-z_2	x_1-x_2, $\frac{1}{2}+y_1+y_2$, $\frac{1}{2}+z_1-z_2$	x_1+x_2, $\frac{1}{2}+y_1-y_2$, $\frac{1}{2}+z_1+z_2$
$-x_1$, $\frac{1}{2}+y_1$, $\frac{1}{2}-z_1$	$2x_1$, $\frac{1}{2}$, $\frac{1}{2}+2z_1$	0, $\frac{1}{2}-2y_1$, $\frac{1}{2}$	0, 0, 0	$2x_1$, $-2y_1$, $2z_1$	x_1+x_2, $\frac{1}{2}-y_1+y_2$, $\frac{1}{2}+z_1+z_2$	x_1-x_2, $\frac{1}{2}-y_1-y_2$, $\frac{1}{2}+z_1-z_2$	x_1-x_2, $-y_1+y_2$, z_1-z_2	x_1+x_2, $-y_1-y_2$, z_1+z_2
x_1, $\frac{1}{2}-y_1$, $\frac{1}{2}+z_1$	0, $\frac{1}{2}+2y_1$, $\frac{1}{2}$	$-2x_1$, $\frac{1}{2}$, $\frac{1}{2}-2z_1$	$-2x_1$, $2y_1$, $-2z_1$	0, 0, 0	$-x_1+x_2$, $\frac{1}{2}+y_1+y_2$, $\frac{1}{2}-z_1+z_2$	$-x_1-x_2$, $\frac{1}{2}+y_1-y_2$, $\frac{1}{2}-z_1-z_2$	$-x_1-x_2$, y_1+y_2, $-z_1-z_2$	$-x_1+x_2$, y_1-y_2, $-z_1+z_2$
x_2, y_2, z_2	x_1-x_2, y_1-y_2, z_1-z_2	$-x_1-x_2$, $-y_1-y_2$, $-z_1-z_2$	$-x_1-x_2$, $\frac{1}{2}+y_1-y_2$, $\frac{1}{2}-z_1-z_2$	x_1-x_2, $\frac{1}{2}-y_1-y_2$, $\frac{1}{2}+z_1-z_2$	0, 0, 0	$-2x_2$, $-2y_2$, $-2z_2$	$-2x_2$, $\frac{1}{2}$, $\frac{1}{2}-2z_2$	0, $\frac{1}{2}-2y_2$, $\frac{1}{2}$
$-x_2$, $-y_2$, $-z_2$	x_1+x_2, y_1+y_2, z_1+z_2	$-x_1+x_2$, $-y_1+y_2$, $-z_1+z_2$	$-x_1+x_2$, $\frac{1}{2}+y_1+y_2$, $\frac{1}{2}-z_1+z_2$	x_1+x_2, $\frac{1}{2}-y_1+y_2$, $\frac{1}{2}+z_1+z_2$	$2x_2$, $2y_2$, $2z_2$	0, 0, 0	0, $\frac{1}{2}+2y_2$, $\frac{1}{2}$	$2x_2$, $\frac{1}{2}$, $\frac{1}{2}+2z_2$
$-x_2$, $\frac{1}{2}+y_2$, $\frac{1}{2}-z_2$	x_1+x_2, $\frac{1}{2}+y_1-y_2$, $\frac{1}{2}+z_1+z_2$	$-x_1+x_2$, $\frac{1}{2}-y_1-y_2$, $\frac{1}{2}-z_1+z_2$	$-x_1+x_2$, y_1-y_2, $-z_1+z_2$	x_1+x_2, $-y_1-y_2$, z_1+z_2	$2x_2$, $\frac{1}{2}$, $\frac{1}{2}+2z_2$	0, $\frac{1}{2}-2y_2$, $\frac{1}{2}$	0, 0, 0	$2x_2$; $-2y_2$, $2z_2$
x_2, $\frac{1}{2}-y_2$, $\frac{1}{2}+z_2$	x_1-x_2, $\frac{1}{2}+y_1+y_2$, $\frac{1}{2}+z_1-z_2$	$-x_1-x_2$, $\frac{1}{2}-y_1+y_2$, $\frac{1}{2}-z_1-z_2$	$-x_1-x_2$, y_1+y_2, $-z_1-z_2$	x_1-x_2, $-y_1+y_2$, z_1-z_2	0, $\frac{1}{2}+2y_2$, $\frac{1}{2}$	$-2x_2$, $\frac{1}{2}$, $\frac{1}{2}-2z_2$	$-2x_2$, $2y_2$, $-2z_2$	0, 0, 0

Table 2.3

Cs^+ atom as 0,38; 0,10; 0,16 and 0,60; 0,23; 0,50 respectively. Three cycles of least squares refinement using these values gave an R of 0,186 and a subsequent difference Fourier yielded the positions of all remaining non-hydrogen atoms except some of the waters of crystallisation. Subsequent refinement was analogous to that of the dysprosium complex (I), except that in the final stages methylenic hydrogen atoms did appear in difference maps. The latter were therefore included in the final model using the technique of constrained refinement (d(C-H) = 1,08 Å) and refining their temperature factors as one single parameter. The water hydrogen atoms could not be located and were omitted. Details of the final refinement parameters are given in Table 2.1. Tables 2.4 and 2.5 show the final atomic coordinates and temperature factors for structures (I) and (II) respectively. Appendices A and B show the respective observed and calculated structure factors.

2.4 Description of the structures and discussion.

The molecular structures with atomic nomenclature of the two compounds appear in Figures 2.1 and 2.2. In complex (I), the structure around the central ion consists of a girdle of four oxygens (one each from the four acetate groups) on either side of which are bonded three water molecules and two nitrogen atoms effectively *trans* to each other. The coordination geometry can best be described by a quasi-mirror passing through Dy^{3+} and the two nitrogen atoms. In this approximation C(1) and C(2) of the puckered ethylenediamine ring are omitted.

In the Yb^{3+} complex, the eight-coordinated square

Table 2.4

Fractional atomic coordinates ($x10^4$) and temperature factors ($Å^2x10^3$) with e.s.d.'s for Na^+ $[DyEDTA(3H_2O)]^-.5H_2O$ (I)

	x	y	z	U
Dy	823(0)	1553(0)	0	†
Na	1372(5)	1321(3)	3203(9)	54(3)
O(1)	963(7)	1822(4)	1862(12)	28(4)
O(2)	-290(8)	1677(4)	790(13)	41(4)
O(3)	2029(8)	1682(4)	380(12)	38(4)
O(4)	173(8)	1640(4)	-1555(13)	33(4)
O(5)	1054(9)	2307(5)	3001(15)	53(5)
O(6)	-1008(9)	2089(5)	1575(15)	63(5)
O(7)	3103(7)	1766(4)	-211(13)	40(4)
O(8)	68(8)	1703(4)	-3391(13)	39(5)
O(9)	22(7)	980(3)	-92(13)	33(3)
O(10)	1341(9)	1104(4)	-1168(13)	36(5)
O(11)	1301(8)	1065(4)	1260(12)	29(4)
N(1)	558(8)	2283(4)	150(18)	35(5)
N(2)	1468(8)	1939(5)	-1523(14)	25(5)
C(1)	753(12)	2477(8)	-899(22)	36(7)
C(2)	1459(11)	2352(6)	-1252(19)	34(6)
C(3)	929(13)	2453(8)	1072(22)	37(8)
C(4)	974(12)	2163(7)	2042(21)	41(7)
C(5)	-217(11)	2337(6)	318(18)	36(6)
C(6)	-501(12)	2016(6)	936(20)	38(6)
C(7)	2216(12)	1807(6)	-1547(20)	37(6)
C(8)	2458(11)	1768(6)	-404(17)	27(5)
C(9)	1151(11)	1854(6)	-2622(22)	36(6)
C(10)	411(10)	1727(5)	-2515(24)	32(5)
W(1)	634(8)	390(4)	1089(13)	47(5)
W(2)	1472(11)	985(6)	5643(19)	85(7)
W(3)	1212(12)	1783(7)	4603(20)	102(8)
W(4)	194(14)	1121(8)	3460(24)	132(10)
W(5)	2594(17)	2154(9)	5720(29)	193(14)

† Anisotropic parameters in the form $T = \exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}klb^*c^*) \times 10^3]$

	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
Dy	13(0)	32(1)	23(1)	1(1)	-2(1)	-1(1)

Table 2.5

Fractional atomic coordinates ($x10^4$) and temperature factors ($Å x10^3$) with e.s.d.'s for $Cs^+[YbEDTA(2H_2O)]^-.3H_2O$ (II)

	x	y	z	U
Yb	3758(0)	964(0)	1549(0)	††
Cs	6039(0)	2308(1)	5008(0)	††
O(1)	4122(5)	77(7)	2834(4)	26(1)
O(2)	2651(5)	-873(6)	922(4)	23(1)
O(3)	3611(5)	3310(7)	1957(4)	23(1)
O(4)	4007(5)	1225(7)	299(4)	24(1)
O(5)	3965(5)	503(8)	4068(4)	33(2)
O(6)	1133(6)	-2197(8)	693(4)	35(2)
O(7)	3173(7)	5687(9)	1651(5)	46(2)
O(8)	3227(5)	698(7)	-1008(4)	30(2)
O(9)	5051(5)	-906(6)	1577(4)	22(1)
O(10)	5516(5)	2011(7)	1972(4)	31(2)
N(1)	2098(6)	860(7)	2041(4)	20(2)
N(2)	2198(6)	2302(8)	561(4)	20(2)
C(1)	1308(7)	2003(11)	1651(5)	27(2)
C(2)	1142(8)	2070(11)	746(6)	29(2)
C(3)	2458(7)	1116(10)	2935(6)	25(2)
C(4)	3614(6)	503(10)	3331(5)	20(2)
C(5)	1632(8)	-665(11)	1879(6)	29(2)
C(6)	1798(7)	-1295(10)	1084(6)	24(2)
C(7)	2516(8)	3892(10)	634(6)	30(2)
C(8)	3125(7)	4366(10)	1487(5)	23(2)
C(9)	2118(6)	1726(10)	-262(5)	21(2)
C(10)	3187(7)	1185(9)	-338(5)	19(2)
W(1)	-1403(6)	3180(9)	809(5)	44(2)
W(2)	-76(7)	608(10)	3591(6)	55(2)
W(3)	8682(8)	822(10)	1954(7)	65(3)

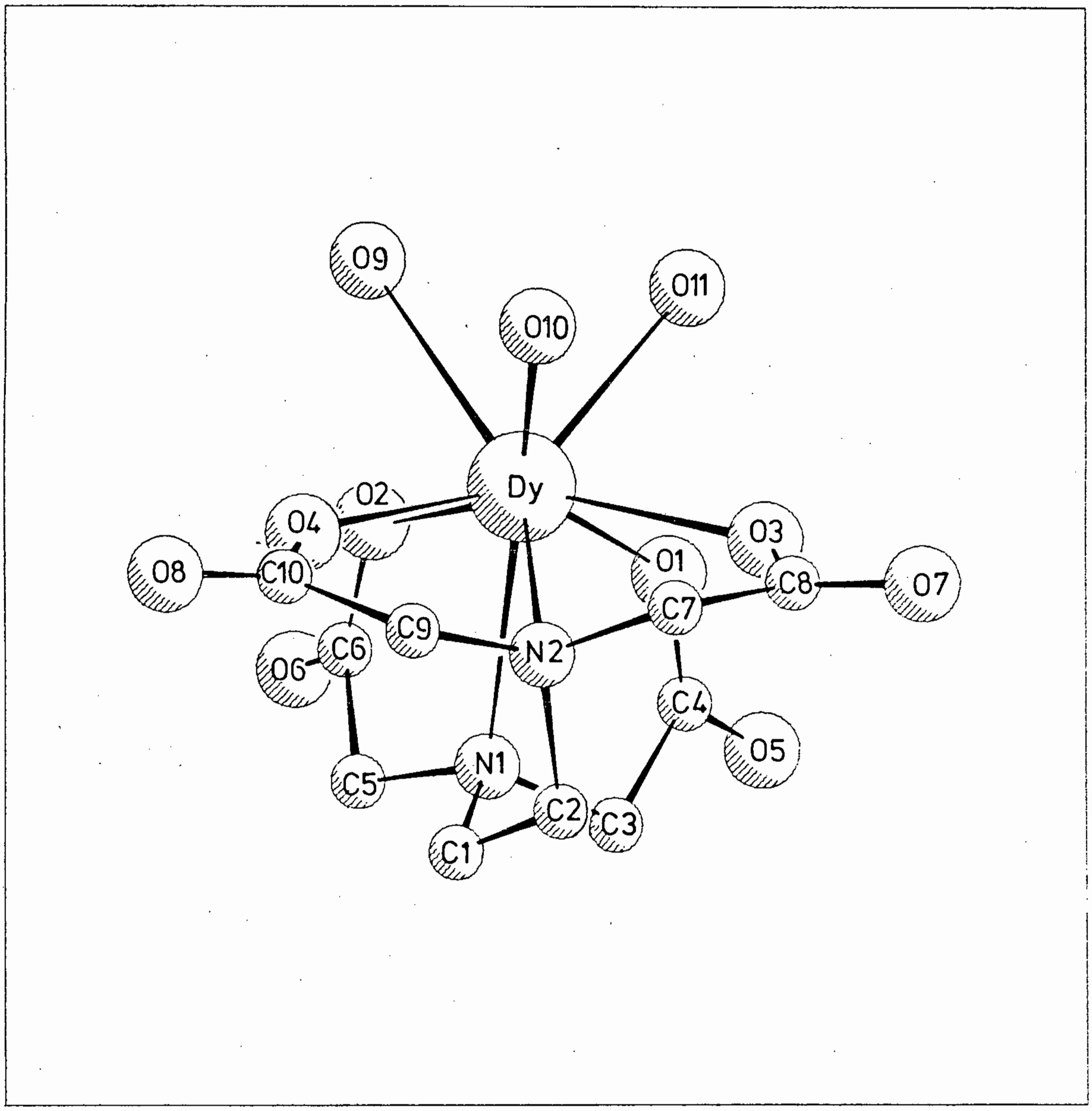
†† Anisotropic parameters in the form $T = \exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}klb^*c^*) \times 10^3]$

	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
Yb	21(0)	12(0)	10(0)	1(0)	2(0)	0
Cs	34(0)	25(0)	31(0)	10(0)	8(0)	2(0)

Table 2.5.1

Hydrogen Atoms: Fractional atomic coordinates (x 10^3) for complex (II)

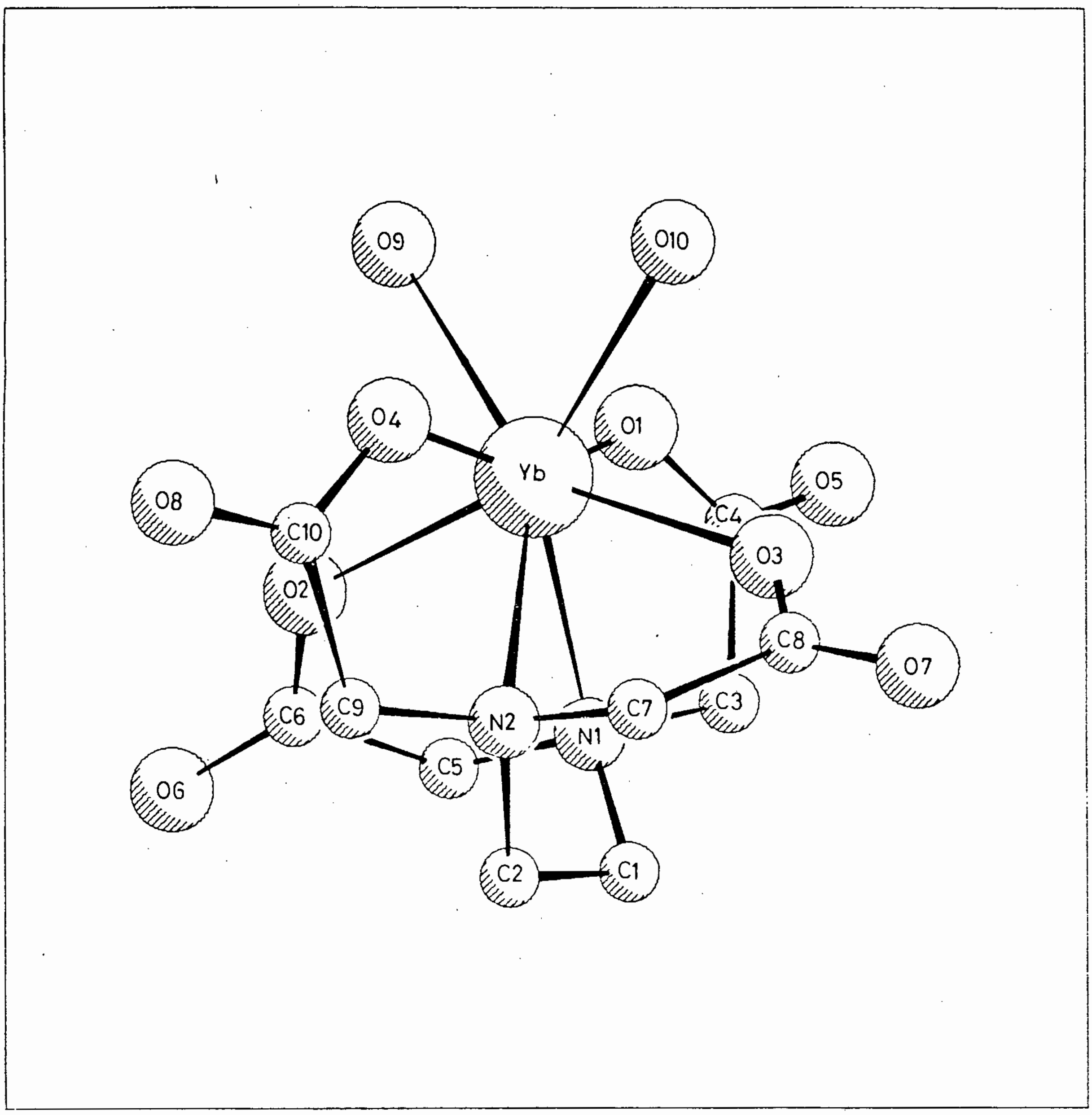
	x	y	z
H(11)	55	175	176
H(12)	159	307	191
H(21)	61	298	49
H(22)	79	104	47
H(31)	245	230	305
H(32)	190	56	320
H(51)	202	-139	238
H(52)	78	-62	182
H(71)	302	410	24
H(72)	179	456	44
H(91)	155	81	-39
H(92)	183	261	-70



Complex (I)

Fig 2.1

antiprismatic geometry (Figure 2.3) shows effectively two-fold symmetry about an axis bisecting the angle N(1)-Yb-N(2). A certain amount of puckering in the five chelate rings of the EDTA moiety is evident in both compounds, but bond lengths and angles (Table 2.6) measured were comparable to those found in similar metal ion-EDTA crystal studies.$^{2.9,2.10}$ Hence in Li[FeEDTA(H_2O)], the 114,2^{o} encountered at a methylene carbon atom and the 115,6^{o} at a carboxylate carbon atom represent examples of maximum angular strain in the chelate rings for

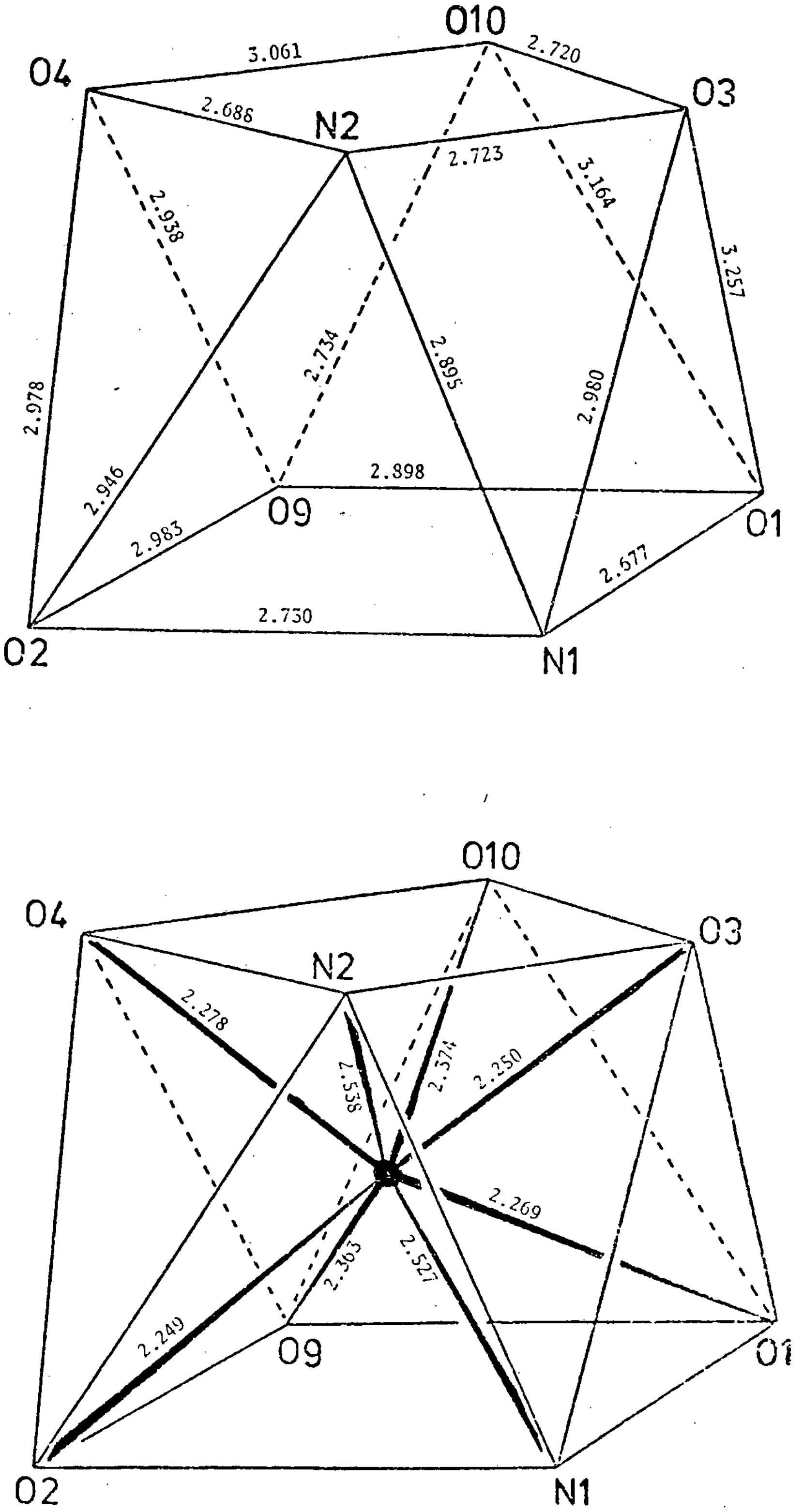


Complex (II)

Fig 2.2

this compound; analogous deviations from ideal tetrahedral and sp^2 geometry in the present study are 111,9° and 115,5° respectively in complex (I) and 114,1° and 115,2° respectively in complex (II).

Assuming that the nature of the cation does not radically influence coordination to the central lanthanide ion, the decreasing atomic radius of the latter is manifested in the



Square antiprismatic geometry about the Yb^{3+} ion.

Fig 2.3

Table 2.6

Intramolecular bond lengths (Å) and selected bond angles (^{o}) with e.s.d.'s for the complex anions

	$[DyEDTA(3H_2O)]^-$	$[YbEDTA(2H_2O)]^-$
M-O(1)	2,464(14)	2,269(6)
M-O(2)	2,396(15)	2,249(6)
M-O(3)	2,420(14)	2,250(6)
M-O(4)	2,285(15)	2,278(6)
M-O(9)	2,553(12)	2,363(6)
M-O(10)	2,351(16)	2,374(6)
M-O(11)	2,483(14)	
M-N(1)	2,642(16)	2,527(7)
M-N(2)	2,614(17)	2,538(7)
N(1)-C(1)	1,493(31)	1,469(11)
C(1)-C(2)	1,498(30)	1,511(12)
N(2)-C(2)	1,496(25)	1,503(11)
N(1)-C(3)	1,458(31)	1,492(11)
C(3)-C(4)	1,561(35)	1,556(11)
O(5)-C(4)	1,277(25)	1,219(11)
O(1)-C(4)	1,229(25)	1,278(10)
N(1)-C(5)	1,523(25)	1,493(11)
C(5)-C(6)	1,466(29)	1,553(13)
O(6)-C(6)	1,276(26)	1,233(11)
O(2)-C(6)	1,280(24)	1,271(11)
N(2)-C(7)	1,520(26)	1,484(11)
C(7)-C(8)	1,469(30)	1,513(13)
O(7)-C(8)	1,269(23)	1,220(11)
O(3)-C(8)	1,298(22)	1,289(11)
N(2)-C(9)	1,496(30)	1,484(10)
C(9)-C(10)	1,505(27)	1,507(11)
O(8)-C(10)	1,254(28)	1,248(11)
O(4)-C(10)	1,289(28)	1,289(10)
O(1)-M-O(4)	139,7(5)	155,6(2)
O(2)-M-O(3)	139,0(5)	137,7(2)
O(1)-M-O(11)	70,4(5)	
O(2)-M-O(9)	67,6(5)	80,6(2)

continued......./

Table 2.6 continued/

O(4)-M-O(10)	80,2(5)	82,3(2)
O(9)-M-N(1)	131,5(4)	129,2(2)
O(10)-M-N(2)	74,1(5)	121,6(2)
O(9)-M-O(10)	72,3(5)	70,5(2)
O(9)-M-O(11)	72,6(5)	
O(10)-M-O(11)	75,0(4)	
N(1)-M-N(2)	68,2(5)	69,7(2)
M-N(1)-C(1)	110,0(14)	111,5(5)
N(1)-C(1)-C(2)	109,8(19)	111,9(7)
N(2)-C(2)-C(1)	111,1(19)	110,8(7)
M-N(2)-C(2)	110,5(13)	112,8(5)
M-N(1)-C(3)	111,2(14)	107,3(5)
N(1)-C(3)-C(4)	109,5(20)	111,9(7)
O(5)-C(4)-C(3)	115,5(21)	118,6(7)
O(1)-C(4)-C(3)	120,7(22)	115,3(7)
M-O(1)-C(4)	123,0(15)	122,9(5)
M-N(1)-C(5)	108,8(11)	107,9(5)
N(1)-C(5)-C(6)	109,9(18)	110,4(7)
O(6)-C(6)-C(5)	116,2(21)	118,0(8)
O(2)-C(6)-C(5)	122,3(21)	115,7(8)
M-O(2)-C(6)	120,9(14)	125,9(6)
M-N(2)-C(7)	107,8(12)	104,7(5)
N(2)-C(7)-C(8)	108,3(18)	114,1(8)
O(7)-C(8)-C(7)	119,2(19)	118,5(8)
O(3)-C(8)-C(7)	120,5(18)	115,2(8)
M-O(3)-C(8)	121,4(12)	124,4(5)
M-N(2)-C(9)	109,1(11)	107,4(5)
N(2)-C(9)-C(10)	111,9(21)	112,4(7)
O(8)-C(10)-C(9)	116,8(24)	118,5(7)
O(4)-C(10)-C(9)	119,2(23)	117,9(7)
M-O(4)-C(10)	125,5(13)	119,7(5)

expulsion of a water molecule from the inner coordination sphere on changing from Dy^{3+} to Yb^{3+}. Hoard *et al*[2.6] report that for $[LaEDTA(3H_2O)]^-$, the displacement of La^{3+} from the mean plane of the four complexed oxygen atoms of EDTA is 0,60 Å on the side away from the nitrogen atoms. In complex (I), this distance is 0,48 Å, a decrease of 0,12 Å, and illustrates the enhanced ability of EDTA to envelope more effectively the smaller cation. In complex (II) this trend is continued to such an extent as to cause the rejection of one water molecule with consequent change in coordination number.

Bell[2.11] discusses the largely electrostatic interaction between lanthanide ion and ligand which causes increasing stability as the size of Ln^{3+} decreases. Thus,[2.6] the average of the four Ln^{3+} - O bond lengths is 2,507 Å in $[LaEDTA(3H_2O)]^-$, 2,319 Å in complex (I) and 2,262 Å in complex (II). The average Ln^{3+} - N and Ln^{3+} - OH_2 bond lengths in the three structures show similar shortening, having average values of 2,755 Å, 2,628 Å and 2,533 Å respectively for the former type of bond, and 2,580 Å, 2,462 Å and 2,369 Å for the latter. (Standard deviations are 0,005 - 0,006 Å for individual Ln - O, Ln - N and Ln - OH_2 bond lengths in $[LaEDTA(3H_2O)]^-$, 0,012 - 0,017 Å for the same bonds in complex (I) and 0,006 - 0,007 Å for these bonds in complex (II)).

2.5 Packing patterns and close contacts.

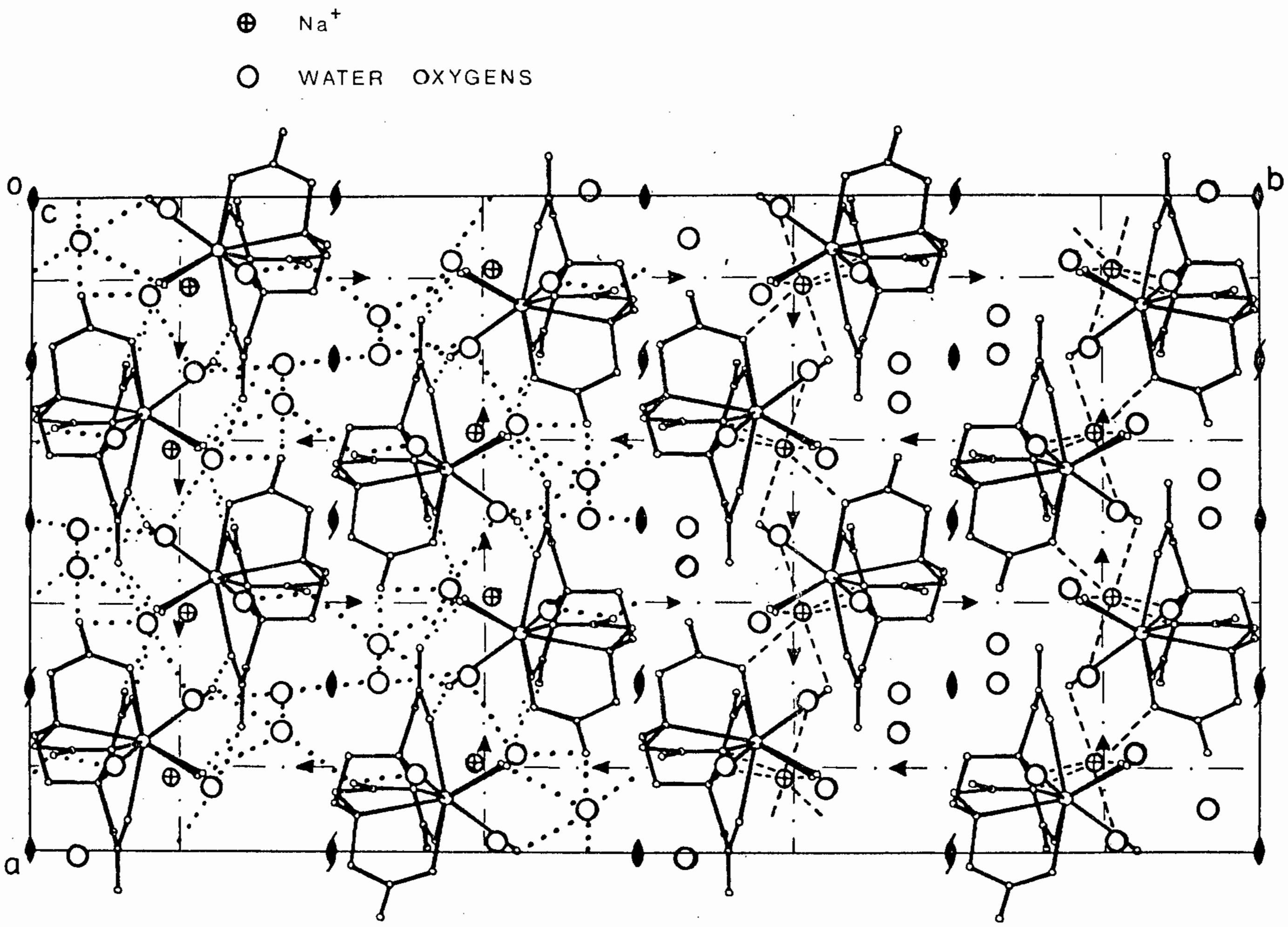
The Dy^{3+} complex (I) crystallises in the space group $\underline{F}dd2$. O....O close contacts in the range 2,47(5) Å to 2,98(2) Å (Table 2.7) are shown by dotted lines in the left

Table 2.7

Close intramolecular and intermolecular approaches (Å) with e.s.d.'s for complex (I)

Symmetry code: (i) $\frac{1}{2} + x, \quad y, \quad \frac{1}{2} + z$
(ii) $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$
(iii) $\frac{1}{4} + x, \frac{1}{4} - y, -\frac{3}{4} + z$
(iv) $\frac{1}{4} - x, \frac{1}{4} + y, \frac{1}{4} + z$
(v) $\frac{1}{2} - x, \frac{1}{2} - y, \quad z$

O(11)....O(1)	2,85(2)	W(5)....O(6^{i})	2,90(4)
O(9) ....O(2)	2,76(2)	W(2)....O(6^{ii})	2,78(3)
O(11)....O(3)	2,81(2)	O(7)....O(2^{iii})	2,76(3)
O(10)....O(4)	2,99(2)	O(7)....O(10^{ii})	2,69(2)
O(10)....O(9)	2,90(2)	O(3)....O(9^{ii})	2,70(2)
O(9) ....O(11)	2,98(2)	O(11)....O(4^{ii})	2,78(2)
O(10)....O(11)	2,95(2)	W(3) ....O(5)	2,70(3)
O(9) ....O(4)	2,95(2)	O(10)....O(8^{ii})	2,63(2)
		W(1) ....O(9)	2,79(2)
		W(1) ....O(11)	2,72(2)
		O(5) ....W(1^{iv})	2,69(2)
		W(2) ....W(4^{ii})	2,77(3)
		W(5) ....W(4^{ii})	2,77(4)
		W(5) ....W(1^{ii})	2,79(4)
		W(5) ....W(5^{v})	2,47(5)



(001) projection of Dy^{3+} structure.

Fig 2.4

half of the [001] projection shown in Figure 2.4 and represent probable H-bonding. A stronger indication of formal H-bonds was not possible due to the uncertainty of the hydrogen positions on any of the water molecules. As regards Na^+....O close contacts, the environment of the Na^+ atom can best be described in terms of its position at the centre of a highly distorted octahedron, depicted by broken lines in the right half of Figure 2.4. The Na^+....O distance varies from 2,40 Å to 2,54 Å and agrees favourably with similar results obtained by Fallon and Gatehouse,[2.12] who measured distorted octahedral Na^+....O distances varying between 2,35 Å and 2,48 Å in sodium acetate trihydrate, and Cameron, Mannan and Rahman,[2.13] where the Na^+....O distance ranged between 2,35(1) Å and 2,56(1) Å in sodium μ-triethylenetetraaminehexaacetatodi-(oxo-vanadium(IV)) decahydrate.

The packing of the Yb^{3+} complex (II) is shown by the four unit cells as a [010] projection in Figure 2.5. The channels of water molecules in the bc-plane are extensively H-bonded (Table 2.8), the O....O close contacts being in the range 2,69(1) Å to 3,16(1) Å. Gupta and Mahata[2.14] found that in caesium hydrogen acetylenedicarboxylate monohydrate, the Cs^+ atom was nine-fold coordinated to surrounding oxygen atoms, the Cs^+....O distance varying from 3,31(3) Å to 3,40(2) Å. In the present study the Cs^+ atom is irregularly surrounded by six O atoms, the close contacts having values less than 3,40 Å.

In the Yb^{3+} complex (II) the change in the crystal packing from $\underline{F}dd2$ to $\underline{P}2_1/c$ is probably influenced by at least three factors, which are not necessarily independent:

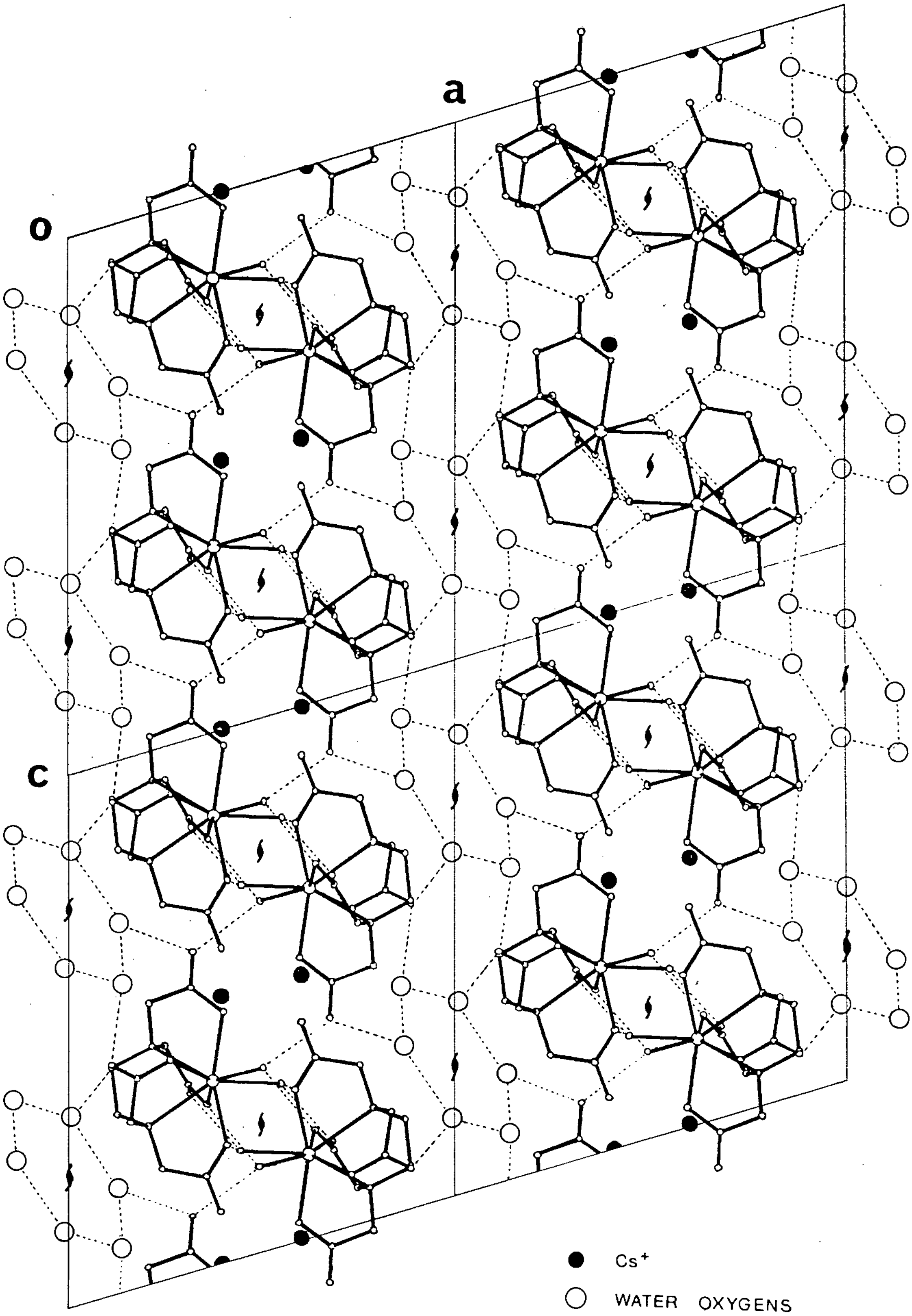
(i) the loss of a water molecule concomitant with the decreasing size of the central ion as the coordi-

Table 2.8

Close intramolecular and intermolecular approaches (Å) with e.s.d.'s for complex (II)

Symmetry code:
(i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(ii) $1 - x, -y, -z$
(iii) $-x, -y, -z$
(iv) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$
(v) $1 + x, y, z$

O(9) ....O(1)	2,90(1)	O(10)....O(1$^{\mathrm{i}}$)	2,80(1)
O(10)....O(1)	3,16(1)	O(3) ....O(9$^{\mathrm{i}}$)	2,71(1)
O(9) ....O(2)	2,98(1)	W(1)....O(6$^{\mathrm{iii}}$)	2,85(1)
O(10)....O(3)	2,72(1)	O(6)....W(2$^{\mathrm{iv}}$)	2,87(1)
O(9) ....O(4)	2,94(1)	O(7)....O(10$^{\mathrm{i}}$)	2,76(1)
O(10)....O(4)	3,06(1)	O(9)....O(8$^{\mathrm{ii}}$)	2,69(1)
O(10)....O(9)	2,73(1)	W(3) ....O(8$^{\mathrm{ii}}$)	2,88(1)
		W(3) ....W(1$^{\mathrm{v}}$)	2,88(1)
		W(2) ....W(1$^{\mathrm{iv}}$)	2,89(1)
		W(3) ....W(2$^{\mathrm{v}}$)	2,82(1)



(010) projection of Yb^{3+} structure.

Fig 2.5

nation number of the Ln^{3+} changes from 9 to 8 results in a different geometry of the ytterbium complex anion;

(ii) the different numbers of waters of crystallisation;

(iii) the large size of the Cs^+ cation.

It is recognised that a substitution of the much smaller Na^+ or K^+ ion for Cs^+ in the ytterbium complex might help in resolving the relative importance of the proposed factors governing the crystal packing pattern for this compound as mentioned above.

CHAPTER 3

THE CRYSTAL STRUCTURES OF A PENTA-COORDINATE PHOSPHORUS COMPOUND: 3,4,8,9-DIBENZ-5,7-DIMETHYL-1-PHENYL-2,6,10,11-TETRAOXATRICYCLO[5,3,1,$0^{1,5}$] PHOSPHA-UNDECANE AND ITS HYDROLYSIS PRODUCT: PHENYL-1-HYDROXY-1-(2'-HYDROXYPHENYL)-ETHLYLIDYNYL PHOSPHINIC ACID

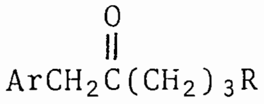
ABSTRACT

Reaction of $PhPCl_2$ with $o\text{-}HOC_6H_4COCH_3$ gives an unusual tricyclic tetraoxaphospha-undecane. Crystals of this compound are monoclinic, $\underline{P}2_1/c$, with $\underline{a}$ = 13,874(7), $\underline{b}$ = 7,924(4), $\underline{c}$ = 16,572(8) Å, β = 94,5(2)°, $\underline{z}$ = 4. The geometry around the phosphorus atom is distorted trigonal bipyramidal, with the two five-membered and one six-membered rings all in apical-equatorial positions. It is postulated that permutational isomerisation in solution is unlikely for this compound due in part to its molecular rigidity. Crystals of the disubstituted phosphinic acid are monoclinic, $\underline{P}2_1/n$, with $\underline{a}$ = 13,886(7), $\underline{b}$ = 7,378(4), $\underline{c}$ = 15,280(8) Å, β = 116,9(2)°, $\underline{z}$ = 4. The phosphorus atom has the expected tetrahedral environment. O....O close contacts less than 2,76(1) Å indicate hydrogen bonding which extends throughout the lattice.

2.1 Introduction

The importance of photochemical reactions in synthetic organic chemistry is well established. An understanding of the molecular orbital excitations involved has proved to be one of the major challenges in this field. Inherent in any mechanistic study of this type of reaction is the need for techniques such as labelling experiments, stereochemistry, kinetics and the trapping of intermediates which besides accounting for the observed phenomena can make useful predictions about how the reaction will respond to changes in substrate or conditions. The famous Diels-Alder cycloaddition process has been characterised and understood on this basis.

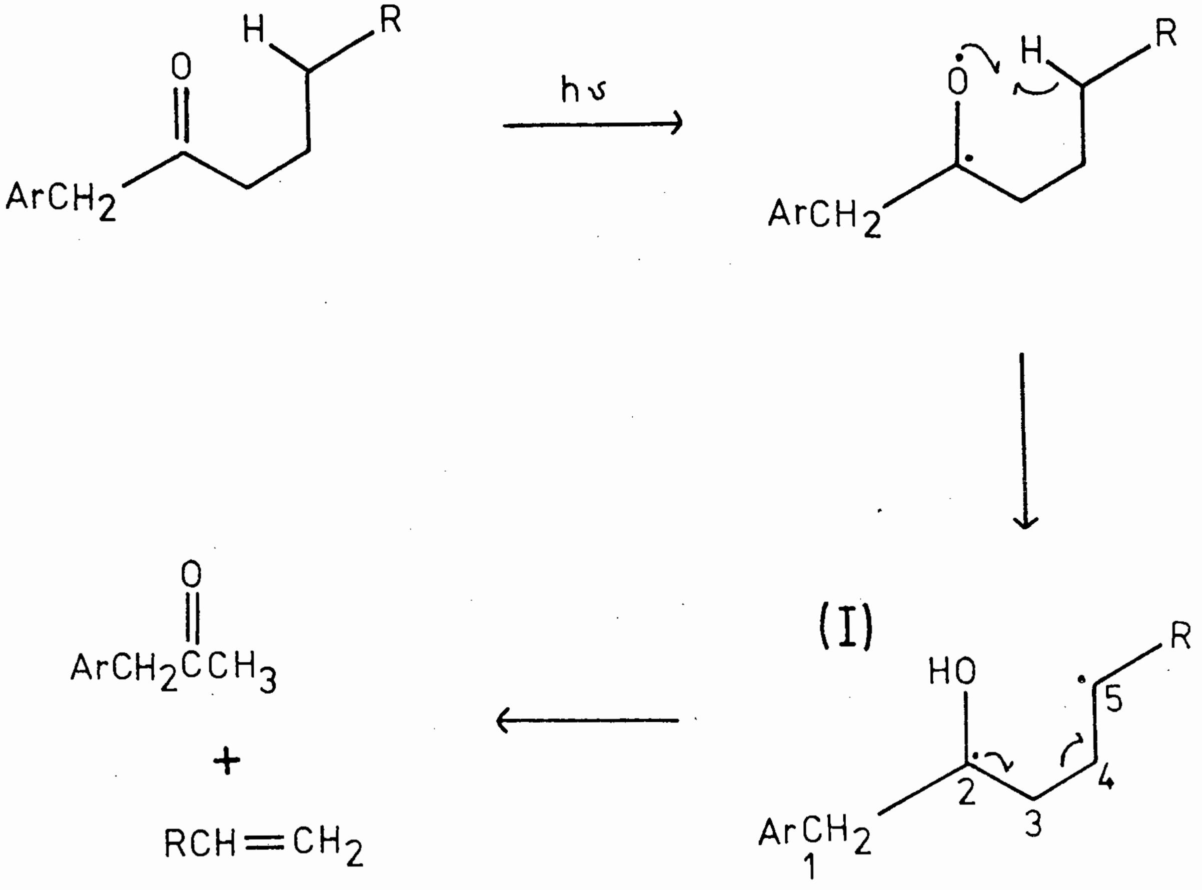
Work in our laboratories has recently been directed towards studies relating to compounds such as



$$ArCH_2\overset{\overset{O}{\|}}{C}(CH_2)_3R$$

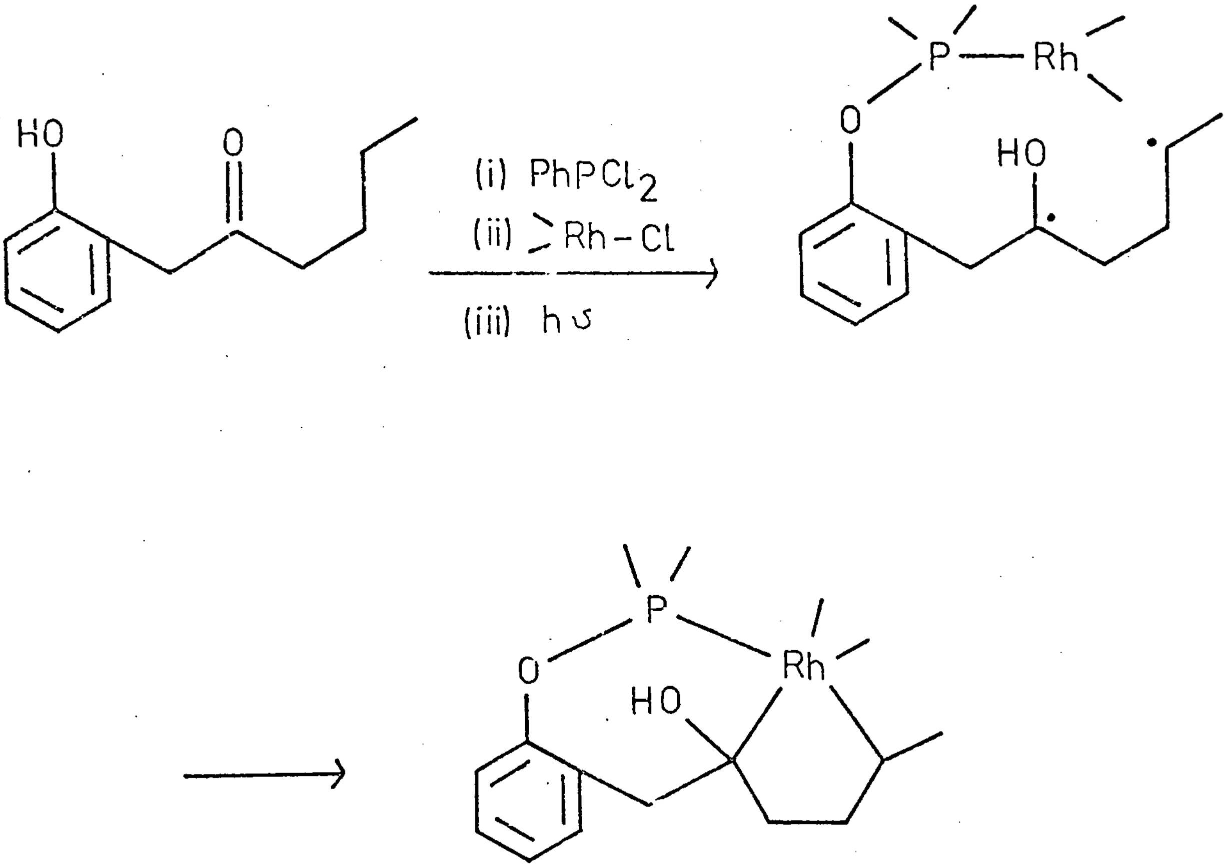
(Ar = aryl and R = H or alkyl or aryl), where under light of appropriate wavelength, an n → π^* excitation of the carbonyl group usually leads to chemical degradation via a postulated diradical intermediate (I, Scheme 3.1). This is generally known as a Norrish Type II process,[3.1, 3.2] and requires a hydrogen atom on the carbon atom γ to the carbonyl group.[3.3]

In addition to the two products shown below, ring closure of the biradical intermediate (I) can occur to yield the cyclobutanol as a minor product. Now Rh(I) and Fe(0) have the property of being able to insert into carbon-carbon bonds and have a capacity to undergo oxidative addition.[3.4] If insertion



Scheme 3.I

of one of these metal atoms between C(2) and C(5) of the excited intermediate (I) could be induced and the product isolated, the existence of such a biradical would be substantiated. However, since the biradical will be short-lived and the concentrations used in photochemistry are of a very low order, the probability of any interaction occurring between the biradical and the free metal derivative would be extremely small. A possible solution would be prior coordination of the metal derivative to the organic species before irradiation, facilitating the proposed trapping of the biradical during photolysis by the metal atom because of its close proximity. In order to minimise the interaction between the keto group and the metal atom, and to place the metal atom stereochemically in a more favourable position for bond formation to occur, a phosphorus atom could form a bridge between the two moieties (Scheme 3.2).



Scheme 3.2

This atom, being a 'soft' ligand, might be expected to form a strong metal-ligand bond and thus a stable complex with a 'soft' metal such as Rh(I).[3.5]

In preliminary investigations along these lines, reaction of $PhPCl_2$ with two equivalents of o-$HOC_6H_4COCH_3$ in triethylamine gave a crystalline product of stoichiometry $PhP(OC_6H_4COCH_3)_2$. The absence of C=O stretching peaks in the infrared spectrum of this compound and the presence of two methyl resonances in its NMR spectrum with one split into a doublet (J = 20 Hz) indicated that it was not the expected product. It was thus decided to solve the structure by x-ray analysis. The characterisation of the product as an unusual tricyclic tetraoxaphospha-undecane (I) is herein described.

An attempt to recrystallise (I) using 'wet' acetone i.e. not completely dry, led to the formation of a new substance. Subsequent x-ray analysis on this compound, also described herein, confirms that (I) undergoes hydrolysis in forming the disubstituted phosphinic acid (II).

3.2 Crystal preperation and data collection.

12,62 g (0,1 mole) o-$HOC_6H_4COCH_3$ in 70 ml benzene was added dropwise at 0^oC to a solution of 10,12 g (0,1 mole) NEt_3 and 8,95 g (0,05 mole) $PhPCl_2$ in 170 ml benzene. The reaction, carried out under N_2, was stirred at 0^oC for a further 3 hours and left overnight. After filtration to remove the amine hydrochloride, the filtrate was concentrated under reduced pressure. The crystalline product (I) was purified by recrystallisation from hot benzene. δ 1,65 (3H, d, J 20 Hz, 5 Me), 2,0 (3H, s, 7-Me), 6,7-7,7 (11H, m, ArH) and 8,0-8,4 (2H, m, ArH). (II) resulted from an attempted recrystallisation of (I) using acetone which had not been rigorously dried.

Oscillation and Weissenberg photographs taken of (I) and

(II) gave the crystallising space groups as $P2_1/c$ for the former and $P2_1/n$ for the latter.[2.8] Crystal data and experimental details of the data collections are listed in Table 3.1.

3.3 Solution and refinement of the structures.

The structure of the tetraoxaphospha-undecane (I) was solved by the automatic centrosymmetric direct methods routine of the SHELX program system,[1.1] in which an E map yielded the positions of all the heavy atoms. Some of the hydrogen atoms were located in subsequent Fourier maps. The final refinement was carried out with the heavy atoms treated anisotropically, the methyl H atoms being refined as rigid groups and the remaining H atoms being constrained at 1,08 Å from their respective C atoms, their positions dictated by the geometry of the molecule. The isotropic temperature factors of the H atoms were treated as two single parameters. Details of the final refinements are reported in Table 3.1.

The disubstituted phosphinic acid (II) was solved in an analogous manner, although hydroxyl hydrogen atoms could not be located in difference Fourier maps and were therefore omitted from the final model.

The positional and thermal parameters of the non-hydrogen atoms are presented in Table 3.2 for compound (I) and Table 3.3 for compound (II). The hydrogen atom positions are listed in Tables 3.2.1 and 3.3.1 respectively. Observed and calculated structure factors appear in Appendices C and D.

Table 3.1

Crystal data and experimental and refinement parameters for the crystal structures of the phospha-undecane (I) and its hydrolysis product (II).

Crystal data	(I)	(II)
Molecular formula	$C_{22}H_{19}O_4P$	$C_{14}H_{15}O_4P$
Mr	378,4	278,2
Space group	$P2_1/c$	$P2_1/n$
a	13,874(7)Å	13,886(7)Å
b	7,924(4)	7,378(4)
c	16,572(8)	15,280(8)
β	94,5(2)°	116,9(2)°
Dm	1,36 Mg M^{-3}	1,20 Mg m^{-3}
Dc	1,38 for z=4	1,22 for z=4
μ(MoKα)	0,133 mm^{-1}	0,159 mm^{-1}
F(ooo)	792	584
Data Collection		
Crystal dimensions	0,38x0,50x0,88 mm	0,14x0,16x0,20mm
Scan mode	ω-2θ	ω-2θ
Scan width	1,0°θ	1,2°θ
Scan speed	$0{,}03^{\circ}\theta s^{-1}$	$0{,}04^{\circ}\theta s^{-1}$
Range scanned (2θ)	6-50°	6-44°
Stability of standard reflections	3,4%	1,4%
Number of reflections collected	3257	1880
Number of 'observed' reflections	2463 with I(rel) >2σI(rel)	1140 with I(rel) >2σI(rel)
Final refinement		
Number of variables	252	177
$R=\Sigma\lvert\lvert Fo\rvert-\lvert Fc\rvert\rvert/\Sigma\lvert Fo\rvert$	0,049	0,058
$R_W=\Sigma w^{\frac{1}{2}}\lvert\lvert Fo\rvert-\lvert Fc\rvert\rvert/\Sigma w^{\frac{1}{2}}\lvert Fo\rvert$	0,065	0,050
Weighting scheme w	$(\sigma^2F+1{,}34\times10^{-2}F^2)^{-1}$	$(\sigma^2F)^{-1}$
U (aromatic H)	0,067 Å^2	0,085 Å^2
U (methyl H)	0,050	0,076

Table 3.2

Non hydrogen atoms. Fractional atomic coordination (x10^4) and anisotropic temperature factors (Å x 10^3) with e.s.d.'s for compound (I).

Thermal parameters are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2}+U_{11}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^* + 2U_{13}hla^*c^*+2U_{23}klb^*c^*)\mathrm{x}10^3]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	2463(1)	828(1)	1680(0)	29(1)	23(1)	34(1)	1(0)	1(0)	3(0)
O(2)	1440(1)	273(3)	1059(1)	31(1)	32(1)	44(1)	-4(1)	-4(1)	6(1)
O(6)	3764(1)	-1529(2)	1913(1)	29(1)	20(1)	59(1)	-1(1)	-3(1)	-2(1)
O(10)	2933(1)	1575(3)	885(1)	37(1)	32(1)	37(1)	4(1)	2(1)	6(1)
O(11)	3457(1)	1190(2)	2318(1)	32(1)	22(1)	33(1)	-1(1)	2(1)	3(1)
C(3)	1562(2)	-1291(4)	717(2)	31(2)	28(2)	38(2)	-6(1)	3(1)	-1(1)
C(4)	2284(2)	-2279(4)	1098(2)	29(2)	22(2)	39(2)	1(1)	5(1)	-5(1)
C(5)	2737(2)	-1436(4)	1844(2)	31(2)	22(2)	41(2)	5(1)	0(1)	0(1)
C(7)	4205(2)	122(4)	2112(2)	30(2)	20(1)	43(2)	-2(1)	0(1)	-2(1)
C(8)	4588(2)	864(3)	1355(2)	31(2)	22(1)	42(2)	-8(1)	4(1)	0(1)
C(9)	3929(2)	1676(3)	811(2)	35(2)	23(2)	35(2)	-4(1)	5(1)	-1(1)
C(12)	2322(2)	-2104(4)	2612(2)	50(2)	37(2)	38(2)	10(1)	1(1)	-9(1)
C(13)	4939(2)	-96(4)	2830(2)	36(2)	31(2)	51(2)	6(1)	-11(1)	-1(1)
C(1A)	1756(2)	2254(4)	2245(2)	34(2)	27(2)	40(2)	-2(1)	6(1)	-2(1)
C(2A)	1918(3)	2388(5)	3085(2)	60(2)	50(2)	41(2)	-2(2)	5(2)	17(2)
C(3A)	1360(3)	3458(6)	3511(2)	74(3)	65(3)	46(2)	-8(2)	14(2)	19(2)
C(4A)	652(3)	4429(5)	3111(2)	54(2)	48(2)	64(2)	-15(2)	16(2)	10(2)
C(5A)	497(2)	4328(4)	2274(2)	41(2)	37(2)	68(2)	-5(2)	1(2)	8(2)
C(6A)	1031(2)	3229(4)	1843(2)	31(2)	29(2)	58(2)	-1(1)	1(1)	6(1)
C(4B)	2465(2)	-3879(4)	818(2)	43(2)	28(2)	42(2)	-1(1)	2(1)	1(1)
C(5B)	1905(3)	-4476(5)	142(2)	53(2)	38(2)	52(2)	-12(2)	-3(2)	3(2)
C(6B)	1175(3)	-3477(5)	-228(2)	63(2)	45(2)	40(2)	-13(2)	-10(2)	2(2)
C(7B)	998(2)	-1877(5)	54(2)	46(2)	49(2)	42(2)	-3(2)	-9(1)	7(2)
C(8C)	5562(2)	895(4)	1210(2)	36(2)	35(2)	52(2)	-9(1)	8(1)	-2(1)
C(9C)	5865(3)	1738(5)	541(2)	44(2)	56(2)	57(2)	-14(2)	20(2)	-9(2)
C(10C)	5191(3)	2577(5)	17(2)	63(3)	49(2)	43(2)	-6(2)	19(2)	-14(2)
C(11C)	4222(3)	2545(4)	157(2)	52(2)	39(2)	38(2)	-2(1)	9(2)	-2(2)

Table 3.2.1

H atoms. Fractional atomic coordinates ($x10^3$) for compound (I)

	x	y	z
H(121)	155	-192	258
H(122)	265	-145	314
H(123)	248	-344	266
H(131)	550	-97	270
H(132)	458	-54	335
H(133)	525	113	296
H(2A)	248	165	340
H(3A)	148	354	416
H(4A)	21	526	345
H(5A)	-5	511	196
H(6A)	89	314	119
H(4B)	303	-465	111
H(5B)	204	-572	-9
H(6B)	74	-396	-75
H(7B)	43	-110	-24
H(8C)	609	27	162
H(9C)	662	174	42
H(10C)	543	325	-50
H(11C)	370	320	-25

Table 3.3

Non Hydrogen Atoms. Fractional atomic coordinates (x 10^4) and anisotropic temperature factors ($\mathrm{\AA}^2$ x 10^3) with e.s.d.'s for compound(II).

Thermal parameters are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*) \times 10^3]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	6521(1)	584(2)	2397(1)	39(1)	30(1)	74(1)	1(1)	29(1)	1(1)
O(1)	7664(3)	1236(4)	2735(3)	39(2)	36(2)	91(2)	1(2)	33(2)	0(2)
O(2)	6194(3)	-941(4)	1597(3)	55(2)	32(2)	63(2)	-9(2)	28(2)	-5(2)
O(3)	4510(3)	3254(6)	3098(3)	71(2)	85(3)	88(3)	-24(2)	-47(2)	-8(2)
O(4)	5911(3)	3911(4)	2491(3)	57(2)	31(2)	82(2)	-11(2)	33(2)	-3(2)
C(1)	5542(4)	2441(7)	1789(4)	44(3)	33(3)	72(3)	4(3)	29(2)	5(2)
C(2)	5594(4)	3020(7)	856(4)	62(3)	46(3)	82(3)	9(3)	42(2)	0(2)
C(3)	4414(4)	1840(7)	1618(4)	34(2)	33(3)	77(3)	14(3)	28(2)	8(2)
C(4)	3811(4)	751(7)	797(4)	41(3)	48(3)	80(3)	-3(3)	20(2)	-1(2)
C(5)	2822(5)	61(8)	635(5)	53(3)	59(3)	90(3)	-6(3)	19(3)	-11(3)
C(6)	2411(5)	433(9)	1288(5)	41(3)	65(3)	114(3)	10(3)	36(3)	-5(3)
C(7)	2985(5)	1508(8)	2091(5)	50(3)	65(3)	104(3)	4(3)	47(2)	1(3)
C(8)	3988(4)	2208(8)	2279(5)	39(3)	49(3)	89(3)	11(3)	35(2)	6(2)
C(11)	6307(4)	-271(7)	3393(4)	33(2)	31(2)	67(3)	-2(2)	24(2)	-5(2)
C(21)	6919(5)	436(8)	4333(5)	65(3)	44(3)	73(3)	-7(3)	29(2)	-8(3)
C(31)	6698(5)	-145(9)	5090(5)	89(3)	81(3)	64(3)	-11(3)	31(3)	15(3)
C(41)	5914(5)	-1395(9)	4925(5)	84(3)	71(3)	88(3)	22(3)	54(3)	25(3)
C(51)	5322(5)	-2098(8)	4004(5)	55(3)	61(3)	105(3)	21(3)	41(3)	2(3)
C(61)	5523(4)	-1544(7)	3235(5)	51(3)	45(3)	72(3)	5(3)	30(2)	-2(2)

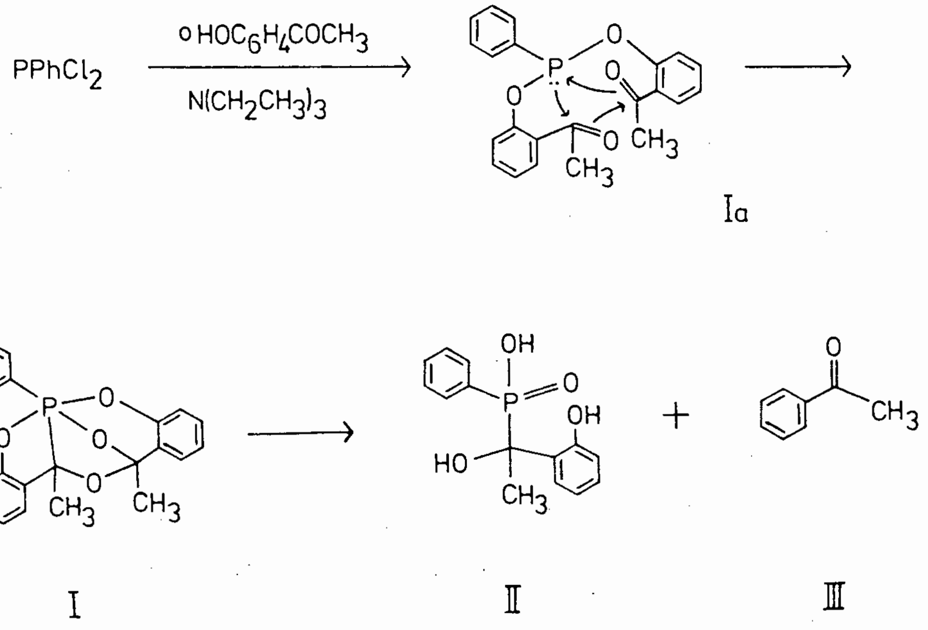
Table 3.3.1

H atoms. Fractional atomic coordinates (x 10^3) for compound (II)

	x	y	z
H(1)	532	192	33
H(2)	642	336	102
H(3)	508	419	55
H(4)	413	45	29
H(5)	237	-77	0
H(6)	164	-12	117
H(7)	265	181	259
H(21)	755	141	447
H(31)	716	40	582
H(41)	576	-184	552
H(51)	470	-309	388
H(61)	506	-211	251

3.4 Description of the structures and discussion.

A possible route for the formation of the phospha-undecane (I) would be initial reaction of two molecules of o-$HOC_6H_4COCH_3$ with $PhPCl_2$ to form the intermediate phosphonite I(a) (Scheme 3·3)· Concerted intramolecular nucleophilic attack would then yield the tricyclic phospha-undecane. This postulated mechanism is supported by the report[3.6] that $PhP(OPh)_2$ reacts with hexafluoroacetone via attack at the carbonyl carbon atom, although in this case the initial P-C-O bond rearranges to give a product containing a P-O-C bond.



Scheme 3.3

As a result of the mechanistic versatility of (I), a discussion using available data concerning the reaction pathway and possible intermediates leading to the hydrolysis products would be purely speculative. Presumably the process involves nucleophilic attack at the phosphorus atom followed by concerted cyclic proton transfer mechanisms.

The molecular structures with atomic nomenclature for compounds (I) and (II) appear in Figures 3.1 and 3.6 respectively, with bond lengths and angles for the two structures in Tables 3.4 and 3.5. The phospha-undecane (I) shows remarkable ability in accommodating the relatively crowded environment around the phosphorus atom, and this is probably due to the presence of five- and six-membered rings involving this atom. It has been mentioned[3.8] that this factor plays a significant role in minimising prohibitive non-bonded interactions within pentacoordinated phosphorus containing molecules. The phosphorus atom in (I) lies at the centre of a distorted trigonal bipyramid (Figure 3.2), with the two five-membered rings and one six-membered ring all in apical-equatorial planes, and both carbon atoms equatorial. The apical-equatorial position for five-membered rings and the tendency for the more electronegative atoms to occupy apical rather than equatorial positions appears to be a general phenomenon in trigonal bipyramidal phosphorus.[3.8]

In (I), the diapical bond axis is slightly distorted, with the angle O(2)-P-O(11) = 174,9(0)°. The apical - equatorial bond angles range from 85,7(1)° to 94,9(0)°, with the equatorial bond angles having values of 112,4(1)°, 117,4(1)° and 130,1(1)°.

The ^1H NMR spectrum of a freshly prepared solution of (I) shows a singlet at 2,00 δ due to the protons on C(13) and a doublet at 1,65 δ (J_{HP} = 20 cps) due to the protons on C(12) (Figure 3.1). The spectrum run on the same solution after 24 hours contains, besides the original set of 3 lines, an additional set of 3 lines consisting also of a singlet and a doublet at values of 2,63 δ and 1,39 δ (J_{HP} = 18 cps) respectively. Given that the ^1H NMR spectrum of phenyl ethanone shows a singlet at 2,59 δ,[3.7] and assuming that in this reaction the introduction of the phosphoryl group has a shielding effect, the spectrum of the aged solutions of (I) can be interpreted in terms of the formation of the hydrolysis products (II) and (III) (Scheme 3.3).

Compound (I)

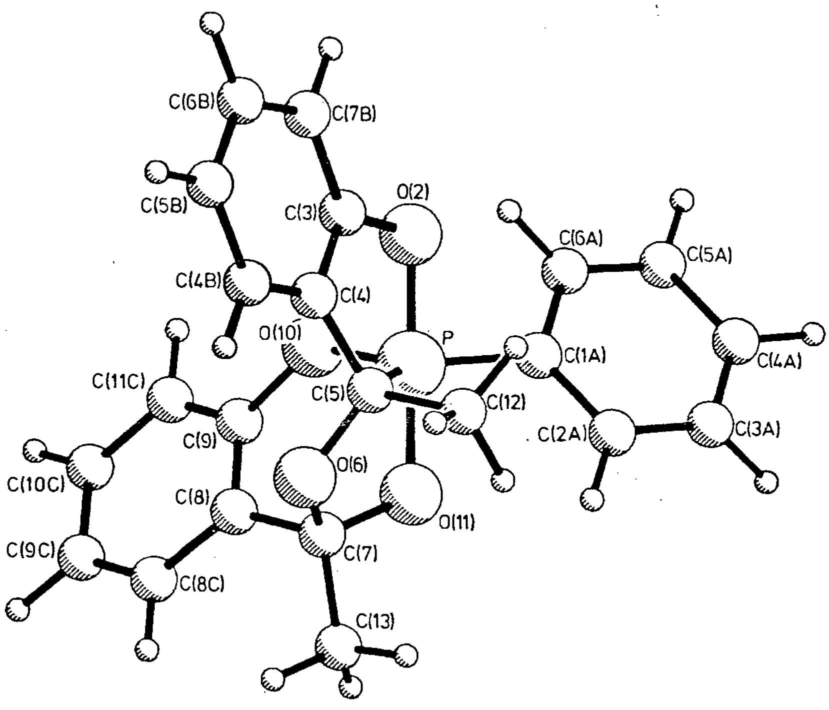


Fig 3.1

Table 3.4

Intramolecular bond lengths (Å) and bond angles (°) with e.s.d.'s for compound (I).

P-O(2)	1,741(1)	C(6B)-C(7B)	1,380(2)
P-O(10)	1,626(1)	C(7B)-C(3)	1,378(2)
P-O(11)	1,696(1)	C(4)-C(5)	1,499(2)
P-C(5)	1,849(1)	C(5)-C(12)	1,533(2)
P-C(1A)	1,806(1)	C(5)-O(6)	1,421(2)
C(1A)-C(2A)	1,397(2)	O(6)-C(7)	1,471(2)
C(2A)-C(3A)	1,379(2)	C(7)-C(13)	1,512(2)
C(3A)-C(4A)	1,377(3)	C(7)-O(11)	1,402(2)
C(4A)-C(5A)	1,388(3)	C(7)-C(8)	1,519(2)
C(5A)-C(6A)	1,379(2)	C(8)-C(9)	1,391(2)
C(6A)-C(1A)	1,395(2)	C(8)-C(8C)	1,392(2)
O(2)-C(3)	1,379(2)	C(8C)-C(9C)	1,388(2)
C(3)-C(4)	1,383(2)	C(9C)-C(10C)	1,393(3)
C(4)-C(4B)	1,380(2)	C(10C)-C(11C)	1,384(2)
C(4B)-C(5B)	1,395(2)	C(11C)-C(9)	1,371(2)
C(5B)-C(6B)	1,390(2)	C(9)-O(10)	1,399(2)

O(2)-P-O(10)	88,5(1)	O(6)-C(7)-C(13)	108,5(1)
O(2)-P-O(11)	174,9(0)	O(11)-C(7)-C(13)	110,0(1)
O(10)-P-O(11)	94,9(0)	C(8)-C(7)-C(13)	115,8(1)
O(2)-P-C(5)	89,5(1)	O(6)-C(7)-C(8)	109,0(1)
O(10)-P-C(5)	112,4(1)	O(11)-C(7)-C(8)	106,3(1)
O(11)-P-C(5)	85,7(1)	C(7)-C(8)-C(9)	117,4(1)
O(2)-P-C(1A)	90,8(1)	C(7)-C(8)-C(8C)	123,9(1)
O(10)-P-C(1A)	117,4(1)	C(8C)-C(8)-C(9)	118,5(1)
O(11)-P-C(1A)	91,1(1)	O(10)-C(9)-C(8)	121,3(1)
C(1A)-P-C(5)	130,1(1)	O(10)-C(9)-C(11C)	117,1(1)
P-O(2)-C(3)	110,4(1)	C(8)-C(9)-C(11C)	121,6(1)
C(5)-O(6)-C(7)	111,6(1)	P-C(1A)-C(2A)	120,9(1)
P-O(10)-C(9)	123,7(1)	P-C(1A)-C(6A)	120,0(1)
P-O(11)-C(7)	109,1(1)	C(2A)-C(1A)-C(6A)	119,1(1)
O(2)-C(3)-C(4)	115,4(1)	C(1A)-C(2A)-C(3A)	120,3(2)

Table 3.4 continued

O(2)-C(3)-C(7B)	123,4(1)	C(2A)-C(3A)-C(4A)	120,4(2)
C(4)-C(3)-C(7B)	121,2(1)	C(3A)-C(4A)-C(5A)	119,8(1)
C(3)-C(4)-C(5)	111,4(1)	C(4A)-C(5A)-C(6A)	120,4(2)
C(3)-C(4)-C(4B)	120,8(1)	C(1A)-C(6A)-C(5A)	120,0(2)
C(4B)-C(4)-C(5)	127,7(1)	C(4)-C(4B)-C(5B)	118,5(1)
P-C(5)-O(6)	104,8(1)	C(4B)-C(5B)-C(6B)	120,1(1)
P-C(5)-C(4)	104,0(1)	C(5B)-C(6B)-C(7B)	121,1(1)
O(6)-C(5)-C(4)	113,3(1)	C(3)-C(7B)-C(6B)	118,3(2)
P-C(5)-C(12)	111,7(1)	C(8)-C(8C)-C(9C)	120,4(2)
O(6)-C(5)-C(12)	110,8(1)	C(8C)-C(9C)-C(10C)	119,8(1)
C(4)-C(5)-C(12)	111,7(1)	C(9C)-C(10C)-C(11C)	120,0(2)
O(6)-C(7)-O(11)	106,8(1)	C(9)-C(11C)-C(10C)	119,6(2)

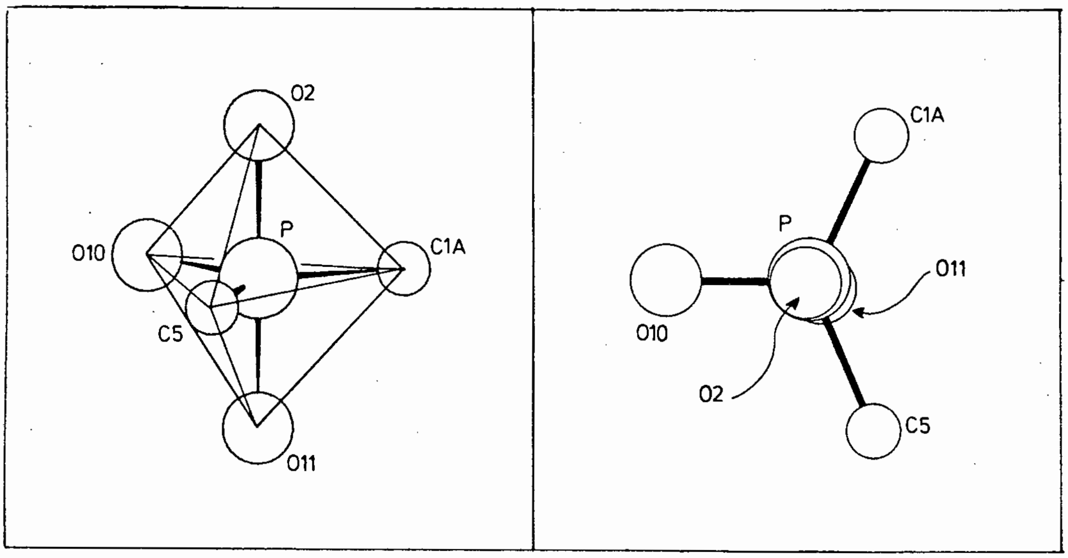
Table 3.5

Intramolecular bond lengths (Å) and bond angles (°) with e.s.d.'s for compound (II)

P-O(1)	1,509(3)	C(6)-C(7)	1,374(7)
P-O(2)	1,570(3)	C(7)-C(8)	1,389(7)
P-C(1)	1,857(5)	O(3)-C(8)	1,367(6)
P-C(11)	1,792(5)	C(8)-C(3)	1,409(7)
C(1)-C(2)	1,522(7)	C(11)-C(21)	1,399(7)
C(1)-O(4)	1,447(6)	C(21)-C(31)	1,391(7)
C(1)-C(3)	1,532(7)	C(31)-C(41)	1,361(8)
C(3)-C(4)	1,404(7)	C(41)-C(51)	1,371(8)
C(4)-C(5)	1,378(7)	C(51)-C(61)	1,387(7)
C(5)-C(6)	1,382(7)	C(61)-C(11)	1,374(6)
O(1)-P-O(2)	112,6(2)	C(3)-C(4)-C(5)	121,1(6)
O(1)-P-C(1)	110,8(2)	C(4)-C(5)-C(6)	120,0(6)
O(2)-P-C(1)	104,5(2)	C(5)-C(6)-C(7)	119,9(6)
O(1)-P-C(11)	111,9(2)	C(6)-C(7)-C(8)	121,4(6)
O(2)-P-C(11)	108,0(2)	O(3)-C(8)-C(3)	123,0(5)

Table 3.5 continued

C(1)-P-C(11)	108,6(2)	O(3)-C(8)-C(7)	117,8(6)
P-C(1)-O(4)	104,4(3)	C(3)-C(8)-C(7)	119,2(6)
P-C(1)-C(3)	109,5(3)	P-C(11)-C(21)	119,0(4)
O(4)-C(1)-C(3)	109,6(4)	P-C(11)-C(61)	120,9(5)
P-C(1)-C(2)	110,0(4)	C(21)-C(11)-C(61)	120,0(5)
O(4)-C(1)-C(2)	109,5(4)	C(11)-C(21)-C(31)	118,7(6)
C(2)-C(1)-C(3)	113,5(5)	C(21)-C(31)-C(41)	120,9(7)
C(1)-C(3)-C(8)	123,4(5)	C(31)-C(41)-C(51)	120,3(7)
C(1)-C(3)-C(4)	118,0(5)	C(41)-C(51)-C(61)	120,1(6)
C(4)-C(3)-C(8)	118,4(5)	C(51)-C(61)-C(11)	120,0(6)

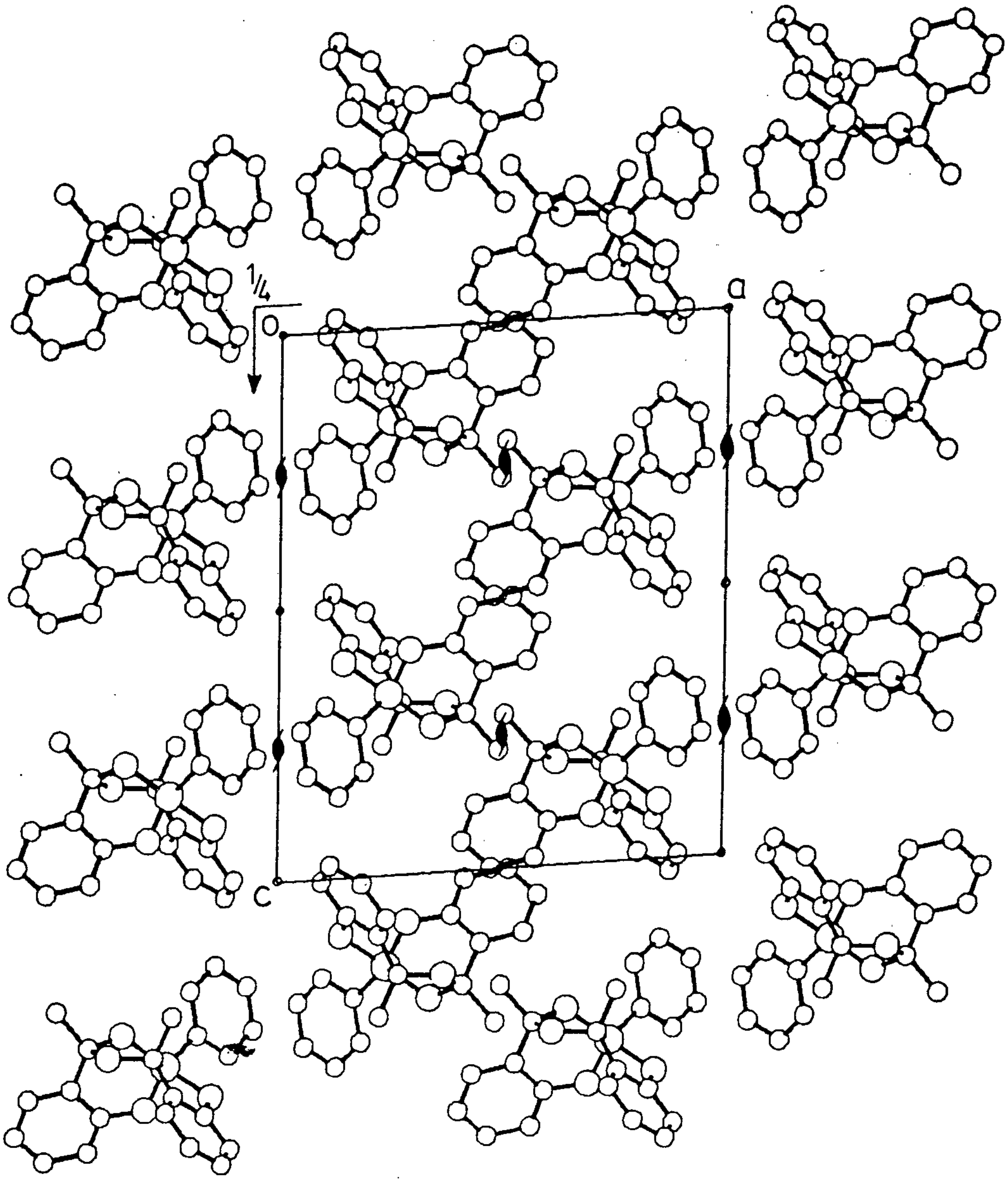


Trigonal bipyramidal geometry about the phosphorus atom in compound (I).

Fig 3.2

The phosphorus atom lies 0,01 Å from the equatorial plane. The phenyl groups have normal geometry. The two five-membered rings are slightly puckered, the P-C(5)-O(6)-C(7)-O(11) ring containing two tetrahedral carbon atoms showing the greater deviation from planarity. Torsion angles in the six-membered dioxaphosphorinene ring vary between 76° for P-O(11)-C(7)-C(8) and -10° for the C(7)-C(8)-C(9)-O(10). A projection of the unit cell looking down the b axis is shown in Figure 3.3.

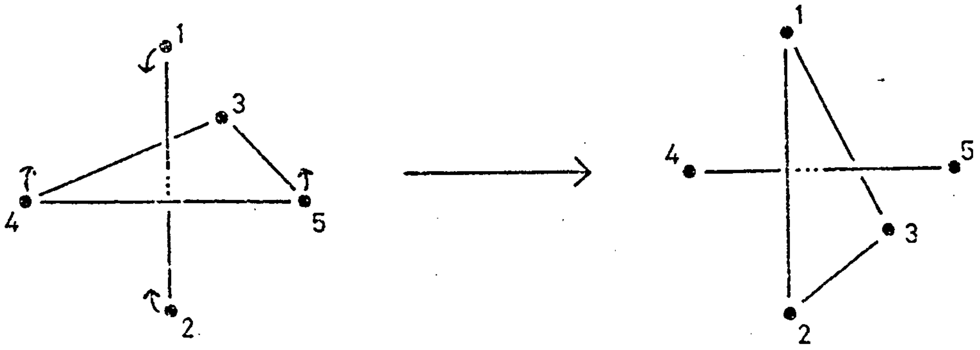
It is well established that many pentacoordinate phosphorus compounds are able to change their ligand distributions by bond deformation processes which may be explained using the Berry pseudorotation[3.9] or the turnstile rotation mechanisms.[3.8] A schematic representation of the two mechanisms is depicted in Figure 3.4. In Berry pseudorotation, pairs of ligands move in planes perpendicular to each other, the planes being



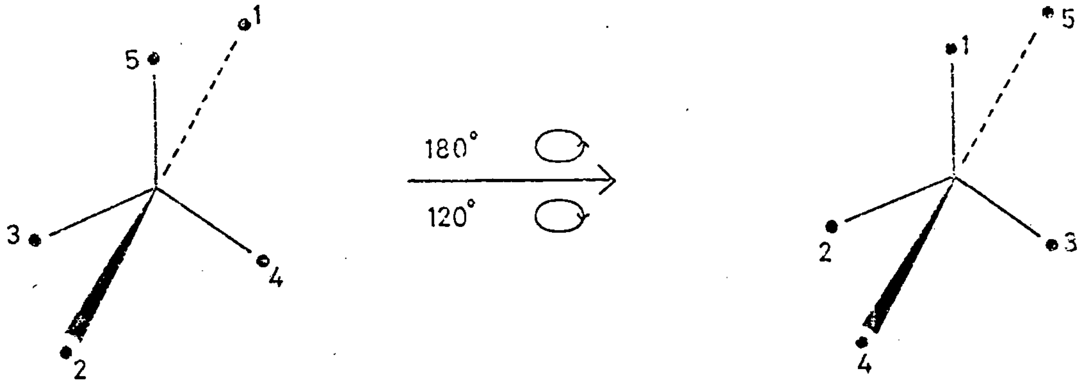
(010) projection of compound(I).

Fig 3.3

defined by the phosphorus atom, the corresponding pairs of ligands, and the fixed equatorial ligand or pivot. The nett result is an interchange of the two apical ligands into positions that are equatorial in the trigonal bipyramid, but there is no internal rotation of some part of the molecule relative to another.



BERRY PSEUDOROTATION



TURNSTILE ROTATION

Fig 3.4

As regards turnstile rotation, referring to Figure 3.4, the orientation of the trigonal bipyramid emphasises that the apical ligand 1 and the equatorial ligand 5 constitute the pair, while the apical ligand 2 and the equatorial ligands 3 and 4 are the *trio* in this mechanism. The isomerism is achieved by first transposing the pair ligands (180° rotation), and then rotating the *trio* ligands 120° either clockwise or anti-cockwise depending on which ligand of the *trio* is to remain equatorial. As can be verified by choosing alternative appropriate ligands as the pair, the example depicted in Figure 3.4 is only one of four equivalent turnstile rotations that accomplishes what one Berry pseudorotation does, when ligand 3 is the pivot.

The schematic representation of the movements of atoms taking place in the turnstile rotation mechanism as discussed is highly misleading in that their actual motion involves a series of angular compressions and expansions, tilting of the ligand pair, and small rotations of the pair relative to the *trio* in opposite directions in realising the same isomerisation. These movements are such as to minimise energy changes in the model situations, and is discussed more fully in the review article by Ramirez and Ugi.[3.8]

Hence the turnstile rotation mechanism, and its extensions, the double and triple turnstile rotations, are essentially alternative processes that accomplish all that the Berry pseudorotation does, but in addition are better able to explain the permutational isomerisations observed in certain cyclic derivatives of pentacoordinated phosphorus compounds which Berry pseudorotation could not do without involving energetically unfavourable intermediates. Energy considerations make it less favourable for atom motions to occur which result in the formation of the intermediate, than other motions which result in the formation of the stable isomer.

Five-coordinated phosphorus having trigonal bipyramidal symmetry, D_{3h}, can exist as 20 isomers, or 10 pairs of enantiomers, when all the ligands are different. Application to the phospha-undecane (I) shows that, when one considers one of each of the enantiomeric pairs, as shown in Figure 3.5(a)-(j) only one is plausible. The other nine exhibit serious drawbacks to their possible formation due to one or more of the following factors:

(i) the plane of one or both five-membered rings lie in diequatorial or diapical positions,

(ii) one or both of the apical positions are occupied by a carbon atom which has a lower electronegativity than an oxygen atom,

(iii) serious steric hindrances exist due to the enforced orientation of bulky groups about the central phosphorus atom.

Hence, referring to Figure 3.5,

(a) C(5) is apical. A model shows prohibitive close contacts involving the phenyl rings precluding this isomer on steric grounds alone; its formation is therefore considered improbable.

(b) C(5) and C(1A) are both apical; its formation is again improbable.

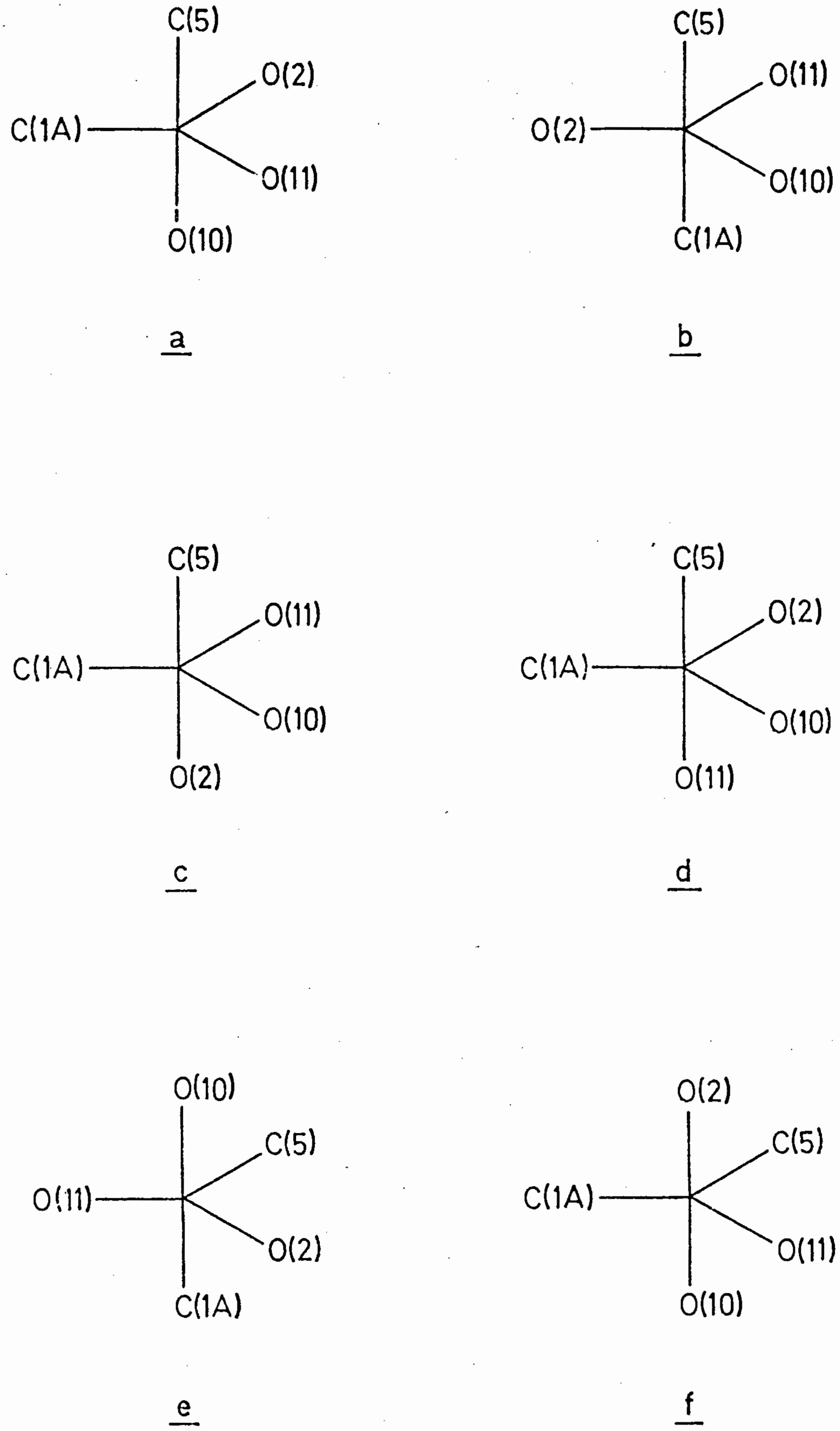
(c) C(5) is apical; the five-membered P-C(5)-C(4)-C(3)-O(2) ring is in a diapical plane; improbable.

(d) C(5) is apical; the five-membered P-C(5)-O(6)-C(7)-O(11) ring is in a diapical plane; improbable.

(e) C(1A) is apical; both five-membered rings are in the diequatorial plane; improbable.

(f) The P-C(5)-O(6)-C(7)-O(11) ring is diequatorial; improbable.

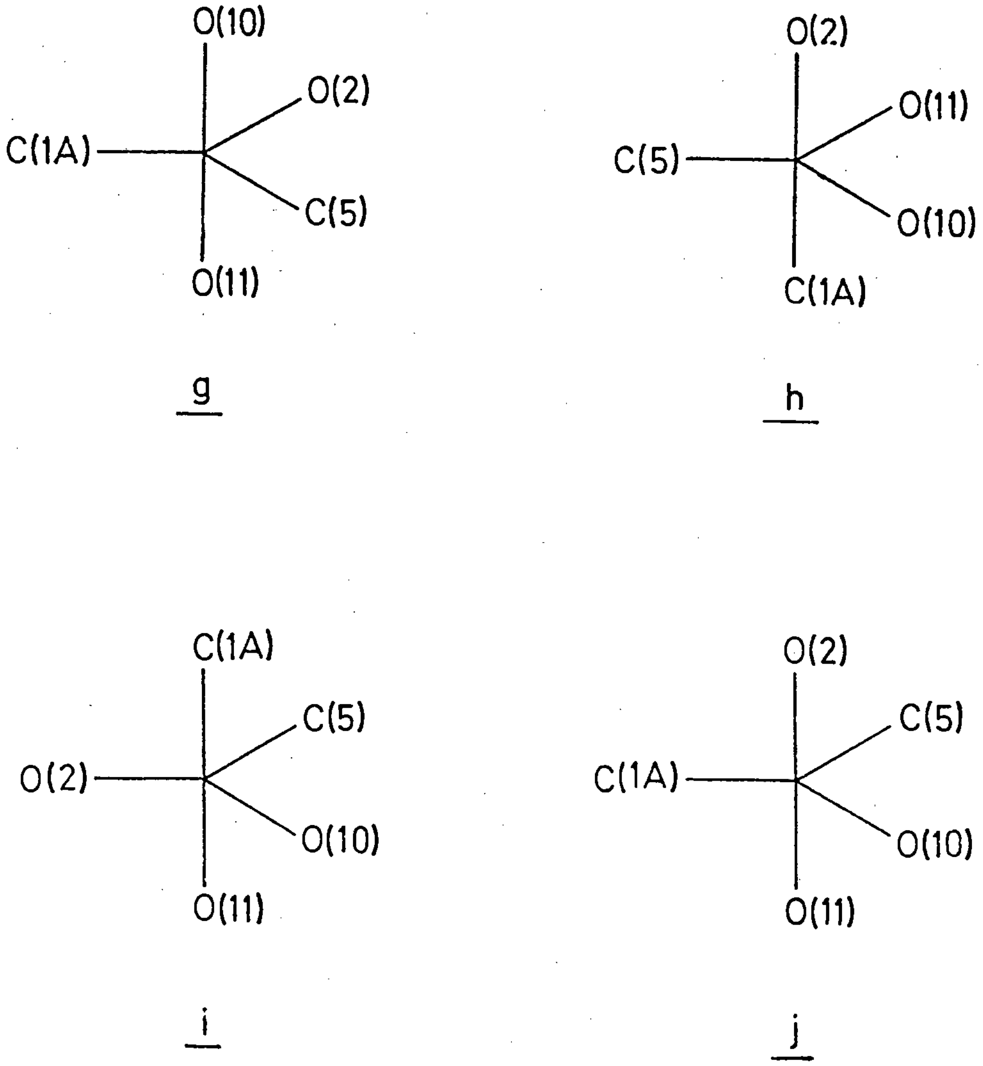
(g) The P-C(5)-C(4)-C(3)-O(2) ring is diequatorial; in addition the six-membered P-O(10)-C(9)-C(8)-C(7)-O(11) ring is diapical; improbable.



a b c d e f

Enantiomeric forms of compound(I).

Fig 3.5



g h

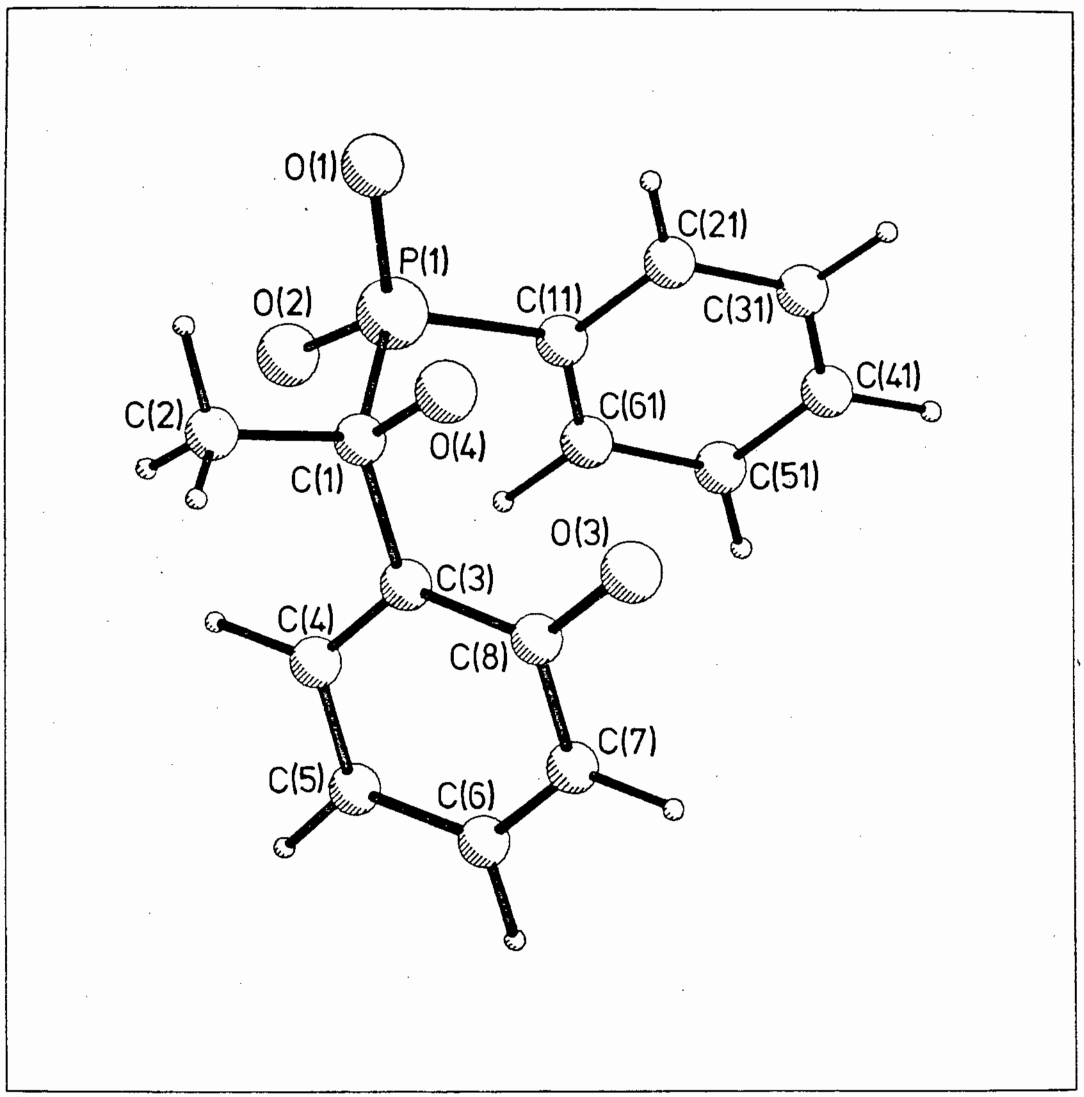
i j

Fig 3.5 (contd.)

(h) C(1A) is apical; the P-C(5)-O(6)-C(7)-O(11) ring is diequatorial; improbable.

(i) C(1A) is apical; the P-C(5)-C(4)-C(3)-O(2) ring is diequatorial; improbable.

(j) This isomer is found in the crystal structure; both apical positions are occupied by oxygen atoms, both five-membered rings are in apical-equatorial planes, and there are no serious steric hindrances.



Compound(II)

Fig 3.6

The molecular rigidity of (I) largely precludes any significant positional changes or rotations of a pair of ligands relative to a trio without rupture of bonds, and therefore the likelihood of permutational isomerism taking place in solution for this compound, either by Berry pseudorotation or by turnstile rotation mechanisms, is considered remote. This conclusion is supported by examination of the ^1H NMR spectrum of (I), whose absorption pattern is temperature independent throughout the range -60°C to 65°C.

The ligands around the phosphorus atom in the disubstituted phosphinic acid (II) are in the expected tetrahedral environment. The P-C(11) bond length of 1,792(5) Å agrees favourably with the average P-C bond length of 1,786(4) Å as determined in diphenylphosphinic acid.[3.10] The P-C(1) bond length is a somewhat longer 1,857(5) Å.

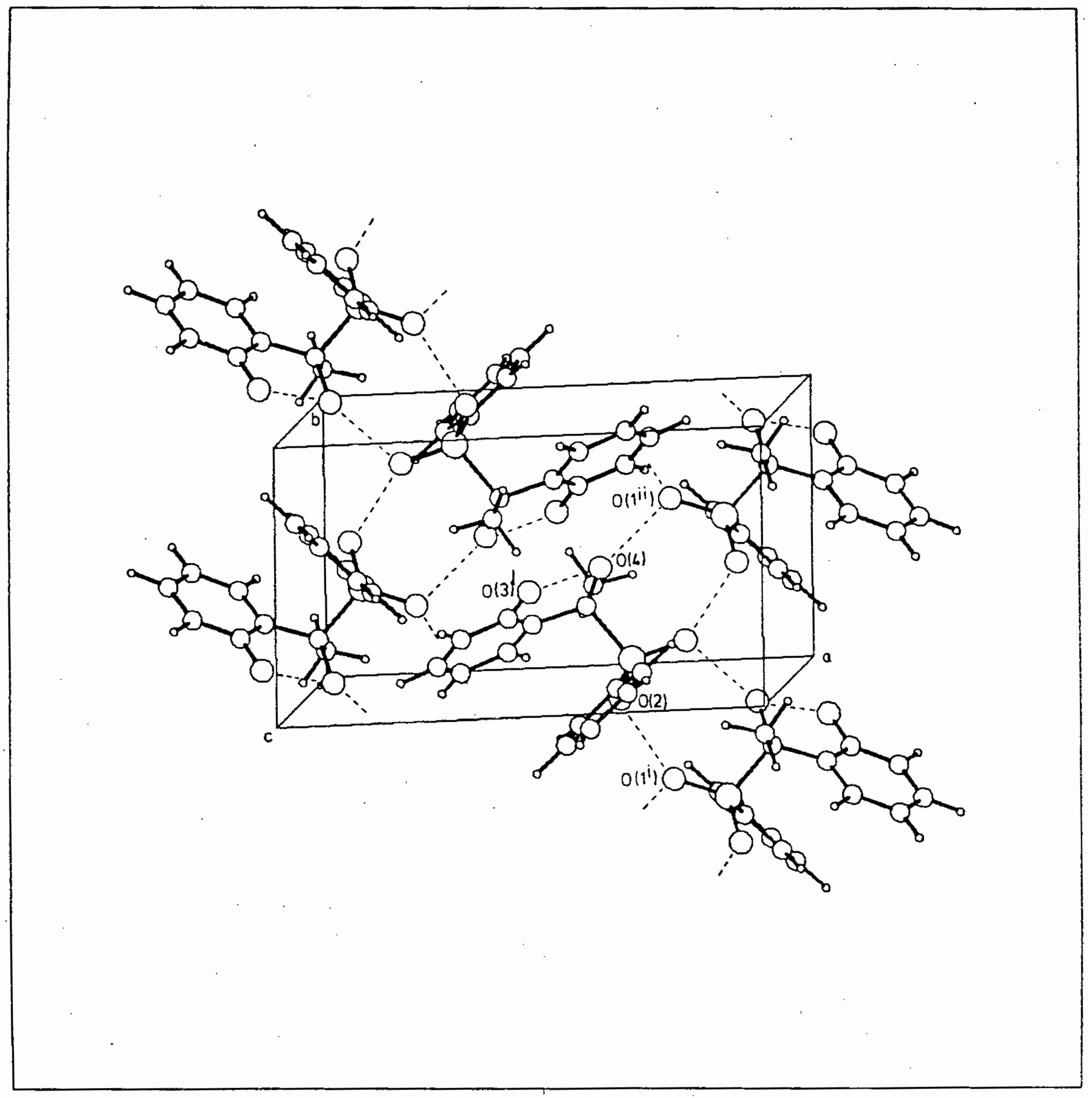
The presence of O....O close contacts (less than 2,76 Å) are indicative of hydrogen bonding which extends throughout the lattice (Table 3.6). Although the hydroxyl hydrogens could not be located, the P-O(1) bond distance of 1,509(3) Å, typical of P=O linkage, and the P-O(2) bond distance of 1,570 (3) Å , typical of P-OH linkage,[3.11] allow a reasonable assessment to be made concerning the donor and acceptor oxygen atoms involved in the H-bonding scheme; O(1) acts as hydrogen acceptor as regards both the O(2)....O(1) and O(4)....O(1) intermolecular bonds, the hydrogen in the O(3)....O(4) intramolecular bond being donated by O(3). This is illustrated in Figure 3.7.

Table 3.6

Close intramolecular and intermolecular approaches (Å) with e.s.d.'s for compound (II)

Symmetry code: (i) $1\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
(ii) $1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

O(2) .... O(1^{i})	2,536(5)
O(4) .... O(1^{ii})	2,756(6)
O(3) .... O(4)	2,551(7)



Unit cell contents of compound(II) showing probable H-bonding

<u>Fig 3.7</u>

CHAPTER 4

CRYSTAL STRUCTURE AND MOLECULAR CONFORMATION OF 2,3-DICYCLOPROPYL-1,4-NAPHTHOQUINONE

ABSTRACT

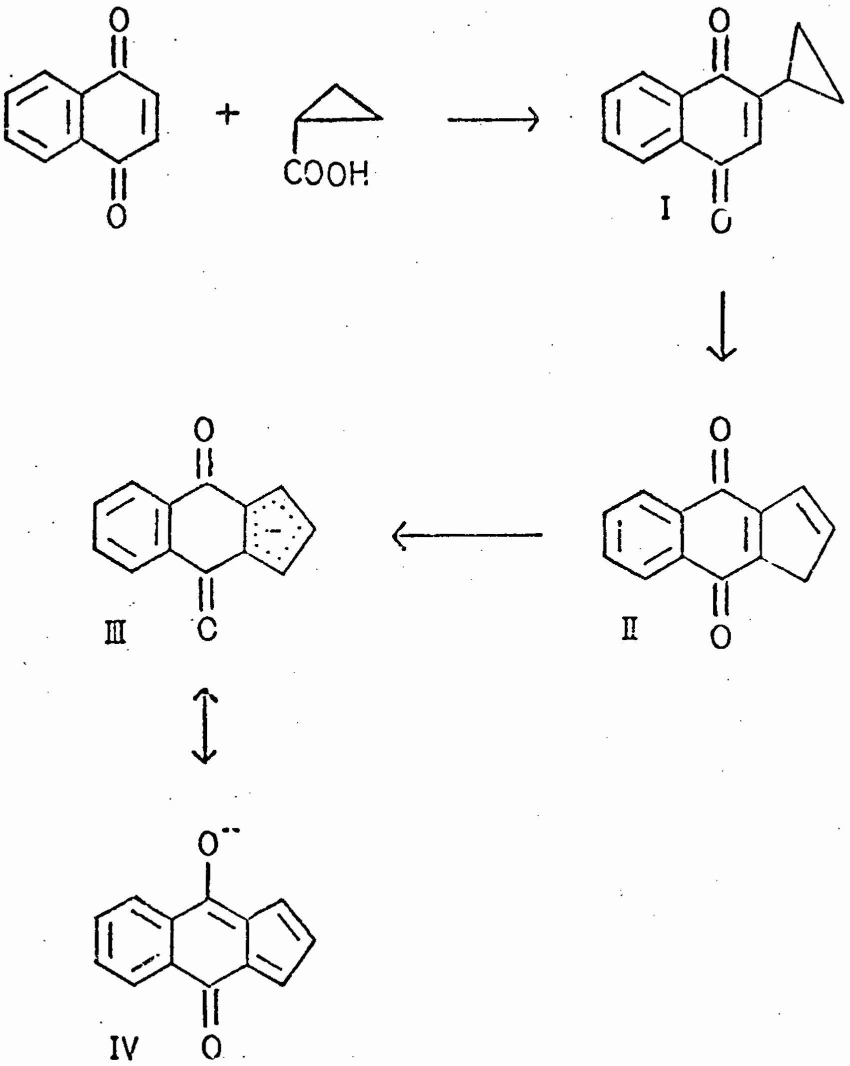
Crystals of the title compound are orthorhombic with $\underline{a}$ = 8,483(4), $\underline{b}$ = 18,249(9), $\underline{c}$ = 15,889(8) Å, space group $\underline{P}bca$, $\underline{z}$ = 8. The quinone ring shows distinct distortions from planarity. The solution NMR spectrum of the compound at various temperatures suggest a measure of restricted rotation about the cyclopropyl - quinonoid bonds. This is partially substantiated by a conformational analysis using the method of atom pair potentials.

4.7 Introduction

A molecule satisfying the so-called Hückel rule (or 4n + 2 rule) is well known to have an unusually high stability.[4.1] Thus the considerable stability possessed by the cyclopentadienide ion has been ascribed to it having six π electrons (n = 1). The synthesis of benz[f]indene-4,9-quinone (II) was attempted with a view to study the chemistry of its anion (III), which is isoelectronic with anthroquinone. The anion, in addition to delocalisation of the negative charge about the five-membered ring, could also be stabilised by the quinone functional group in forming the canonical form (IV). The route that was proposed in the attempted synthesis of (III) was as shown in Scheme 4.1.[4.2]

Reaction of 1,4-naphthoquinone with cyclopropyl carboxylic acid in the presence of silver ions and peroxodisulphonate would yield 2-cyclopropyl-1,4-naphthoquinone(I). The thermal and photochemical isomerisations of vinylcyclopropanes to cyclopentenes are well established processes and similar treatment of (I) would hopefully yield the benz[f]indene-4,9-quinone. Reaction of this with base would then afford the desired anion.

An early fraction in the chromatographed products of the first stage in the above reaction scheme yielded 2,3-dicylopropyl-1,4-naphthoquinone in the form of yellow crystals. The interesting nature of the ^1H NMR spectrum at room temperature of this by-product, which exhibited a highly symmetrical pattern about the methylene and methine proton absorption region, prompted further investigations as regards its structure and conformation.



Scheme 4.1

4.2 Crystal preparation and data collection

Ammonium peroxodisulphonate (6,2g) in water (50 ml) was added at a bath temperature of 80-85°C to a stirred mixture of cyclopropyl carboxylic acid (0,95 g), silver nitrate (1g) and naphthoquinone (1,58 g) in water (25 ml) and cyclohexane (25 ml) over a period of 45 minutes. The reaction mixture was stirred for 10 minutes after addition was completed, and then worked up by cooling and extracting with ether. The ether extract was washed with 10% sodium bicarbonate solution until excess acid had been removed, and then once with water. The ethereal solution was dried with sodium sulphate and evaporated off under reduced pressure. The resulting brown oil (1,87 g) was chromatographed on a silica column using 2½ - 10% ethyl acetate/light petroleum ether as eluant. An early fraction afforded 2,3-dicyclopropyl-1,4-naphthoquinone as yellow needles (0,62 g, 26%). δ 1,08 (8H, d, J 8Hz, cyclopropyl CH_2), 2,00 (2H, quintet, J 8Hz, cyclopropyl CH), 7,65 (2H, m, 6- and 7-H) and 8,08 (2H, m, 5- and 8-H). A later fraction afforded the 2-cyclopropyl-1,4-naphthoquinone analogue as the major product (0,96 g, 48,5%).

Preliminary oscillation Weissenberg and precession photographs gave the crystallising space group as Pbca, the conditions limiting possible reflections being[2.8]

okl : k = 2n
hol : l = 2n
hko : h = 2n
hoo : h = 2n
oko : k = 2n
ool : l = 2n

Crystal data and experimental details of the data collection are listed in Table 4.1.

Table 4.1

Crystal data and experimental and refinement parameters for the structure analysis					
Crystal data		Data collection		Final refinement	
Molecular formula	$C_{16}H_{14}O_2$	Crystal dimensions	0,1x0,1x0,5mm	Number of variables	106
Mr	238	Scan mode	ω-2θ	$R=\Sigma\|\|Fo\|-\|Fc\|\|/\Sigma\|Fo\|$	0,096
Space group	Pbca	Scan width	1,1$^{o}\theta$	$R_w=\Sigma w^{\frac{1}{2}}\|\|Fo\|-\|Fc\|\|/\Sigma w^{\frac{1}{2}}\|Fo\|$	0,071
a	8,483(4)Å	Scan speed	0,03^{o} θ s^{-1}	Weighting scheme	$w=(\sigma^2F)^{-1}$
b	18,249(9)	Range scanned(2θ)	6^{o}-40^{o}	U (aromatic H)	0,167 Å^2
c	15,889(8)	Stability of standard reflections	0,84%	U (methine H)	0,112 Å^2
V	2459,7Å^3			U (methylene H)	0,117 Å^2
Dm	1,27Mg m^{-3}	No. of reflections collected	1358		
Dc	1,29 for z=8	No. of 'observed' reflections	489 with I(rel) >2σI(rel)		
μ(MoKα)	0,047 mm^{-1}				
F(000)	1008				

4.3 Solution and refinment of the structure

The structure was solved by the automatic centrosymmetric direct-methods routine of the SHELX program system,[1.1] in which an E map yielded the positions of all the heavy atoms. Due to the paucity of observed reflections, the structure refinement proceeded with isotropic temperature factors for the non-H atoms; a subsequent different Fourier indicated the positions of most of the hydrogen atoms. These were then included in the model by the technique of constrained refinement, with d(C-H) = 1,08 Å, their positions being dictated by the geometry of the molecule. The positions of the two methine hydrogens H(21) and H(31) derived in this way, however, were deemed unsatisfactory because they gave rise to unacceptable angles between the C-(methylene H) bond and adjacent C-C bonds. The methine hydrogen atoms were therefore omitted from a structure factor calculation and their positions found in a difference electron density map. All H atoms in the cyclopropyl rings were finally allowed to refine with a simple bond length constraint of 1,08 Å from their parent atoms. The final geometry of the cyclopropyl moieties compared favourably with that previously found in N,N-dimethyl-2-phenylcyclopropylamine hydrochloride[4.3] and α-cyano-3-phenoxybenzyl-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate[4.4] in which no constraints had been applied to the hydrogens. The isotropic temperature factors of all the H atoms were treated as three single parameters, whose final values are reported in Table 4.1. Final atomic parameters, principal bond lengths and angles are shown in Tables 4.2, 4.3 and 4.4 respectively. Observed and calculated structure factors appear in Appendix E.

Table 4.2

Fractional atomic coordinates (x 10^4) and temperature factors (Å x 10^3) and their e.s.d.'s in parenthesis

	x	y	z	U
C(1)	23(16)	3167(7)	2039(8)	46(4)
C(2)	29(14)	2879(7)	2922(8)	39(4)
C(21)	-668(16)	2143(8)	3074(8)	53(4)
C(22)	356(18)	1574(9)	3475(11)	75(5)
C(23)	18(19)	1509(9)	2554(11)	71(4)
C(3)	535(14)	3315(7)	3563(9)	41(4)
C(31)	276(18)	3088(8)	4433(9)	60(5)
C(32)	17(19)	3629(8)	5178(9)	65(5)
C(33)	1531(20)	3205(8)	5133(10)	72(5)
C(4)	1358(16)	4024(8)	3382(8)	56(5)
C(41)	1624(15)	4242(6)	2474(9)	43(4)
C(5)	2551(16)	4845(7)	2300(8)	56(4)
C(6)	2717(17)	5049(6)	1451(8)	64(5)
C(7)	1988(17)	4649(7)	828(9)	70(5)
C(8)	1076(18)	4036(8)	983(9)	67(5)
C(81)	911(15)	3829(7)	1843(8)	42(4)
O(1)	-761(10)	2841(5)	1512(6)	70(3)
O(4)	1854(10)	4425(5)	3930(6)	81(4)

Table 4.2.1

Hydrogen atoms. Fractional atomic coordinates (x 10^3).

	x	y	z
H(21)	-192	219	320
H(221)	-20	119	390
H(222)	159	168	358
H(231)	-114	132	235
H(232)	94	157	209
H(31)	-5	254	464
H(321)	-83	337	559
H(322)	-5	420	502
H(331)	150	272	553
H(332)	256	353	499
H(5)	309	516	280
H(6)	347	551	129
H(7)	210	484	19
H(8)	54	373	48

Table 4.3

Bond lengths (Å) and their e.s.d.'s

O(1)-C(1)	1,223(13)	C(3)-C(4)	1,497(15)
C(1)-C(2)	1,498(12)	O(4)-C(4)	1,212(13)
C(2)-C(21)	1,488(16)	C(4)-C(41)	1,513(16)
C(21)-C(22)	1,495(19)	C(41)-C(5)	1,381(14)
C(21)-C(23)	1,536(19)	C(5)-C(6)	1,406(15)
C(22)-C(23)	1,496(21)	C(6)-C(7)	1,377(14)
C(2)-C(3)	1,362(14)	C(7)-C(8)	1,383(16)
C(3)-C(31)	1,460(17)	C(8)-C(81)	1,423(14)
C(31)-C(32)	1,556(19)	C(41)-C(81)	1,393(15)
C(31)-C(33)	1,554(19)	C(1)-C(81)	1,458(15)
C(32)-C(33)	1,501(20)		

Table 4.4

Selected bond angles (°) and their e.s.d.'s.

O(1)-C(1)-C(2)	118,2(1,3)	C(31)-C(33)-C(32)	61,2(1,0)
C(21)-C(2)-C(3)	122,1(1,3)	C(32)-C(31)-C(33)	57,7(0,9)
C(31)-C(3)-C(4)	119,8(1,2)	H(21)-C(21)-C(2)	110,4(6,2)
O(4)-C(4)-C(41)	118,3(1,3)	H(21)-C(21)-C(22)	123,0(6,3)
C(4)-C(41)-C(5)	119,0(1,4)	H(221)-C(22)-C(21)	117,2(6,5)
C(41)-C(5)-C(6)	117,4(1,3)	H(222)-C(22)-C(23)	110,9(7,2)
C(5)-C(6)-C(7)	120,3(1,3)	H(231)-C(23)-C(21)	93,0(6,6)
C(6)-C(7)-C(8)	123,5(1,4)	H(232)-C(23)-C(22)	121,5(6,7)
C(7)-C(8)-C(81)	116,2(1,4)	H(31)-C(31)-C(3)	125,7(6,5)
C(8)-C(81)-C(1)	118,4(1,3)	H(31)-C(31)-C(32)	108,7(6,4)
C(21)-C(22)-C(23)	61,8(1,0)	H(321)-C(32)-C(31)	105,6(6,8)
C(21)-C(23)-C(22)	59,1(1,0)	H(322)-C(32)-C(33)	122,2(6,8)
C(22)-C(21)-C(23)	59,1(0,9)	H(331)-C(33)-C(31)	106,8(6,7)
C(31)-C(32)-C(33)	61,1(1,0)	H(332)-C(33)-C(32)	114,5(6,7)

4.4 Description of the structure and discussion

Figure 4.1 shows the molecule viewed perpendicular to the two aromatic rings. A distinctive feature of the structure is the considerable distortion from planarity occurring in the quinone ring, as shown by the endocyclic torsion angles given in Figure 4.2.

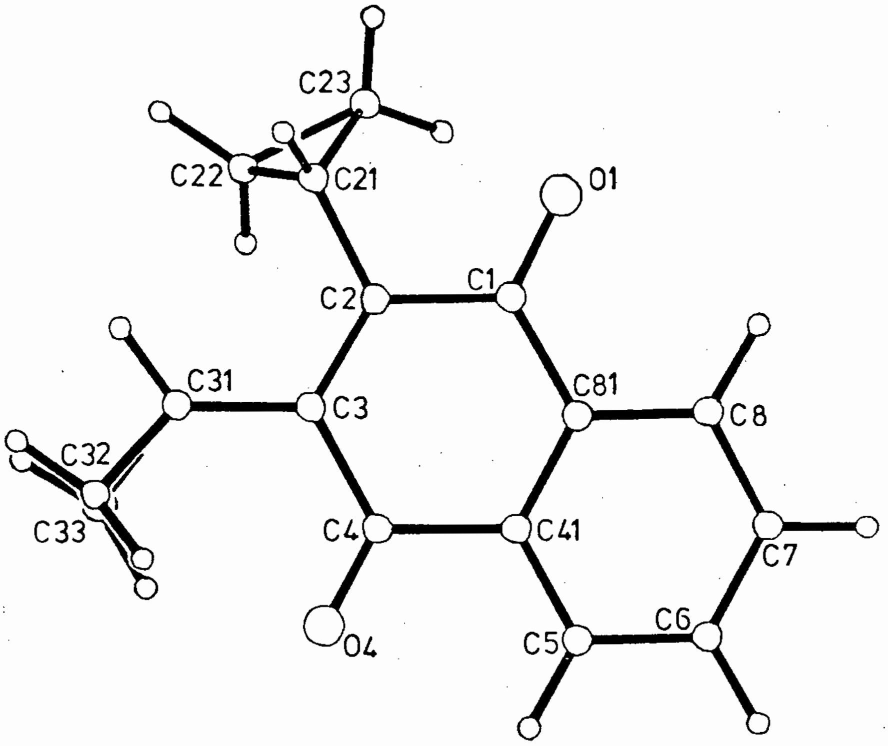


Fig 4.1

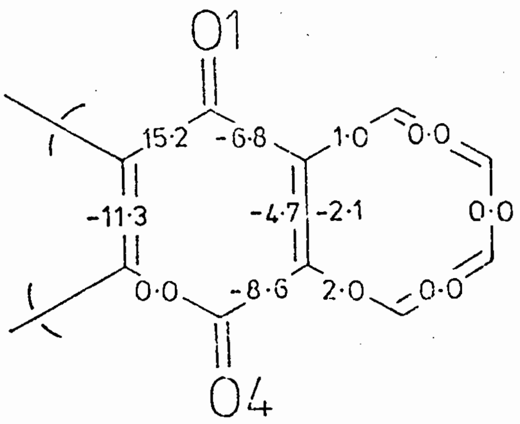


Fig 4.2

This is probably due to the intramolecular close contacts C(23)....C(1) of 3,13 Å and C(23)....O(1) of 3,01 Å. Thus C(1) and O(1) are displaced 0,14 Å and 0,39 Å respectively from the least squares plane containing C(2), C(3), C(4), C(41) and C(81). There are no significant intermolecular close contacts.

A conformational study of the compound was carried out by calculating the van der Waal's energy using empirical atom pair potentials. This method of evaluating molecular energies is well established and has recently been reviewed by Kitaigorodsky[4.5] and Mirsky[4.6]. The coefficients of the atom-atom potentials are of the form

$$u(r) = a \exp(-br)/r^d - c/r^6$$

where r is the distance between any pair of atoms and the coefficients a,b,c and d are those given by Giglio,[4.7] such that u(r) is evaluated in calories when r is in Å. These potential curves were derived primarily to give good agreement for the calculation of molecular positions in crystal structures and the energy values mean little in an absolute sense. No account was taken of possible torsional potentials for the σ bonds, partial atomic charges or dipole interactions. The program EENY[4.8] calculates molecular coordinates as defined by appropriate torsion angles and sums the energy for all non-bonded pairs of atoms whose seperation is dependent on the torsion angles.

In the present study, if an idealised structure in which the aromatic and quinonoid rings are exactly planar and the cyclopropyl moieties are identical is assumed, and the molecule is divided into three residues linked by two torsion angles:

τ1[C(1)-C(2)-C(21)-H(21) and τ2[C(4)-C(3)-C(31)-H(31) as shown in Figure 4.3, then for equal but opposite values of τ1 and τ2, the molecule possesses Cs symmetry, the mirror plane bisecting residue 1 and lying perpendicular to the aromatic and quinonoid rings.

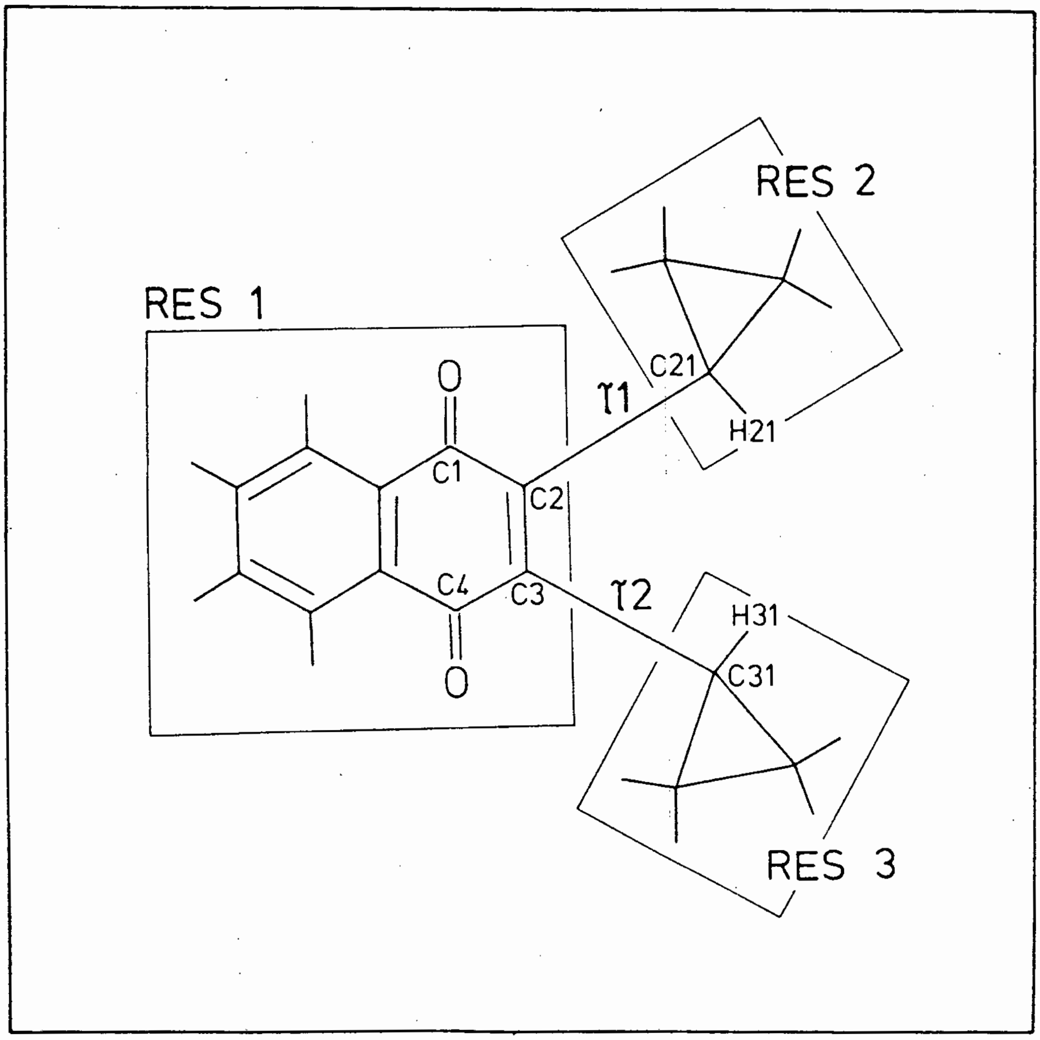


Fig 4.3

Hence any conformational arrangement defined by torsion angles τ1 and τ2 which gives rise to an energy minimum will have an equivalent arrangement at values of -τ1 and -τ2, which is its mirror image. The atomic coordinates used in the energy analysis however were not for the idealised molecule, but those obtained from the refined crystal structure. An energy map was calculated with both the torsion angles varying over the complete angular range 0-360^{o} in 10^{o} increments. This map, shown in Figure 4.4, yielded six energy minima labelled A,B,C and A',B',C'. These are displayed as a three-dimensional energy surface in Figure 4.5 for greater clarity.[4.10]

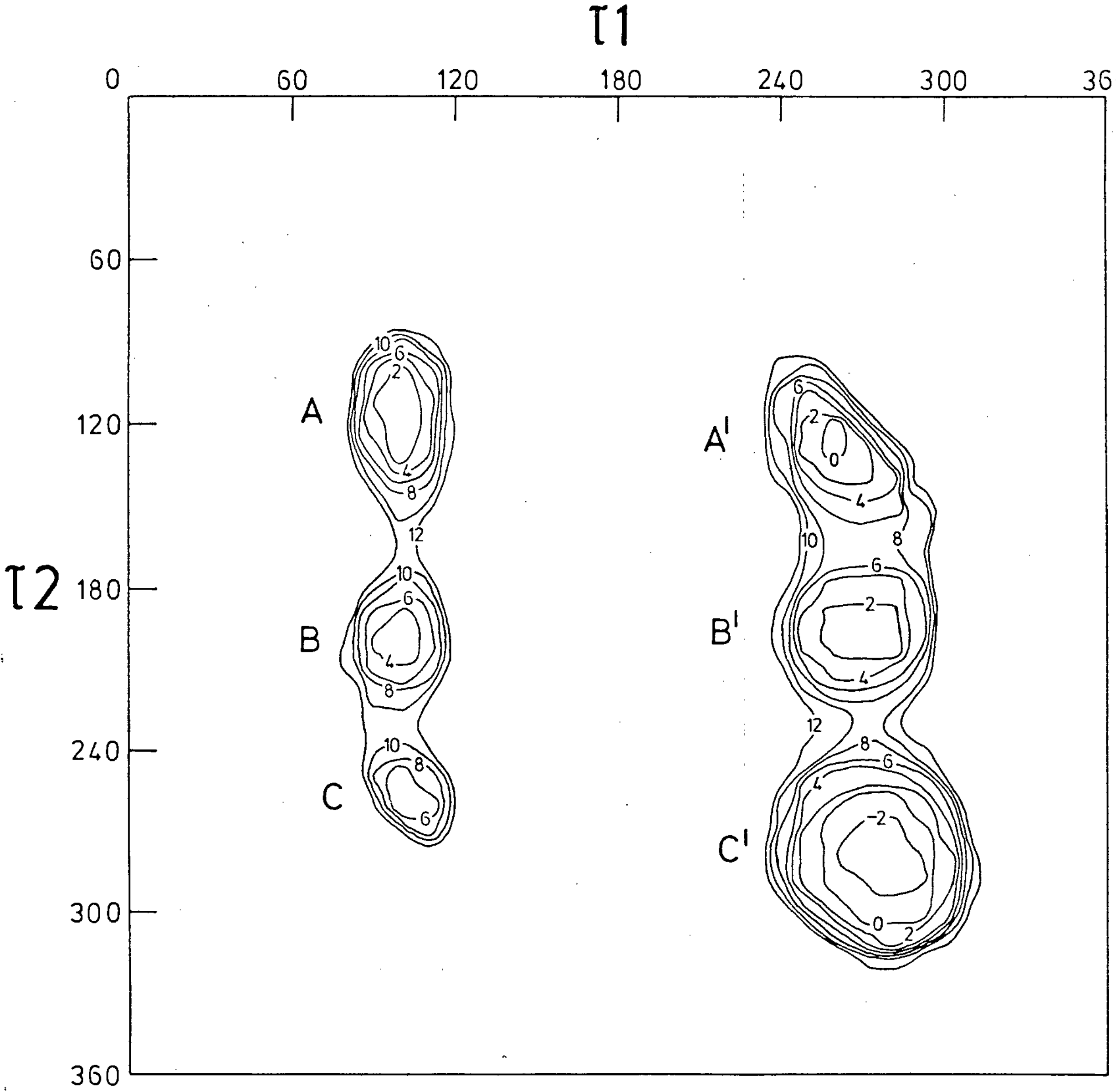


Fig 4.4

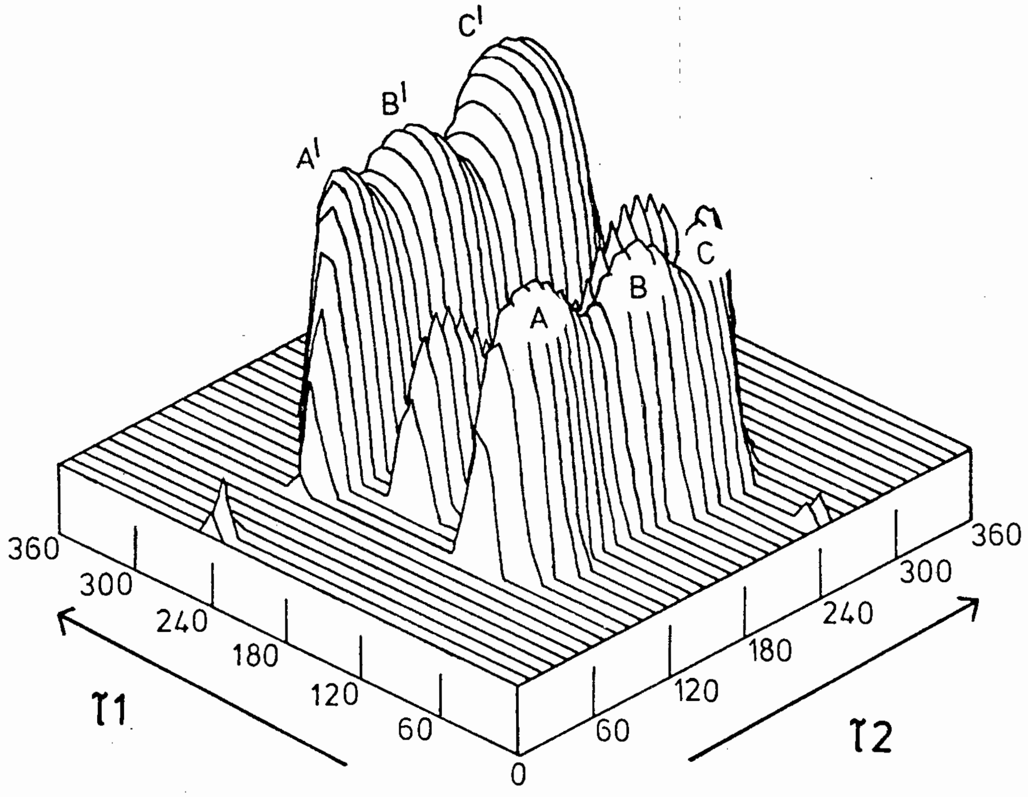
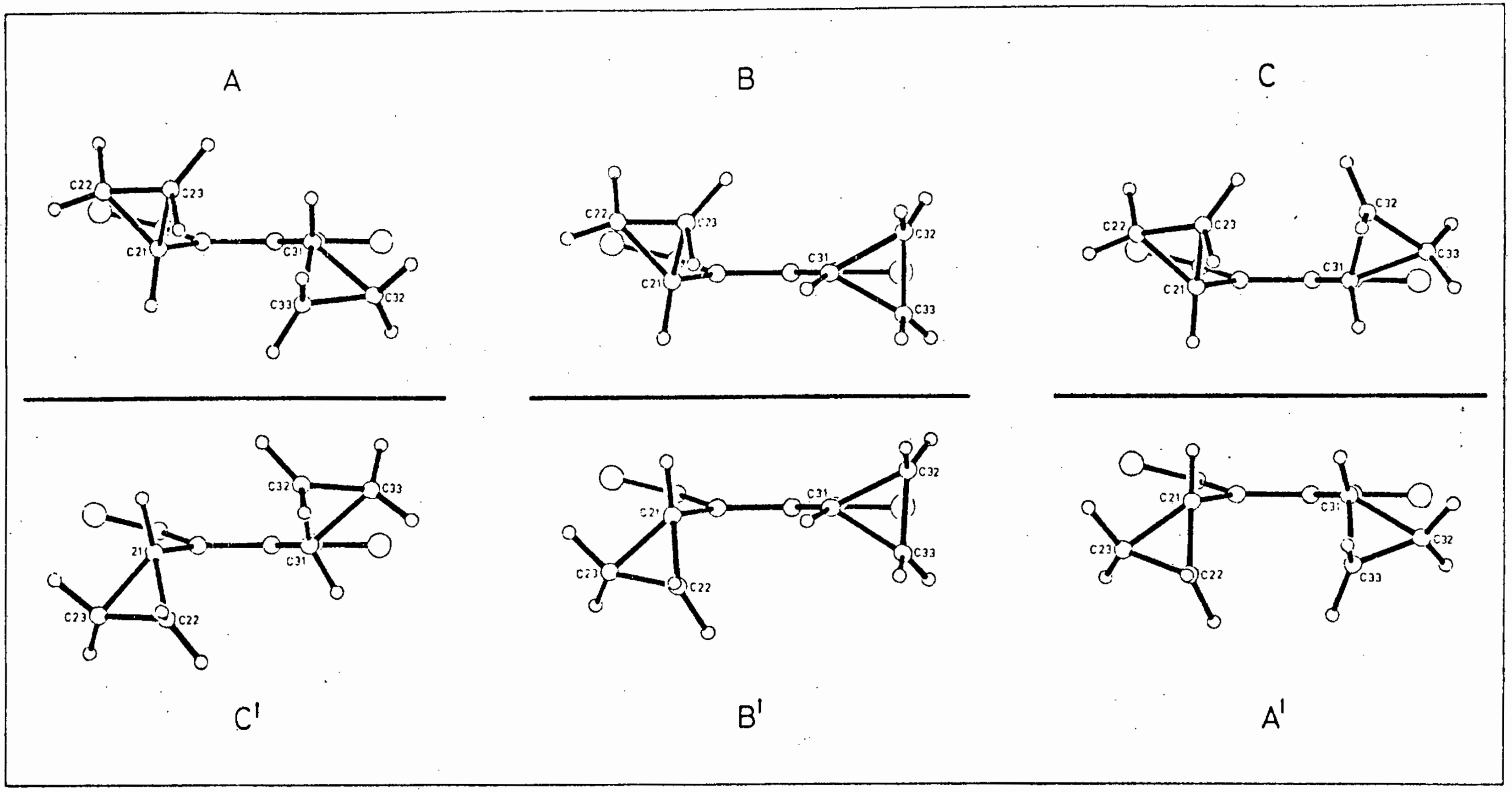


Fig 4.5

The torsion angles at the exact minima were obtained using the method of steepest descent incorporated in the program, and these are shown in Table 4.5 together with calculated energies at these positions. Energy barriers between the different conformations are of the order of 40 kJ mol^{-1}.

The peaks obtained correspond to the molecular conformations shown in Figure 4.6, which do indeed display mirror image pairs, although mirror symmetry is inexact. The conformation in the crystal structure with $\tau 1 = 271{,}3^{o}$ and $\tau 2 = 195{,}4^{o}$



Molecular conformations corresponding to the energy minima. The view is along a line joining the midpoints of C(2)— C(3) and C(6)— C(7). Aromatic H atoms and selected C atoms have been omitted for clarity.

Fig 4.6

Table 4.5

Torsion angles (degrees) and energies (kcal) for potential energy minima

	A	B	C	A'	B'	C'
$\tau 1$	100,1	97,8	105,3	261,0	268,7	276,6
$\tau 2$	114,4	198,8	259,2	127,6	195,5	284,8
μ(min)	-,4	2,5	3,7	-,8	,3	-3,3

is gratifying close to that of B' in Figure 4.6, where $\tau 1$ = 268,7^{o} and $\tau 2$ = 195,5^{o}.

As was mentioned above, the room temperature ^{1}H NMR spectrum of 2,3 dicyclopropyl-1,4-naphthoquinone exhibits a highly symmetrical pattern around the methylene and methine proton absorption region. On heating or cooling, the simple doublet observed collapses and the true complexity of the spectrum becomes evident (Figure 4.7). In general, a reversible temperature dependence in the ^{1}H NMR spectrum of a compound can be the result of one or more of the following:

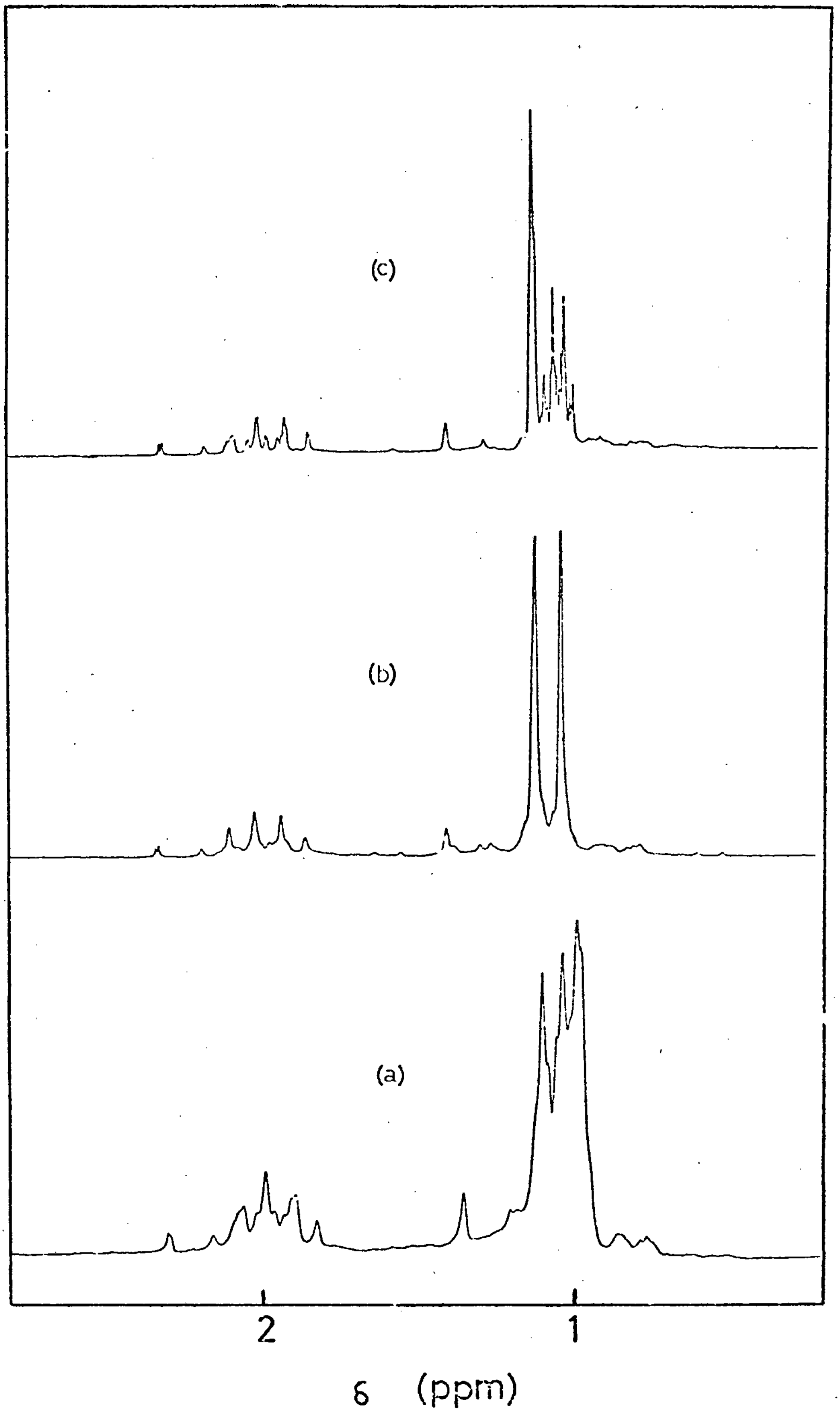
(i) Rate processes involving intermolecular proton transfers.

(ii) Rotations about single bonds with partial double bond character or intramolecular close contacts causing rotational restrictions.

(iii) Inversion of carbocyclic and heterocyclic rings.

(iv) Valence isomerisations and intramolecular rearrangements.

(v) Temperature sensitive solvent interactions.



Methine and methylene ^1H NMR spectrum of compound at (a) -35° C (b) 28° C and (c) 76° C

Fig 4.7

In the present study this dependence is most likely due to measurable differences in energy between molecular conformations, described in terms of the torsion angles $\tau 1$ and $\tau 2$, such that molecules spend a variable length of time in any one given conformation relative to another. As the temperature changes, so too does the population distribution, and the ^{1}H NMR spectrum, which sees the average of the conformations, is accordingly affected. Hence 'free' rotation about the C(2)-C(21) and C(3)-C(31) bonds is restricted in the sense that the barriers separating the energy minima are sufficiently large that the molecule spends more of its time in those of lowest energy, yet sufficiently small that interconversion between minima is fast on the NMR time scale.

Although the protons lying *cis* to the methine proton (Figure 4.8) are thermodynamically equivalent, they are in general magnetically non-equivalent as the couplings HaHb and HaHb' are observed to differ. The analogous also holds for those protons lying *trans* to the methine proton. Thus the spectrum of the cyclopropyl protons constitutes a complex AA' BB' C spin system, the appearance of which is determined by the signs and magnitudes of these couplings.

Figure 4.8 shows a schematic representation of the methine and methylene chemical shift changes considered to be taking place as a function of temperature. At -35°C, the overall environment of the cyclopropyl rings is such that the chemical shifts of the Ha and Hb protons are different. The ^{1}H NMR spectrum in this region hence appears as the nett resultant of a complicated absorption pattern, of the AA' BB' C type discussed above, incorporating both vicinal and

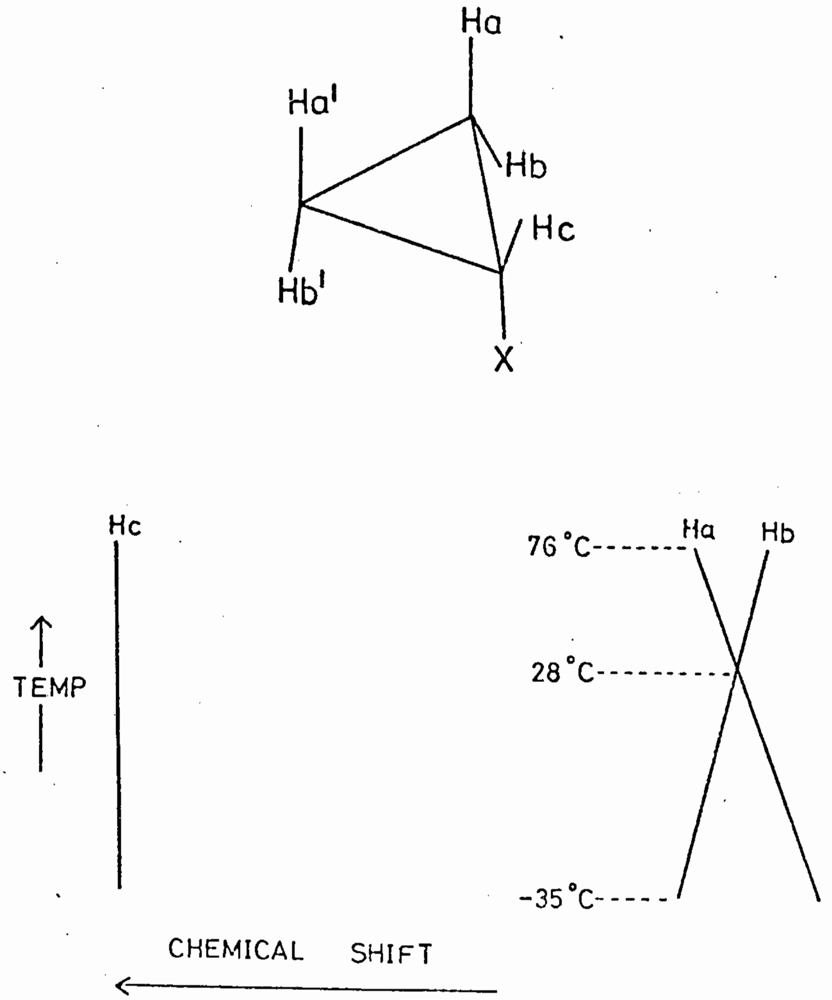


Fig 4.8

geminal coupling, and whose interpretation cannot be explained in terms of first order splitting rules. At room temperature, the conformational population distribution is such that the chemical shift difference between the Ha and Hb protons becomes negligible i.e. δHa = δHb 'by accident',[4.9] and the spectrum degenerates into a deceptively simple spectrum of the A A' A'' A''' C type with a quintet/doublet pattern as observed. The splitting in the multiplets is here an average of the coupling constants involved. As the temperature continues to rise, the chemical shift differences are no longer zero (the chemical shifts of the cyclopropyl protons vary characteristically with the orientation of substituents), and the pattern again becomes complex.

Whether in fact the proton resonances actually 'cross over', as is implied in Figure 4.8, or merely change direction can only be ascertained by a complete analysis of the spectra. This detailed analysis, if possible, could hopefully also yield information as to the nature of the conformational minima, ideally matching those obtained from solid state coordinates, and their relative populations as a function of temperature.

APPENDIX A

Observed and calculated structure factors for $Na^+[DyEDTA(3H_2O)]^-.5H_2O$

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	752	731	8	8	0	97	87	14	16	0	97	81	2	28	0	306	341	3	5	1	367	376
8	0	0	69	63	10	8	0	626	627	16	16	0	179	153	8	28	0	126	135	5	5	1	119	99
12	0	0	603	584	14	8	0	510	501	2	18	0	236	226	10	28	0	296	297	7	5	1	265	309
16	0	0	178	187	2	10	0	555	550	4	18	0	444	463	12	28	0	199	190	9	5	1	616	556
20	0	0	166	181	4	10	0	180	180	8	18	0	343	344	4	30	0	243	271	11	5	1	314	315
4	2	0	794	790	6	10	0	839	844	10	18	0	157	158	6	30	0	345	380	13	5	1	239	246
6	2	0	616	590	8	10	0	378	354	14	18	0	77	32	8	30	0	234	241	15	5	1	444	439
8	2	0	510	514	10	10	0	289	303	16	18	0	419	430	10	30	0	143	146	17	5	1	254	254
10	2	0	258	279	12	10	0	83	96	0	20	0	291	296	0	32	0	264	255	19	5	1	166	165
12	2	0	156	171	14	10	0	311	300	2	20	0	127	133	4	32	0	183	212	1	7	1	413	450
16	2	0	597	592	16	10	0	122	128	4	20	0	319	342	8	32	0	210	197	3	7	1	224	207
18	2	0	206	209	18	10	0	459	462	6	20	0	130	127	4	34	0	333	339	5	7	1	487	436
20	2	0	282	323	0	12	0	892	859	8	20	0	221	239	8	34	0	302	301	7	7	1	505	509
2	4	0	821	855	2	12	0	293	324	10	20	0	222	237	0	36	0	256	264	9	7	1	481	464
4	4	0	210	217	4	12	0	120	130	12	20	0	440	540	2	36	0	202	205	11	7	1	241	236
6	4	0	138	142	6	12	0	154	169	14	20	0	200	208	4	36	0	142	119	13	7	1	383	382
8	4	0	99	69	8	12	0	250	248	16	20	0	110	123	3	1	1	554	507	15	7	1	150	147
10	4	0	322	322	10	12	0	647	655	2	22	0	271	330	5	1	1	563	548	17	7	1	261	281
12	4	0	345	352	12	12	0	454	449	4	22	0	167	190	7	1	1	348	332	19	7	1	282	282
14	4	0	434	419	14	12	0	271	297	6	22	0	442	433	9	1	1	676	632	1	9	1	123	110
20	4	0	214	219	16	12	0	171	153	8	22	0	197	196	11	1	1	389	362	3	9	1	678	709
2	6	0	271	301	4	14	0	662	672	10	22	0	143	195	13	1	1	284	288	5	9	1	379	365
4	6	0	160	142	6	14	0	459	459	12	22	0	75	91	15	1	1	356	356	7	9	1	550	528
6	6	0	730	665	8	14	0	589	591	14	22	0	169	225	17	1	1	270	282	9	9	1	545	507
8	6	0	63	51	10	14	0	64	62	16	22	0	177	181	19	1	1	205	207	11	9	1	358	349
10	6	0	419	406	14	14	0	87	78	0	24	0	74	53	3	3	1	84	83	13	9	1	369	373
14	6	0	198	206	16	14	0	351	348	2	24	0	407	437	5	3	1	562	565	15	9	1	195	187
16	6	0	292	285	18	14	0	116	150	4	24	0	165	204	7	3	1	684	688	17	9	1	277	282
18	6	0	452	454	0	16	0	712	748	10	24	0	438	455	9	3	1	183	154	19	9	1	224	237
20	6	0	193	192	2	16	0	360	366	14	24	0	318	295	11	3	1	380	401	1	11	1	634	657
0	8	0	203	240	4	16	0	104	96	2	26	0	227	256	13	3	1	366	340	3	11	1	548	551
2	8	0	553	604	8	16	0	376	359	6	26	0	469	480	17	3	1	312	312	5	11	1	355	359
4	8	0	306	306	10	16	0	130	156	14	26	0	207	215	19	3	1	279	290	7	11	1	440	421
6	8	0	362	330	12	16	0	566	567	0	28	0	191	154	1	5	1	461	495	9	11	1	528	520

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	11	1	233	218	5	19	1	293	297	7	27	1	125	133	20	2	2	117	121	2	12	2	149	155
13	11	1	255	233	7	19	1	363	368	9	27	1	254	240	2	4	2	250	220	4	12	2	571	569
15	11	1	334	340	9	19	1	133	117	11	27	1	212	221	4	4	2	449	438	6	12	2	496	470
17	11	1	189	190	11	19	1	263	265	13	27	1	124	123	6	4	2	605	579	8	12	2	457	467
19	11	1	157	169	13	19	1	280	262	1	29	1	227	247	8	4	2	606	572	10	12	2	279	250
1	13	1	553	547	15	19	1	159	143	5	29	1	266	265	10	4	2	403	394	14	12	2	217	223
3	13	1	156	165	17	19	1	184	177	7	29	1	207	205	12	4	2	189	176	16	12	2	264	268
5	13	1	319	371	1	21	1	169	174	11	29	1	210	214	14	4	2	212	217	18	12	2	340	345
7	13	1	366	377	3	21	1	565	594	1	31	1	121	159	16	4	2	336	339	0	14	2	127	140
9	13	1	218	236	5	21	1	95	119	3	31	1	266	270	18	4	2	320	322	2	14	2	662	697
11	13	1	409	396	7	21	1	209	230	5	31	1	130	166	20	4	2	196	216	4	14	2	130	122
13	13	1	340	351	9	21	1	315	310	7	31	1	127	156	0	6	2	649	674	6	14	2	95	84
17	13	1	319	321	11	21	1	137	128	9	31	1	217	213	2	6	2	130	435	8	14	2	171	186
19	13	1	256	260	13	21	1	141	143	11	31	1	153	169	4	6	2	451	445	10	14	2	539	518
1	15	1	431	457	15	21	1	336	336	1	33	1	149	159	6	6	2	71	54	12	14	2	218	231
3	15	1	442	445	1	23	1	377	392	3	33	1	212	246	8	6	2	557	516	14	14	2	277	273
5	15	1	344	327	3	23	1	170	150	5	33	1	197	218	10	6	2	239	252	16	14	2	155	138
7	15	1	312	309	5	23	1	313	319	7	33	1	155	172	12	6	2	533	511	2	16	2	417	412
9	15	1	370	346	7	23	1	202	187	9	33	1	162	166	14	6	2	248	254	4	16	2	132	139
11	15	1	165	191	9	23	1	160	151	1	35	1	174	172	16	6	2	165	171	6	16	2	570	579
13	15	1	251	223	11	23	1	207	205	5	35	1	192	183	2	8	2	432	412	10	16	2	268	243
15	15	1	279	275	13	23	1	280	260	2	0	2	431	441	4	8	2	734	703	12	16	2	164	159
17	15	1	187	182	15	23	1	158	172	6	0	2	814	807	6	8	2	106	99	14	16	2	330	356
1	17	1	320	337	1	25	1	282	330	10	0	2	312	295	8	8	2	632	611	18	16	2	342	367
3	17	1	413	430	3	25	1	272	281	14	0	2	413	404	16	8	2	463	455	0	18	2	290	316
5	17	1	289	277	5	25	1	319	337	18	0	2	516	504	0	10	2	605	778	2	18	2	696	734
7	17	1	251	261	7	25	1	208	212	0	2	2	410	401	2	10	2	392	390	4	18	2	135	116
9	17	1	276	311	9	25	1	177	153	2	2	2	630	604	4	10	2	472	480	8	18	2	103	99
11	17	1	370	366	11	25	1	223	220	4	2	2	234	208	6	10	2	253	251	10	18	2	433	422
13	17	1	119	164	13	25	1	115	111	6	2	2	59	27	8	10	2	460	494	12	18	2	75	78
15	17	1	228	231	15	25	1	170	168	8	2	2	371	328	10	10	2	137	120	14	18	2	371	376
17	17	1	149	194	1	27	1	115	103	10	2	2	777	735	12	10	2	532	543	2	20	2	375	404
1	19	1	418	440	3	27	1	293	273	12	2	2	177	175	14	10	2	166	155	4	20	2	308	262
3	19	1	229	235	5	27	1	229	271	14	2	2	444	420	16	10	2	241	219	6	20	2	537	446

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	20	2	335	340	2	32	2	199	222	1	7	3	648	653	13	13	3	387	364	13	21	3	196	199
10	20	2	229	220	6	32	2	323	326	3	7	3	376	362	17	13	3	203	209	15	21	3	300	296
12	20	2	90	83	0	34	2	74	26	5	7	3	593	607	1	15	3	462	462	1	23	3	321	323
14	20	2	251	231	2	34	2	274	277	7	7	3	364	351	3	15	3	539	537	3	23	3	179	179
16	20	2	242	237	4	36	2	133	140	9	7	3	281	293	5	15	3	267	248	5	23	3	309	304
0	22	2	483	498	1	1	3	570	614	11	7	3	327	334	7	15	3	302	300	7	23	3	381	390
2	22	2	267	274	3	1	3	410	405	13	7	3	257	264	9	15	3	379	402	9	23	3	186	191
4	22	2	352	365	5	1	3	335	354	15	7	3	145	146	11	15	3	265	258	11	23	3	313	320
8	22	2	226	221	7	1	3	207	234	17	7	3	320	327	13	15	3	181	178	13	23	3	219	208
10	22	2	203	216	9	1	3	596	572	19	7	3	263	271	15	15	3	291	298	15	23	3	127	140
12	22	2	349	339	11	1	3	345	341	1	9	3	353	327	17	15	3	160	165	1	25	3	190	209
14	22	2	165	184	13	1	3	314	304	3	9	3	339	347	1	17	3	279	253	3	25	3	259	279
16	22	2	171	179	15	1	3	212	217	5	9	3	378	373	3	17	3	336	343	5	25	3	289	291
2	24	2	104	132	17	1	3	244	233	7	9	3	436	423	5	17	3	352	338	7	25	3	208	296
4	24	2	445	443	19	1	3	158	150	9	9	3	203	210	7	17	3	215	225	9	25	3	235	237
6	24	2	74	11	1	3	3	452	462	11	9	3	368	365	9	17	3	392	417	11	25	3	225	226
8	24	2	411	436	3	3	3	294	267	13	9	3	325	319	11	17	3	206	210	13	25	3	163	166
0	26	2	435	424	5	3	3	581	534	15	9	3	281	262	13	17	3	338	329	1	27	3	157	149
2	26	2	162	156	7	3	3	466	473	17	9	3	277	275	15	17	3	221	229	3	27	3	324	314
4	26	2	233	233	11	3	3	350	337	19	9	3	224	223	17	17	3	196	208	5	27	3	192	208
8	26	2	266	272	13	3	3	384	385	1	11	3	515	529	1	19	3	296	278	7	27	3	169	152
10	26	2	128	125	15	3	3	229	199	3	11	3	576	585	3	19	3	162	157	9	27	3	286	309
12	26	2	337	335	17	3	3	241	249	5	11	3	308	295	5	19	3	202	277	11	27	3	177	183
14	26	2	85	57	19	3	3	264	256	7	11	3	289	288	7	19	3	446	451	1	29	3	271	259
2	28	2	182	205	1	5	3	192	204	9	11	3	435	424	9	19	3	117	101	5	29	3	281	294
4	28	2	350	364	3	5	3	520	504	11	11	3	257	241	11	19	3	342	341	7	29	3	315	302
6	28	2	248	255	5	5	3	252	248	15	11	3	304	324	13	19	3	257	272	11	29	3	188	174
8	28	2	180	164	7	5	3	161	179	17	11	3	218	219	15	19	3	105	103	1	31	3	175	159
10	28	2	95	104	9	5	3	466	459	1	13	3	609	569	1	21	3	93	85	3	31	3	215	227
0	30	2	136	155	11	5	3	332	347	3	13	3	180	166	3	21	3	385	371	5	31	3	163	143
2	30	2	260	278	13	5	3	203	188	5	13	3	524	533	5	21	3	218	229	7	31	3	116	118
4	30	2	161	171	15	5	3	414	408	7	13	3	534	536	7	21	3	177	182	9	31	3	183	177
8	30	2	122	103	17	5	3	235	248	9	13	3	104	139	9	21	3	405	398	1	33	3	107	106
10	30	2	271	275	19	5	3	159	159	11	13	3	316	345	11	21	3	183	193	3	33	3	190	166

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	33	3	134	148	0	8	4	314	305	16	14	4	356	335	6	26	4	465	483	1	5	5	521	526
7	33	3	140	135	2	8	4	731	717	0	16	4	717	712	8	26	4	94	105	3	5	5	663	662
1	35	3	180	165	4	8	4	307	296	2	16	4	203	207	10	26	4	217	211	5	5	5	597	604
5	35	3	165	165	6	8	4	183	185	4	16	4	288	288	0	28	4	305	336	7	5	5	312	329
0	0	4	653	683	8	8	4	194	192	6	16	4	133	132	2	28	4	297	294	9	5	5	551	531
4	0	4	187	195	10	8	4	469	457	8	16	4	306	321	8	28	4	123	119	11	5	5	159	169
8	0	4	547	551	12	8	4	113	100	10	16	4	81	63	10	28	4	265	269	13	5	5	303	277
12	0	4	635	617	14	8	4	393	404	12	16	4	512	534	2	30	4	113	107	15	5	5	306	314
16	0	4	148	170	16	8	4	83	56	16	16	4	180	195	4	30	4	303	277	17	5	5	196	197
2	2	4	137	153	18	8	4	84	48	2	18	4	108	76	6	30	4	173	175	1	7	5	459	451
4	2	4	830	818	2	10	4	230	256	4	18	4	439	435	8	30	4	264	256	3	7	5	331	327
6	2	4	367	366	4	10	4	337	319	6	18	4	264	266	0	32	4	366	370	5	7	5	301	316
8	2	4	706	683	6	10	4	651	665	8	18	4	450	450	2	32	4	91	103	7	7	5	420	427
10	2	4	129	100	8	10	4	77	102	16	18	4	371	379	4	32	4	182	202	9	7	5	166	168
12	2	4	105	103	10	10	4	211	214	0	20	4	278	267	8	32	4	104	90	11	7	5	364	373
16	2	4	321	342	12	10	4	70	65	2	20	4	348	331	4	34	4	234	229	13	7	5	311	316
18	2	4	164	151	14	10	4	264	263	4	20	4	83	90	1	1	5	282	302	15	7	5	237	236
0	4	4	582	576	16	10	4	154	168	8	20	4	130	134	3	1	5	352	370	17	7	5	273	270
2	4	4	737	716	18	10	4	384	421	10	20	4	341	333	5	1	5	411	395	1	9	5	390	379
4	4	4	264	279	0	12	4	691	687	12	20	4	432	423	7	1	5	318	283	3	9	5	259	239
6	4	4	63	41	2	12	4	624	620	14	20	4	230	238	9	1	5	453	458	5	9	5	571	551
8	4	4	420	427	4	12	4	292	284	16	20	4	154	134	11	1	5	320	332	7	9	5	332	325
10	4	4	384	379	6	12	4	125	116	2	22	4	129	128	13	1	5	241	251	9	9	5	153	155
12	4	4	544	544	8	12	4	277	282	4	22	4	253	251	15	1	5	288	290	11	9	5	258	263
14	4	4	185	197	10	12	4	414	392	6	22	4	429	439	17	1	5	193	197	13	9	5	258	264
16	4	4	165	171	12	12	4	258	265	8	22	4	200	230	1	3	5	380	363	15	9	5	123	123
2	6	4	86	111	14	12	4	245	249	10	22	4	112	155	3	3	5	230	208	17	9	5	214	245
4	6	4	200	193	16	12	4	107	113	14	22	4	227	220	5	3	5	375	390	1	11	5	259	256
6	6	4	837	810	2	14	4	257	263	0	24	4	153	168	7	3	5	549	558	3	11	5	391	395
8	6	4	242	243	4	14	4	526	516	2	24	4	317	317	9	3	5	197	192	5	11	5	117	120
10	6	4	235	224	6	14	4	334	334	10	24	4	414	416	11	3	5	402	402	7	11	5	197	195
14	6	4	233	260	8	14	4	452	471	12	24	4	102	126	13	3	5	443	441	9	11	5	382	373
16	6	4	235	228	12	14	4	119	105	14	24	4	204	283	15	3	5	182	177	11	11	5	180	169
18	6	4	466	470	14	14	4	245	221	2	26	4	201	276	17	3	5	255	249	13	11	5	108	165

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	11	5	345	331	3	21	5	342	334	5	33	5	133	132	10	8	6	131	134	0	18	6	236	225
17	11	5	241	233	5	21	5	250	250	2	0	6	403	431	12	8	6	121	92	2	18	6	386	364
1	13	5	467	467	7	21	5	178	162	6	0	6	462	490	16	8	6	458	451	6	18	6	101	87
3	13	5	114	121	9	21	5	242	226	10	0	6	438	432	0	10	6	540	547	8	18	6	120	116
5	13	5	384	387	11	21	5	199	211	14	0	6	407	376	2	10	6	180	193	10	18	6	393	395
7	13	5	415	399	13	21	5	94	98	18	0	6	390	392	4	10	6	307	312	12	18	6	167	170
9	13	5	106	93	1	23	5	242	230	0	2	6	416	440	6	10	6	85	87	14	18	6	293	292
11	13	5	220	218	3	23	5	161	155	2	2	6	653	666	8	10	6	295	276	2	20	6	227	221
13	13	5	248	242	5	23	5	195	178	4	2	6	177	196	10	10	6	116	123	4	20	6	327	325
17	13	5	144	181	7	23	5	274	269	6	2	6	129	121	12	10	6	412	398	6	20	6	354	328
1	15	5	222	243	9	23	5	131	132	8	2	6	124	122	14	10	6	242	233	8	20	6	215	195
3	15	5	510	512	11	23	5	252	243	10	2	6	348	376	16	10	6	128	138	10	20	6	154	144
5	15	5	139	142	13	23	5	198	191	12	2	6	211	213	2	12	6	230	223	14	20	6	127	140
7	15	5	239	225	1	25	5	177	187	14	2	6	459	447	4	12	6	386	399	0	22	6	318	302
9	15	5	387	371	3	25	5	225	211	2	4	6	307	330	6	12	6	325	324	2	22	6	199	199
11	15	5	173	196	5	25	5	180	189	4	4	6	460	489	8	12	6	329	322	4	22	6	169	169
13	15	5	229	229	7	25	5	200	205	6	4	6	446	441	10	12	6	219	227	8	22	6	185	175
15	15	5	293	293	9	25	5	232	217	8	4	6	303	298	14	12	6	211	209	10	22	6	231	232
1	17	5	394	394	11	25	5	147	154	10	4	6	263	255	16	12	6	258	261	12	22	6	335	372
3	17	5	374	372	1	27	5	120	100	12	4	6	124	90	0	14	6	331	311	2	24	6	67	90
5	17	5	331	321	3	27	5	329	326	14	4	6	287	281	2	14	6	421	410	4	24	6	380	356
7	17	5	210	191	5	27	5	149	146	16	4	6	323	331	4	14	6	309	306	6	24	6	116	117
9	17	5	237	232	7	27	5	135	137	0	6	6	799	772	6	14	6	132	111	8	24	6	292	278
11	17	5	232	232	9	27	5	246	253	2	6	6	288	296	8	14	6	182	167	0	26	6	428	385
13	17	5	225	227	11	27	5	129	133	4	6	6	357	381	10	14	6	364	380	4	26	6	172	189
15	17	5	222	219	1	29	5	298	309	6	6	6	77	73	12	14	6	182	172	8	26	6	249	249
1	19	5	352	346	5	29	5	254	248	8	6	6	283	281	14	14	6	334	327	2	28	6	150	154
3	19	5	134	129	7	29	5	223	228	10	6	6	192	191	16	14	6	121	103	4	28	6	277	268
5	19	5	304	292	1	31	5	160	149	12	6	6	543	553	2	16	6	440	419	6	28	6	206	187
7	19	5	308	302	3	31	5	292	273	14	6	6	162	157	4	16	6	127	124	8	28	6	274	277
11	19	5	307	311	5	31	5	104	96	16	6	6	164	179	6	16	6	564	551	0	30	6	169	162
13	19	5	302	292	7	31	5	160	162	2	8	6	121	109	10	16	6	281	292	2	30	6	319	304
15	19	5	94	98	1	33	5	198	193	4	8	6	529	555	12	16	6	108	84	4	30	6	111	99
1	21	5	220	206	3	33	5	134	131	8	8	6	476	489	14	16	6	221	220	2	32	6	163	167

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	1	7	408	390	3	9	7	207	216	13	17	7	212	213	8	0	8	305	324	0	12	8	356	352
3	1	7	507	523	5	9	7	358	370	1	19	7	331	321	12	0	8	402	419	2	12	8	310	298
5	1	7	245	246	7	9	7	400	402	3	19	7	78	86	2	2	8	145	133	4	12	8	195	186
7	1	7	199	205	9	9	7	223	233	5	19	7	264	269	4	2	8	521	538	6	12	8	95	91
9	1	7	225	218	11	9	7	285	287	7	19	7	238	236	6	2	8	173	155	8	12	8	176	170
11	1	7	235	208	13	9	7	258	247	9	19	7	128	103	8	2	8	336	353	10	12	8	389	361
13	1	7	264	270	15	9	7	157	182	11	19	7	261	249	14	2	8	110	113	12	12	8	251	267
15	1	7	254	256	1	11	7	214	191	13	19	7	225	212	0	4	8	413	420	14	12	8	273	280
17	1	7	151	154	3	11	7	433	432	1	21	7	160	162	2	4	8	266	279	2	14	8	114	97
1	3	7	461	463	5	11	7	252	242	3	21	7	294	263	4	4	8	189	186	4	14	8	403	412
3	3	7	302	290	7	11	7	126	138	5	21	7	147	139	6	4	8	186	167	6	14	8	263	262
5	3	7	381	394	9	11	7	400	393	7	21	7	203	202	8	4	8	164	165	8	14	8	291	287
7	3	7	307	323	11	11	7	209	217	9	21	7	248	230	10	4	8	293	296	10	14	8	103	108
9	3	7	103	98	13	11	7	113	123	11	21	7	173	169	12	4	8	319	326	0	16	8	527	526
11	3	7	265	282	15	11	7	301	298	1	23	7	284	287	14	4	8	236	239	4	16	8	237	222
13	3	7	298	299	1	13	7	405	405	3	23	7	170	164	2	6	8	218	220	8	16	8	211	218
15	3	7	87	90	3	13	7	96	116	5	23	7	228	221	4	6	8	202	207	10	16	8	99	99
1	5	7	226	204	5	13	7	359	336	7	23	7	236	216	6	6	8	490	514	12	16	8	401	394
3	5	7	435	436	7	13	7	364	365	9	23	7	88	91	8	6	8	241	254	4	18	8	379	380
5	5	7	299	306	11	13	7	295	310	11	23	7	219	199	10	6	8	203	203	6	18	8	90	66
7	5	7	206	224	13	13	7	272	272	1	25	7	265	239	12	6	8	80	58	8	18	8	377	372
9	5	7	406	418	1	15	7	255	228	3	25	7	232	234	14	6	8	197	187	0	20	8	435	424
11	5	7	85	99	3	15	7	369	350	5	25	7	173	173	0	8	8	177	172	2	20	8	288	281
13	5	7	196	204	5	15	7	301	315	7	25	7	209	173	2	8	8	433	440	4	20	8	202	191
15	5	7	314	307	7	15	7	116	115	9	25	7	186	180	10	8	8	442	455	8	20	8	81	79
1	7	7	260	265	9	15	7	354	342	1	27	7	162	156	12	8	8	81	59	10	20	8	143	155
3	7	7	137	148	11	15	7	200	179	3	27	7	320	309	14	8	8	379	349	2	22	8	168	160
5	7	7	350	354	13	15	7	164	161	5	27	7	164	163	2	10	8	259	248	4	22	8	177	144
7	7	7	323	315	1	17	7	217	227	7	27	7	155	122	4	10	8	192	175	6	22	8	370	356
9	7	7	198	183	3	17	7	271	274	1	29	7	210	194	6	10	8	574	563	8	22	8	211	171
11	7	7	230	224	5	17	7	255	239	5	29	7	213	188	8	10	8	112	98	10	22	8	152	139
13	7	7	266	281	7	17	7	167	184	1	31	7	109	121	10	10	8	198	180	0	24	8	139	119
15	7	7	204	220	9	17	7	224	202	0	0	8	577	643	12	10	8	85	63	2	24	8	442	412
1	9	7	243	279	11	17	7	242	243	4	0	8	259	260	14	10	8	165	196	2	26	8	164	154

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	26	8	92	91	7	9	9	296	294	5	21	9	120	122	8	10	10	223	227	5	7	11	160	169
6	26	8	339	326	9	9	9	176	182	7	21	9	165	163	10	10	10	174	168	7	7	11	260	257
0	28	8	186	165	11	9	9	263	267	1	23	9	210	192	2	12	10	126	126	9	7	11	112	133
2	28	8	259	242	13	9	9	189	192	3	23	9	84	83	4	12	10	317	295	1	9	11	215	206
1	1	9	276	295	1	11	9	170	196	5	23	9	220	200	6	12	10	294	294	3	9	11	172	168
3	1	9	328	360	3	11	9	229	220	7	23	9	231	223	8	12	10	277	249	5	9	11	220	216
5	1	9	180	183	5	11	9	217	229	1	25	9	174	173	10	12	10	127	135	7	9	11	167	173
7	1	9	250	246	7	11	9	181	183	3	25	9	131	128	0	14	10	272	236	9	9	11	194	177
9	1	9	259	251	9	11	9	331	315	2	0	10	286	315	2	14	10	349	336	1	11	11	130	139
11	1	9	229	218	11	11	9	178	175	6	0	10	528	549	10	14	10	322	302	3	11	11	352	348
13	1	9	155	139	13	11	9	154	153	10	0	10	195	205	2	16	10	205	190	5	11	11	167	156
1	3	9	360	385	1	13	9	288	271	0	2	10	139	145	6	16	10	387	372	7	11	11	152	190
5	3	9	345	347	3	13	9	91	78	2	2	10	374	382	2	18	10	347	312	1	13	11	233	213
7	3	9	223	228	5	13	9	330	320	4	2	10	151	150	4	18	10	116	117	5	13	11	241	241
9	3	9	73	26	7	13	9	291	272	6	2	10	95	72	2	20	10	190	169	7	13	11	167	196
11	3	9	186	202	11	13	9	246	240	8	2	10	138	140	4	20	10	157	145	1	15	11	215	207
13	3	9	322	300	1	15	9	273	264	10	2	10	386	391	6	20	10	268	271	3	15	11	163	169
1	5	9	103	98	3	15	9	199	188	12	2	10	146	155	0	22	10	299	283	5	15	11	185	156
3	5	9	348	352	5	15	9	218	213	2	4	10	130	146	2	22	10	145	135	1	17	11	126	130
5	5	9	150	174	7	15	9	207	188	4	4	10	294	303	1	1	11	188	170	3	17	11	213	189
7	5	9	208	185	9	15	9	237	222	6	4	10	251	262	3	1	11	327	323	0	0	12	378	411
9	5	9	293	305	11	15	9	206	195	8	4	10	285	314	5	1	11	225	233	4	0	12	106	106
11	5	9	178	195	1	17	9	231	246	10	4	10	111	121	7	1	11	204	203	2	2	12	125	120
13	5	9	120	115	3	17	9	295	259	0	6	10	210	248	9	1	11	252	288	4	2	12	293	316
1	7	9	282	302	5	17	9	237	225	2	6	10	170	154	1	3	11	287	302	6	2	12	119	136
3	7	9	185	185	7	17	9	207	215	4	6	10	243	250	5	3	11	254	273	0	4	12	277	303
5	7	9	280	292	9	17	9	205	203	8	6	10	267	259	7	3	11	232	225	2	4	12	203	238
7	7	9	211	213	11	17	9	194	191	10	6	10	129	112	1	5	11	95	83	4	4	12	90	95
9	7	9	199	219	1	19	9	277	265	12	6	10	306	325	3	5	11	282	290	2	6	12	293	233
11	7	9	266	250	5	19	9	263	244	4	8	10	341	367	5	5	11	126	124	4	6	12	138	152
13	7	9	256	245	7	19	9	240	216	8	8	10	320	323	7	5	11	165	162	6	6	12	278	277
1	9	9	208	193	9	19	9	112	121	0	10	10	464	461	9	5	11	274	291	2	8	12	354	363
3	9	9	348	343	1	21	9	169	165	4	10	10	288	282	1	7	11	245	233	2	10	12	188	170
5	9	9	298	295	3	21	9	340	321	6	10	10	105	70	3	7	11	207	209	4	10	12	112	119

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	12	12	252	249	2	12	12	222	225															

APPENDIX B

Observed and calculated structure factors for $Cs^+[YbEDTA(2H_2O)]^-.3H_2O$

H	K	L	FO	FC
6	0	0	73	-83
7	0	0	75	-88
8	0	0	229	257
9	0	0	160	-174
10	0	0	102	110
12	0	0	110	-102
13	0	0	108	103
14	0	0	62	-55
2	1	0	36	30
3	1	0	100	112
4	1	0	81	-94
5	1	0	54	63
6	1	0	85	-98
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8	0	2	18	-10
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2	1	2	205	-213
3	1	2	145	139
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5	1	2	158	-167
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8	2	2	86	-86
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H	K	L	FO	FC
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H	K	L	FO	FC
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10	2	3	118	-119
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H	K	L	FO	FC
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-12	6	3	43	-41
-11	6	3	59	62
-10	6	3	61	-68
-9	6	3	20	20
-8	6	3	34	40
-7	6	3	96	-96
-6	6	3	108	115
-5	6	3	53	-53
-4	6	3	84	-31
-3	6	3	139	130
-2	6	3	143	-136
-1	6	3	85	81
1	6	3	116	-112
2	6	3	175	169
3	6	3	100	-107
4	6	3	19	18
5	6	3	40	42
6	6	3	101	-101
7	6	3	84	85
8	6	3	28	-29
9	6	3	21	-24
10	6	3	55	59
11	6	3	45	-47
-11	7	3	16	-14
-10	7	3	39	41
-9	7	3	94	-96
-8	7	3	77	78

H	K	L	FO	FC
-6	7	3	53	-50
-5	7	3	108	105
-4	7	3	130	-120
-3	7	3	31	22
-2	7	3	39	35
-1	7	3	147	-142
0	7	3	161	161
1	7	3	100	-97
2	7	3	27	22
3	7	3	66	65
4	7	3	125	-128
5	7	3	106	108
6	7	3	46	-47
7	7	3	56	-57
8	7	3	73	72
9	7	3	60	-61
10	7	3	31	32
-10	8	3	71	-73
-9	8	3	66	69
-8	8	3	29	-30
-7	8	3	48	-47
-6	8	3	92	90
-5	8	3	62	-57
-3	8	3	54	49
-2	8	3	71	-65
-1	8	3	51	47
0	8	3	13	11
1	8	3	80	-78
2	8	3	84	81
3	8	3	24	-22
4	8	3	63	-61
5	8	3	113	111
6	8	3	75	-82
7	8	3	15	12

H	K	L	FO	FC
8	8	3	52	55
-8	9	3	91	-94
-7	9	3	44	45
-6	9	3	33	36
-5	9	3	120	-118
-4	9	3	127	123
-3	9	3	80	-74
-2	9	3	17	-19
-1	9	3	127	124
0	9	3	157	-150
1	9	3	100	95
2	9	3	16	-16
3	9	3	92	-90
4	9	3	116	117
5	9	3	81	-86
6	9	3	20	14
7	9	3	44	47
-4	10	3	40	-37
-3	10	3	70	69
-2	10	3	76	-75
-1	10	3	51	49
1	10	3	57	-54
2	10	3	83	85
3	10	3	55	-56
4	10	3	13	17
-15	0	4	123	111
-14	0	4	116	-107
-13	0	4	40	37
-12	0	4	101	103
-11	0	4	171	-184
-10	0	4	154	167
-9	0	4	49	-50
-8	0	4	88	-101
-7	0	4	91	100

H	K	L	FO	FC
-6	0	4	280	-337
-4	0	4	36	-33
-3	0	4	171	-187
-2	0	4	220	237
-1	0	4	170	-158
0	0	4	65	-73
1	0	4	71	72
2	0	4	166	-152
4	0	4	69	63
5	0	4	106	-105
6	0	4	18	18
7	0	4	58	61
8	0	4	70	-72
9	0	4	52	52
10	0	4	20	-17
11	0	4	38	-37
12	0	4	47	43
13	0	4	71	-66
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-14	1	4	28	-26
-13	1	4	11	5
-11	1	4	45	-45
-10	1	4	65	73
-9	1	4	32	-32
-8	1	4	43	-46
-7	1	4	115	131
-6	1	4	126	-144
-5	1	4	119	130
-4	1	4	60	-63
-3	1	4	179	-186
-2	1	4	291	296
-1	1	4	222	-217
0	1	4	133	120
1	1	4	55	53

H	K	L	FO	FC
2	1	4	273	-258
3	1	4	307	298
4	1	4	181	-174
5	1	4	32	-34
6	1	4	144	147
7	1	4	183	-187
8	1	4	122	122
9	1	4	14	-13
10	1	4	69	-70
11	1	4	126	125
12	1	4	112	-108
13	1	4	35	30
-14	2	4	14	14
-13	2	4	46	-49
-12	2	4	26	29
-11	2	4	15	-15
-10	2	4	63	-75
-9	2	4	99	110
-8	2	4	57	-62
-7	2	4	34	40
-6	2	4	34	36
-5	2	4	151	-166
-4	2	4	139	141
-3	2	4	189	-188
-2	2	4	10	7
-1	2	4	156	144
0	2	4	300	-275
1	2	4	274	254
2	2	4	84	-75
3	2	4	111	-109
4	2	4	147	145
5	2	4	169	-168
6	2	4	68	88
7	2	4	16	14

H	K	L	FO	FC
8	2	4	94	-99
9	2	4	95	96
10	2	4	86	-85
11	2	4	45	44
12	2	4	17	18
13	2	4	65	-57
-14	3	4	84	-77
-13	3	4	136	138
-12	3	4	125	-129
-11	3	4	26	25
-10	3	4	81	87
-9	3	4	150	-161
-8	3	4	167	182
-7	3	4	98	-101
-6	3	4	60	-63
-5	3	4	199	211
-4	3	4	220	-221
-3	3	4	120	112
-2	3	4	26	-21
-1	3	4	94	-89
0	3	4	138	135
1	3	4	84	-79
2	3	4	91	-81
3	3	4	105	101
4	3	4	67	-65
5	3	4	10	5
6	3	4	39	37
7	3	4	63	-59
8	3	4	12	6
9	3	4	32	34
10	3	4	52	-49
11	3	4	56	52
12	3	4	42	-40
-13	4	4	13	8

H	K	L	FO	FC
-12	4	4	44	-46
-11	4	4	61	64
-10	4	4	22	23
-9	4	4	90	-101
-8	4	4	84	89
-7	4	4	89	-84
-6	4	4	27	26
-5	4	4	92	91
-4	4	4	189	-186
-3	4	4	205	193
-2	4	4	68	-62
-1	4	4	104	-97
0	4	4	250	229
1	4	4	276	-245
2	4	4	145	137
3	4	4	18	17
4	4	4	173	-172
5	4	4	229	230
6	4	4	140	-141
8	4	4	126	126
9	4	4	143	-146
10	4	4	96	93
11	4	4	31	-33
12	4	4	47	-42
-13	5	4	29	-26
-12	5	4	42	46
-11	5	4	50	-53
-10	5	4	27	28
-9	5	4	17	16
-8	5	4	42	-45
-7	5	4	91	99
-6	5	4	101	-104
-5	5	4	36	34
-4	5	4	36	33

H	K	L	FO	FC
-3	5	4	125	-116
-2	5	4	148	138
-1	5	4	112	-105
0	5	4	9	-1
1	5	4	106	99
2	5	4	131	-125
3	5	4	104	104
4	5	4	59	-60
5	5	4	44	-45
6	5	4	47	50
7	5	4	58	-57
8	5	4	65	63
9	5	4	24	-26
10	5	4	21	-17
11	5	4	41	38
-12	6	4	61	-61
-11	6	4	107	107
-10	6	4	89	-93
-8	6	4	65	47
-7	6	4	104	-104
-6	6	4	140	141
-5	6	4	73	-69
-4	6	4	35	-32
-3	6	4	160	146
-2	6	4	152	-146
-1	6	4	24	22
0	6	4	76	67
1	6	4	103	-95
2	6	4	109	106
3	6	4	21	-18
4	6	4	22	-22
5	6	4	62	60
6	6	4	39	-39
7	6	4	26	-26

H	K	L	FO	FC
8	6	4	41	36
9	6	4	26	-26
10	6	4	33	28
-11	7	4	32	28
-10	7	4	68	-74
-9	7	4	80	79
-8	7	4	23	-23
-7	7	4	66	-63
-6	7	4	108	107
-5	7	4	120	-114
-4	7	4	69	63
-3	7	4	68	64
-2	7	4	148	-141
-1	7	4	137	130
0	7	4	73	-72
1	7	4	51	-52
2	7	4	149	144
3	7	4	177	-175
4	7	4	121	121
5	7	4	21	23
6	7	4	125	-127
7	7	4	123	128
8	7	4	85	-84
-10	8	4	45	48
-9	8	4	27	-27
-8	8	4	16	17
-7	8	4	27	28
-6	8	4	32	-29
-5	8	4	29	29
-4	8	4	41	-41
-3	8	4	14	16
-2	8	4	30	29
-1	8	4	19	-20
0	8	4	69	69

H	K	L	FO	FC
1	8	4	59	-57
3	8	4	50	47
4	8	4	26	-26
5	8	4	24	19
6	8	4	19	-18
-8	9	4	64	-64
-7	9	4	26	24
-6	9	4	56	50
-5	9	4	97	-97
-4	9	4	73	72
-3	9	4	18	-18
-2	9	4	34	-31
-1	9	4	82	81
0	9	4	76	-81
1	9	4	26	22
2	9	4	37	44
3	9	4	68	-70
4	9	4	48	48
5	9	4	17	-12
6	9	4	19	-16
-4	10	4	64	81
-3	10	4	91	-88
-2	10	4	51	51
-1	10	4	32	27
0	10	4	86	-87
1	10	4	98	100
2	10	4	64	-63
3	10	4	13	-10
-15	1	5	46	49
-14	1	5	67	-64
-13	1	5	79	84
-12	1	5	31	-37
-11	1	5	56	-39
-10	1	5	118	132

H	K	L	FO	FC
-9	1	5	95	-107
-8	1	5	28	35
-7	1	5	77	94
-6	1	5	141	-161
-5	1	5	150	161
-4	1	5	26	-18
-3	1	5	164	-164
-2	1	5	208	198
-1	1	5	83	-83
0	1	5	22	15
1	1	5	155	142
2	1	5	133	-123
3	1	5	57	57
4	1	5	40	-34
5	1	5	87	-87
6	1	5	170	166
7	1	5	107	-106
8	1	5	15	14
9	1	5	78	76
10	1	5	104	-104
11	1	5	61	59
12	1	5	20	-19
13	1	5	45	-38
-15	2	5	56	-51
-13	2	5	79	81
-12	2	5	121	-127
-11	2	5	122	129
-10	2	5	42	-46
-9	2	5	89	-101
-8	2	5	169	187
-7	2	5	137	-150
-6	2	5	79	88
-5	2	5	135	142
-4	2	5	221	-229

H	K	L	FO	FC
-3	2	5	195	192
-2	2	5	134	-120
-1	2	5	49	-47
0	2	5	259	238
1	2	5	150	-148
2	2	5	48	39
3	2	5	152	140
4	2	5	154	-147
5	2	5	105	105
6	2	5	61	-59
7	2	5	41	-35
8	2	5	106	103
9	2	5	49	-47
10	2	5	15	14
11	2	5	37	35
12	2	5	78	-78
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-9	3	5	19	-27
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-6	3	5	26	25
-5	3	5	24	21
-4	3	5	36	-32
-3	3	5	50	47
-2	3	5	81	-73
-1	3	5	32	28
0	3	5	26	25
1	3	5	61	-53
2	3	5	75	68
4	3	5	39	-39
5	3	5	50	52
6	3	5	63	-59

H	K	L	FO	FC
8	3	5	23	15
9	3	5	35	-37
10	3	5	42	40
11	3	5	19	-18
12	3	5	15	15
-12	4	5	34	-31
-11	4	5	51	57
-10	4	5	13	-18
-9	4	5	22	-22
-8	4	5	61	60
-7	4	5	52	-50
-6	4	5	18	-16
-5	4	5	124	125
-4	4	5	102	-101
-3	4	5	115	105
-1	4	5	102	-98
0	4	5	139	127
1	4	5	94	-84
2	4	5	15	-12
3	4	5	171	158
4	4	5	124	-119
5	4	5	93	87
7	4	5	83	-79
8	4	5	118	118
9	4	5	81	-80
10	4	5	13	12
11	4	5	62	62
12	4	5	82	-80
-13	5	5	74	-73
-12	5	5	17	16
-11	5	5	89	92
-10	5	5	160	-167
-9	5	5	136	139
-8	5	5	52	-55

H	K	L	FO	FC
-7	5	5	67	-92
-6	5	5	188	189
-5	5	5	209	-210
-4	5	5	110	108
-3	5	5	93	84
-2	5	5	204	-196
-1	5	5	219	205
0	5	5	110	-103
1	5	5	67	-62
2	5	5	128	123
3	5	5	163	-155
4	5	5	107	104
5	5	5	20	23
6	5	5	101	-95
7	5	5	114	114
8	5	5	45	-42
9	5	5	34	-32
10	5	5	49	47
11	5	5	50	-45
-9	6	5	19	15
-7	6	5	17	-19
-6	6	5	46	45
-5	6	5	44	-41
-4	6	5	43	38
-3	6	5	18	-13
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1	6	5	53	51
2	6	5	66	64
3	6	5	97	-97
4	6	5	77	78
5	6	5	55	-53
6	6	5	20	-19

H	K	L	FO	FC
7	6	5	93	94
8	6	5	78	-78
9	6	5	53	52
-8	7	5	38	36
-7	7	5	39	-41
-6	7	5	32	28
-5	7	5	20	-20
-4	7	5	60	-56
-3	7	5	112	107
-2	7	5	75	-74
-1	7	5	13	-11
0	7	5	49	45
1	7	5	75	-75
2	7	5	79	79
3	7	5	25	-22
4	7	5	22	-20
5	7	5	64	66
6	7	5	103	-103
7	7	5	59	57
9	7	5	60	-55
-10	8	5	27	30
-9	8	5	68	71
-8	8	5	140	-139
-7	8	5	129	124
-6	8	5	52	-51
-5	8	5	60	-56
-4	8	5	163	158
-3	8	5	172	-165
-2	8	5	93	88
-1	8	5	24	24
0	8	5	129	-122
1	8	5	147	143
2	8	5	78	-79
3	8	5	32	-31

H	K	L	FO	FC
4	8	5	104	102
5	8	5	93	-94
6	8	5	59	60
8	8	5	54	-55
-8	7	5	24	-23
-7	9	5	17	13
-6	9	5	16	-10
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-3	9	5	41	-42
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-1	9	5	34	-29
0	9	5	49	-52
1	9	5	80	76
2	9	5	100	-97
3	9	5	51	53
4	9	5	41	41
5	9	5	92	-97
6	9	5	95	98
-3	10	5	42	43
-2	10	5	44	-46
-1	10	5	49	49
0	10	5	32	-29
1	10	5	21	-18
2	10	5	47	48
-15	0	6	31	17
-14	0	6	79	-72
-13	0	6	134	133
-12	0	6	97	-102
-11	0	6	15	-4
-10	0	6	134	139
-9	0	6	211	-230
-8	0	6	148	162
-7	0	6	79	-89
-6	0	6	55	-57

H	K	L	FO	FC
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-4	0	6	265	-295
-3	0	6	153	164
-2	0	6	201	193
-1	0	6	389	-388
0	0	6	403	388
1	0	6	266	-248
2	0	6	19	-17
3	0	6	279	267
4	0	6	299	-287
5	0	6	206	199
6	0	6	12	10
7	0	6	133	-135
8	0	6	179	178
9	0	6	121	-120
10	0	6	27	25
11	0	6	52	51
12	0	6	89	-88
-15	1	6	31	-27
-14	1	6	48	42
-13	1	6	68	-69
-12	1	6	39	44
-11	1	6	17	7
-10	1	6	47	-52
-9	1	6	76	82
-8	1	6	41	[illegible]
-7	1	6	12	9
-5	1	6	84	-88
-4	1	6	32	28
-3	1	6	11	-7
-2	1	6	54	51
-1	1	6	16	12
0	1	6	37	-27
1	1	6	29	-27

H	K	L	FO	FC
2	1	6	75	-69
3	1	6	81	75
4	1	6	104	-97
5	1	6	76	76
7	1	6	48	-44
8	1	6	93	91
9	1	6	107	-104
10	1	6	52	50
11	1	6	16	9
12	1	6	67	-63
-15	2	6	61	-61
-14	2	6	36	37
-13	2	6	13	0
-12	2	6	42	-41
-11	2	6	49	51
-10	2	6	53	-60
-9	2	6	42	45
-8	2	6	9	[illegible]
-7	2	6	18	-15
-6	2	6	85	93
-5	2	6	83	-88
-4	2	6	26	22
-3	2	6	72	-66
-2	2	6	15	-16
-1	2	6	88	76
0	2	6	42	-39
1	2	6	156	142
2	2	6	65	-62
4	2	6	54	47
5	2	6	122	-113
6	2	6	122	117
7	2	6	84	-03
8	2	6	23	15
9	2	6	59	59

H	K	L	FO	FC
10	2	6	59	-58
11	2	6	65	65
12	2	6	34	-31
-14	3	6	58	54
-13	3	6	22	21
-12	3	6	95	-93
-11	3	6	153	159
-10	3	6	154	-166
-8	3	6	115	118
-7	3	6	241	-256
-6	3	6	228	239
-5	3	6	44	-43
-4	3	6	165	-162
-3	3	6	289	278
-2	3	6	348	-334
-1	3	6	126	118
0	3	6	59	53
1	3	6	289	-274
2	3	6	316	300
3	3	6	154	-145
5	3	6	137	136
6	3	6	225	-218
7	3	6	133	131
8	3	6	19	-16
9	3	6	84	-82
10	3	6	119	113
11	3	6	79	-79
-13	4	6	38	-40
-12	4	6	71	72
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-10	4	6	12	3
-9	4	6	32	32
-8	4	6	77	-82
-7	4	6	76	75

H	K	L	FO	FC
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-5	4	6	35	-33
-4	4	6	71	71
-3	4	6	45	-38
-1	4	6	74	66
0	4	6	48	-45
1	4	6	32	-30
2	4	6	24	21
3	4	6	48	-44
4	4	6	41	34
5	4	6	52	48
6	4	6	89	-67
7	4	6	102	100
8	4	6	50	-45
9	4	6	28	-27
10	4	6	57	56
11	4	6	80	-75
-13	5	6	44	-44
-12	5	6	52	56
-11	5	6	18	-16
-10	5	6	17	-18
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-8	5	6	64	-63
-7	5	6	52	52
-6	5	6	46	-48
-5	5	6	14	13
-4	5	6	21	23
-3	5	6	86	-82
-2	5	6	87	83
-1	5	6	95	-86
1	5	6	63	58
2	5	6	74	-66
3	5	6	80	77
4	5	6	78	-78

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	6	17	-12	-3	7	6	94	-88	2	9	6	96	-98	10	1	7	40	40	-10	3	7	50	50
6	5	6	47	45	-2	7	6	66	65	3	9	6	47	45	11	1	7	14	15	-8	3	7	46	-53
7	5	6	40	-43	-1	7	6	17	-6	4	9	6	31	30	12	1	7	56	-51	-7	3	7	78	81
8	5	6	55	56	0	7	6	44	-40	5	9	6	77	-82	-15	2	7	48	-43	-6	3	7	81	-81
9	5	6	51	-50	1	7	6	84	77	-4	10	6	66	-67	-14	2	7	78	74	-5	3	7	23	21
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-10	6	6	107	-108	3	7	6	13	-14	-2	10	6	53	49	-12	2	7	38	39	-3	3	7	60	-59
-9	6	6	162	168	4	7	6	72	70	-1	10	6	84	-85	-11	2	7	34	37	-2	3	7	69	64
-8	6	6	114	-111	5	7	6	72	-67	0	10	6	68	68	-10	2	7	116	-118	-1	3	7	14	-14
-7	6	6	19	14	6	7	6	49	49	1	10	6	26	-25	-9	2	7	131	141	1	3	7	35	-33
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-5	6	6	205	-197	-10	8	6	38	38	-14	1	7	45	41	-7	2	7	116	-121	4	3	7	10	2
-4	6	6	222	213	-9	8	6	42	-38	-13	1	7	19	10	-6	2	7	178	182	5	3	7	16	11
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1	6	6	123	115	-3	8	6	17	18	-8	1	7	114	123	-1	2	7	265	249	-14	4	7	45	42
2	6	6	33	34	-2	8	6	35	35	-7	1	7	137	-151	0	2	7	161	-147	-13	4	7	57	-49
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4	6	6	156	153	0	8	6	41	42	-5	1	7	41	47	2	2	7	250	229	-11	4	7	13	-13
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7	6	6	99	96	4	8	6	50	-52	-2	1	7	69	-62	5	2	7	14	13	-8	4	7	49	-47
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9	6	6	62	62	6	8	6	17	-19	0	1	7	139	124	7	2	7	158	153	-6	4	7	46	41
-11	7	6	65	-65	-7	9	6	107	101	1	1	7	196	-178	8	2	7	88	-88	-5	4	7	84	-84
-10	7	6	86	90	-6	9	6	83	-79	2	1	7	111	99	9	2	7	33	-34	-4	4	7	78	78
-9	7	6	45	-40	-4	9	6	65	64	4	1	7	137	-127	10	2	7	100	97	-3	4	7	69	-64
-8	7	6	22	-19	-3	9	6	108	-104	5	1	7	154	148	11	2	7	93	-93	-2	4	7	12	9
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-5	7	6	38	38	0	9	6	38	-36	8	1	7	112	111	-12	3	7	32	35	2	4	7	80	71
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5	4	7	29	25	-9	6	7	94	-97	-4	8	7	42	-39	-3	0	8	343	339	6	1	8	123	119
6	4	7	57	-54	-8	6	7	75	76	-3	8	7	83	-84	-2	0	8	194	-185	7	1	8	46	-41
7	4	7	83	82	-7	6	7	25	-24	-2	8	7	156	150	-1	0	8	45	43	8	1	8	25	-25
8	4	7	33	-32	-6	6	7	37	-36	-1	8	7	170	-163	0	0	8	14	21	9	1	8	42	41
9	4	7	51	-49	-5	6	7	67	82	0	8	7	86	85	1	0	8	316	-295	10	1	8	15	-17
10	4	7	55	58	-4	6	7	83	-80	1	8	7	63	63	2	0	8	333	303	11	1	8	14	0
11	4	7	48	-57	-3	6	7	53	52	2	8	7	165	-165	3	0	8	98	-89	-15	2	8	67	-63
-13	5	7	37	-34	-1	6	7	36	-34	3	8	7	168	167	4	0	8	68	-70	-14	2	8	75	70
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-11	5	7	85	-83	3	6	7	28	-17	5	8	7	17	-14	6	0	8	193	-188	-12	2	8	26	-32
-10	5	7	16	18	6	6	7	19	12	6	8	7	89	89	7	0	8	122	119	-11	2	8	80	86
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0	5	7	211	-199	-2	7	7	22	18	2	9	7	22	23	-8	1	8	157	-167	-1	2	8	200	186
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2	5	7	144	-135	0	7	7	54	54	-2	10	7	31	-29	-6	1	8	82	-87	1	2	8	32	32
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7	5	7	27	25	6	7	7	12	-5	-11	0	8	45	46	-1	1	8	16	-14	7	2	8	38	31
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-12	6	7	37	-37	-7	8	7	86	83	-6	0	8	67	91	3	1	8	18	-14	-14	3	8	19	21
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-11	3	8	25	-27	-3	4	8	70	-66	-11	6	8	48	-48	4	7	8	87	-84	-5	1	9	190	-193
-10	3	8	19	-12	-2	4	8	166	160	-10	6	8	46	43	5	7	8	80	83	-4	1	9	161	152
-9	3	8	75	78	-1	4	8	173	-163	-9	6	8	13	-9	6	7	8	34	-38	-3	1	9	42	39
-8	3	8	50	-48	0	4	8	88	84	-8	6	8	19	-19	7	7	8	35	-35	-2	1	9	183	-174
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-6	3	8	119	117	3	4	8	150	146	-6	6	8	86	-87	-7	8	8	19	-20	0	1	9	145	-132
-5	3	8	180	-180	4	4	8	52	-50	-5	6	8	41	33	-6	8	8	18	15	1	1	9	89	83
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-2	3	8	97	-94	7	4	8	79	-75	-2	6	8	101	96	-1	8	8	35	-31	4	1	9	131	123
-1	3	8	252	235	8	4	8	36	37	-1	6	8	20	-20	0	8	8	52	49	5	1	9	32	-30
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1	3	8	70	62	10	4	8	44	-43	1	6	8	165	160	2	8	8	18	21	7	1	9	108	106
2	3	8	133	1[illegible]1	-13	5	8	39	-35	2	6	8	166	-160	4	8	8	35	-35	8	1	9	100	-93
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6	3	8	30	-27	-8	5	8	61	-60	6	6	8	134	133	-6	9	8	22	-15	-14	2	9	58	-55
7	3	8	143	138	-7	5	8	76	78	7	6	8	58	-59	-5	9	8	44	42	-12	2	9	42	40
8	3	8	175	-170	-6	5	8	51	-51	8	6	8	39	-37	-4	9	8	55	-53	-11	2	9	106	-116
9	3	8	112	109	-5	5	8	22	-21	9	6	8	91	91	-3	9	8	37	39	-10	2	9	99	102
10	3	8	16	16	-4	5	8	93	87	-11	7	8	79	79	-2	9	8	23	22	-8	2	9	105	-107
11	3	8	107	-102	-3	5	8	98	-91	-9	7	8	95	-92	-1	9	8	73	-73	-7	2	9	110	106
-14	4	8	104	-97	-2	5	8	96	92	-8	7	8	145	142	0	9	8	56	60	-6	2	9	98	-96
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-11	4	8	99	-100	1	5	8	65	63	-4	7	8	169	-164	3	9	8	91	91	-2	2	9	107	103
-10	4	8	138	137	2	5	8	59	-57	-3	7	8	117	113	-14	1	9	52	46	-1	2	9	21	-23
-9	4	8	138	-141	3	5	8	39	37	-2	7	8	44	-44	-13	1	9	85	-87	0	2	9	124	-118
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-7	4	8	116	118	6	5	8	60	58	0	7	8	149	145	-10	1	9	89	-94	2	2	9	123	-112
-6	4	8	184	-182	7	5	8	51	-50	1	7	8	126	-123	-9	1	9	142	153	3	2	9	25	-22
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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
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6	2	9	97	92	-4	4	9	51	46	9	5	9	16	-7	4	7	9	80	-80	-6	0	10	116	-125
7	2	9	14	-17	-3	4	9	174	-167	-12	6	9	61	-54	5	7	9	55	54	-5	0	10	43	48
8	2	9	91	-89	-2	4	9	153	142	-11	6	9	71	68	7	7	9	30	-28	-4	0	10	28	19
9	2	9	128	127	-1	4	9	45	-42	-10	6	9	51	-52	-9	8	9	21	22	-3	0	10	123	-123
10	2	9	76	-69	0	4	9	58	-56	-9	6	9	18	-18	-8	8	9	24	21	-2	0	10	47	49
-14	3	9	33	-30	1	4	9	113	111	-8	6	9	68	65	-7	8	9	51	-50	-1	0	10	74	-68
-13	3	9	32	33	2	4	9	144	-140	-7	6	9	93	-91	-6	8	9	37	36	0	0	10	26	-27
-12	3	9	31	-35	3	4	9	59	55	-6	6	9	67	67	-4	8	9	45	-46	1	0	10	103	98
-10	3	9	53	56	5	4	9	85	-82	-5	6	9	18	-15	-3	8	9	72	69	2	0	10	42	-40
-9	3	9	45	-42	6	4	9	90	90	-4	6	9	69	-65	-2	8	9	47	-45	3	0	10	62	-59
-8	3	9	45	46	7	4	9	59	-5[illegible]	-3	6	9	121	116	-1	8	9	16	-15	4	0	10	65	65
-7	3	9	13	-12	9	4	9	44	44	-2	6	9	107	-105	0	8	9	74	71	5	0	10	22	-23
-6	3	9	58	-52	10	4	9	53	-52	-1	6	9	34	31	1	8	9	89	-89	6	0	10	40	-36
-5	3	9	44	44	-13	5	9	73	69	0	6	9	48	41	2	8	9	41	39	7	0	10	67	64
-4	3	9	62	-62	-12	5	9	55	-55	1	6	9	124	-119	3	8	9	38	39	8	0	10	102	-96
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1	3	9	30	-32	-8	5	9	69	67	5	6	9	77	76	-5	9	9	106	-104	-12	1	10	41	40
2	3	9	65	-62	-7	5	9	15	-4	6	6	9	87	-87	-4	9	9	91	90	-11	1	10	84	-86
3	3	9	85	79	-6	5	9	48	-43	7	6	9	37	36	-3	9	9	34	-33	-10	1	10	69	69
4	3	9	73	-70	-5	5	9	111	110	-10	7	9	61	60	-2	9	9	52	-50	-8	1	10	64	-63
5	3	9	19	19	-4	5	9	55	-53	-9	7	9	86	-86	-1	9	9	115	115	-7	1	10	133	135
6	3	9	20	17	-3	5	9	41	-39	-8	7	9	78	82	0	9	9	122	-126	-6	1	10	130	-127
7	3	9	32	-31	-2	5	9	102	93	-7	7	9	19	-17	1	9	9	59	56	-5	1	10	81	82
8	3	9	49	48	-1	5	9	129	-123	-6	7	9	64	-63	2	9	9	30	28	-4	1	10	63	63
-13	4	9	27	-26	0	5	9	36	38	-5	7	9	103	103	-15	0	10	117	116	-3	1	10	185	-181
-12	4	9	60	60	2	5	9	72	-71	-4	7	9	97	-94	-14	0	10	69	-65	-2	1	10	182	177
-11	4	9	108	-112	3	5	9	158	151	-2	7	9	62	61	-13	0	10	27	-29	-1	1	10	165	-157
-10	4	9	81	81	4	5	9	66	-66	-1	7	9	70	-69	-12	0	10	100	102	0	1	10	54	46
-8	4	9	69	-66	5	5	9	39	-39	0	7	9	102	100	-11	0	10	121	-121	1	1	10	166	156
-7	4	9	134	134	6	5	9	115	112	1	7	9	52	-53	-10	0	10	62	54	2	1	10	206	-198
-5	4	9	103	-97	7	5	9	148	-148	2	7	9	14	-16	-8	0	10	97	-93	3	1	10	168	162

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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
-3	6	14	100	-100	-12	2	15	75	-74	-11	4	15	66	-62	-4	6	15	49	-51	-7	1	16	109	109
-2	6	14	79	77	-11	2	15	77	-74	-10	4	15	30	27	-3	6	15	81	79	-6	1	16	119	-117
0	6	14	95	-94	-10	2	15	21	20	-9	4	15	36	36	-2	6	15	86	-87	-5	1	16	56	56
1	6	14	123	121	-9	2	15	34	31	-8	4	15	67	-88	-1	6	15	17	17	-4	1	16	68	70
2	6	14	86	-88	-8	2	15	86	-81	-7	4	15	84	83	0	6	15	46	44	-3	1	16	142	-144
-7	7	14	52	-53	-7	2	15	92	89	-6	4	15	42	-39	1	6	15	70	-70	-2	1	16	141	142
-6	7	14	43	-42	-6	2	15	24	-21	-5	4	15	40	-35	2	6	15	55	57	-1	1	16	79	-78
-5	7	14	103	105	-5	2	15	63	-62	-4	4	15	77	75	-5	7	15	66	68	0	1	16	28	-29
-4	7	14	115	-115	-4	2	15	112	111	-3	4	15	88	-87	-4	7	15	42	-43	1	1	16	113	114
-3	7	14	87	86	-3	2	15	122	-122	-2	4	15	65	65	-3	7	15	13	8	2	1	16	129	-131
-2	7	14	15	12	-2	2	15	58	57	0	4	15	76	-75	-2	7	15	44	44	3	1	16	102	102
-1	7	14	99	-100	-1	2	15	28	31	1	4	15	76	75	-1	7	15	65	-66	5	1	16	61	-60
0	7	14	95	97	0	2	15	125	-122	2	4	15	54	-54	-12	0	16	88	85	-12	2	16	17	16
1	7	14	58	-58	1	2	15	134	128	4	4	15	61	60	-11	0	16	51	-47	-11	2	16	20	19
-13	1	15	69	-62	2	2	15	53	-54	5	4	15	85	-80	-10	0	16	12	5	-10	2	16	60	-60
-12	1	15	15	13	3	2	15	48	-47	-10	5	15	65	60	-9	0	16	50	52	-9	2	16	73	74
-11	1	15	39	34	4	2	15	125	124	-9	5	15	71	-66	-8	0	16	99	-94	-8	2	16	67	-66
-10	1	15	82	-80	5	2	15	120	-119	-8	5	15	35	34	-7	0	16	82	78	-7	2	16	27	24
-9	1	15	101	102	6	2	15	39	36	-7	5	15	50	-50	-6	0	16	22	-24	-6	2	16	72	69
-8	1	15	41	[illegible]	-12	3	15	16	-10	-6	5	15	104	-102	-5	0	16	54	-49	-5	2	16	101	-94
-7	1	15	65	-66	-11	3	15	21	-17	-5	5	15	55	53	-4	0	16	100	99	-4	2	16	94	93
-6	1	15	101	103	-10	3	15	39	38	-4	5	15	15	-9	-3	0	16	75	-77	-3	2	16	65	-64
-5	1	15	94	-99	-9	3	15	71	-71	-3	5	15	35	-36	-2	0	16	16	-10	-2	2	16	34	-33
-4	1	15	32	31	-8	3	15	35	36	-2	5	15	109	108	-1	0	16	86	80	-1	2	16	122	120
-3	1	15	35	35	-6	3	15	29	-23	-1	5	15	105	-102	0	0	16	102	-97	0	2	16	137	-135
-2	1	15	110	-112	-5	3	15	77	76	0	5	15	42	40	1	0	16	68	61	1	2	16	77	77
-1	1	15	134	130	-4	3	15	60	-62	1	5	15	57	55	2	0	16	44	42	3	2	16	58	-61
0	1	15	76	-76	-1	3	15	59	-58	2	5	15	113	-114	3	0	16	93	-89	4	2	16	92	91
1	1	15	32	-31	0	3	15	64	62	3	5	15	86	85	4	0	16	52	52	5	2	16	70	-67
2	1	15	111	108	1	3	15	23	-18	4	5	15	21	-19	5	0	16	19	-12	-11	3	16	42	-38
3	1	15	119	-115	2	3	15	24	-24	-8	6	15	67	64	-12	1	16	62	62	-10	3	16	73	68
4	1	15	41	44	3	3	15	37	39	-7	6	15	95	-96	-11	1	16	90	-91	-9	3	16	76	-75
5	1	15	21	21	4	3	15	23	-27	-6	6	15	61	64	-10	1	16	57	56	-8	3	16	41	40
6	1	15	78	-75	5	3	15	16	14	-5	6	15	14	11	-8	1	16	59	-57	-7	3	16	44	41

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	3	16	106	-104	1	5	16	53	52	-1	2	17	110	-108	-10	0	18	142	141	-6	3	18	46	51
-5	3	16	89	88	2	5	16	51	-51	0	2	17	78	81	-9	0	18	121	-122	-5	3	18	66	67
-4	3	16	11	-4	-7	6	16	75	-73	2	2	17	60	-60	-8	0	18	40	37	-4	3	18	131	-138
-3	3	16	53	-52	-6	6	16	32	29	3	2	17	96	98	-7	0	18	51	52	-3	3	16	128	137
-2	3	16	97	97	-5	6	16	23	21	4	2	17	85	-86	-6	0	18	159	-159	-2	3	16	62	-65
-1	3	16	60	-59	-4	6	16	58	-56	-10	3	17	16	4	-5	0	18	140	146	-1	3	18	29	-32
0	3	16	29	-27	-3	6	16	65	67	-5	3	17	22	23	-4	0	18	61	-65	0	3	18	92	95
1	3	16	71	70	-2	6	16	16	-9	-4	3	17	37	-38	-3	0	18	35	-37	1	3	18	102	-107
2	3	16	59	-60	-1	6	16	59	-60	-3	3	17	34	38	-2	0	18	129	134	-7	4	18	36	-34
3	3	16	37	34	0	6	16	61	62	-2	3	17	16	-19	-1	0	18	131	-142	-6	4	15	35	35
4	3	16	35	32	-11	1	17	72	-70	-1	3	17	18	-16	0	0	18	63	68	-5	4	18	16	-17
-10	4	16	58	57	-10	1	17	55	57	0	3	17	42	45	2	0	18	96	-98	-4	4	18	31	-27
-9	4	16	88	-89	-8	1	17	71	-74	1	3	17	58	-59	3	0	18	93	99	-3	4	16	67	67
-8	4	15	99	94	-7	1	17	122	122	2	3	17	32	33	-10	1	18	14	3	-2	4	18	63	-65
-7	4	16	42	-42	-6	1	17	78	-77	3	3	17	12	9	-9	1	18	13	10	-1	4	18	28	29
-6	4	16	54	-54	-5	1	17	12	-6	-9	4	17	67	-66	-6	1	18	33	-33	0	4	18	34	33
-5	4	16	112	112	-4	1	17	81	82	-8	4	17	32	26	-5	1	18	48	50	-4	5	16	17	9
-4	4	16	121	-121	-3	1	17	118	-117	-6	4	17	85	-68	-4	1	18	43	-47	-3	5	16	35	-32
-3	4	16	64	64	-2	1	17	92	94	-5	4	17	95	91	-2	1	18	46	49	-9	1	19	66	-66
-2	4	16	37	39	0	1	17	81	-82	-4	4	17	48	-44	-1	1	18	58	-61	-8	1	19	63	65
-1	4	16	115	-120	1	1	17	116	115	-3	4	17	20	-20	0	1	18	49	54	-7	1	19	29	-27
0	4	16	151	154	2	1	17	72	-76	-2	4	17	77	81	1	1	18	15	-18	-6	1	19	22	-21
1	4	16	90	-90	3	1	17	19	15	-1	4	17	93	-96	2	1	18	37	-34	-5	1	19	50	56
2	4	16	22	-18	4	1	17	41	47	0	4	17	52	53	-10	2	18	18	-16	-4	1	19	58	-63
3	4	16	83	84	-11	2	17	14	4	2	4	17	62	-65	-9	2	18	[illegible]	10	-3	1	19	37	37
-8	5	16	42	-39	-10	2	17	42	42	-8	5	17	54	58	-5	2	18	[illegible]	-23	-2	1	19	31	33
-7	5	16	52	52	-9	2	17	84	-87	-7	5	17	107	-108	-4	2	18	16	19	-1	1	19	74	-76
-6	5	16	30	-32	-8	2	17	94	93	-6	5	17	81	84	-3	2	18	24	-28	0	1	19	70	73
-5	5	16	24	24	-7	2	17	25	-25	-5	5	17	28	-31	0	2	18	34	-33	1	1	19	30	-29
-4	5	16	31	31	-6	2	17	82	-81	-4	5	17	46	-43	1	2	18	40	43	-8	2	19	39	39
-3	5	16	75	-75	-5	2	17	126	125	-3	5	17	83	88	2	2	18	28	-31	-7	2	19	86	-69
-2	5	16	54	63	-4	2	17	94	-94	-2	5	17	70	-73	-9	3	18	59	-52	-6	2	19	83	83
-1	5	16	22	-23	-3	2	17	22	21	-1	5	17	23	16	-8	3	16	123	124	-5	2	19	32	-33
0	5	16	14	-14	-2	2	17	54	51	0	5	17	62	59	-7	3	18	128	-134	-4	2	19	32	-29

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
-3	2	19	86	90	-6	3	19	15	-3	-6	0	20	28	23	-2	0	20	36	-39	-4	1	20	54	59
-2	2	19	97	-99	-4	3	19	20	14	-5	0	20	58	60	-7	1	20	28	26	-3	1	20	36	-37
-1	2	19	46	49	-2	3	19	20	-13	-4	0	20	103	-108	-6	1	20	32	30	-5	2	20	43	-44
0	2	19	30	27	-7	0	20	89	-87	-3	0	20	114	116	-5	1	20	61	-63	-3	2	20	19	12

APPENDIX C

Observed and calculated structure factors for $C_{22}H_{19}O_4P$.

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
3	0	0	104	-117	14	2	0	7	6	7	5	0	15	15	-6	1	1	26	-25	5	2	1	26	-28
4	0	0	6	-5	1	3	0	29	-30	8	5	0	19	-20	-5	1	1	16	-15	6	2	1	16	17
5	0	0	12	11	2	3	0	3	3	9	5	0	12	-12	-4	1	1	61	-63	7	2	1	3	2
6	0	0	66	-63	3	3	0	21	20	10	5	0	5	6	-3	1	1	46	-48	9	2	1	40	-39
7	0	0	8	8	4	3	0	44	-41	11	5	0	21	21	-2	1	1	59	-63	10	2	1	20	21
8	0	0	40	40	5	3	0	49	-46	0	6	0	5	-5	-1	1	1	65	70	12	2	1	14	-13
9	0	0	9	-8	6	3	0	3	-4	2	6	0	17	18	1	1	1	109	-121	13	2	1	9	-5
10	0	0	31	-31	7	3	0	21	22	3	6	0	17	16	2	1	1	68	68	14	2	1	14	14
11	0	0	10	-9	8	3	0	31	29	4	6	0	57	-58	3	1	1	49	49	-14	3	1	5	-6
12	0	0	20	19	9	3	0	47	-46	5	6	0	18	-19	5	1	1	13	12	-13	3	1	4	4
14	0	0	11	-10	10	3	0	14	-15	6	6	0	13	13	6	1	1	5	-3	-12	3	1	4	2
2	1	0	4	-4	11	3	0	22	21	7	6	0	20	20	7	1	1	63	62	-11	3	1	9	-8
3	1	0	16	-15	12	3	0	27	26	8	6	0	10	10	8	1	1	8	9	-10	3	1	11	9
4	1	0	20	-18	13	3	0	8	-8	9	6	0	17	-17	9	1	1	40	-39	-9	3	1	13	13
5	1	0	31	28	0	4	0	41	-43	10	6	0	38	39	10	1	1	22	-21	-8	3	1	6	7
7	1	0	32	-28	1	4	0	6	6	12	6	0	14	-13	11	1	1	8	7	-7	3	1	9	-10
8	1	0	19	-17	2	4	0	42	41	1	7	0	6	5	12	1	1	5	6	-6	3	1	36	-36
9	1	0	19	17	3	4	0	57	-55	2	7	0	13	-12	13	1	1	5	2	-5	3	1	6	-5
11	1	0	9	10	4	4	0	16	13	3	7	0	8	-8	-14	2	1	9	9	-4	3	1	25	23
12	1	0	7	-8	5	4	0	24	22	4	7	0	6	-5	-12	2	1	31	-32	-3	3	1	14	11
13	1	0	5	-5	6	4	0	19	19	6	7	0	13	13	-10	2	1	22	22	-2	3	1	57	57
14	1	0	8	8	7	4	0	7	-9	8	7	0	9	-9	-9	2	1	11	-8	-1	3	1	19	-17
0	2	0	35	-33	8	4	0	27	-27	1	8	0	14	-16	-7	2	1	15	-14	0	3	1	53	-50
1	2	0	9	8	10	4	0	26	27	3	8	0	5	-4	-6	2	1	14	-13	1	3	1	76	75
2	2	0	50	48	11	4	0	18	-19	4	8	0	4	-4	-5	2	1	5	4	2	3	1	23	-22
3	2	0	7	8	12	4	0	8	8	6	8	0	18	18	-4	2	1	32	-35	3	3	1	53	-51
4	2	0	33	32	13	4	0	5	-6	7	8	0	6	7	-3	2	1	53	-52	4	3	1	34	32
5	2	0	15	-13	14	4	0	13	12	-14	1	1	5	6	-2	2	1	51	50	5	3	1	19	-18
6	2	0	12	11	1	5	0	30	-30	-13	1	1	27	28	-1	2	1	115	122	6	3	1	39	37
7	2	0	8	7	2	5	0	18	-17	-11	1	1	18	-19	0	2	1	22	-22	8	3	1	13	12
9	2	0	8	-8	3	5	0	17	-16	-10	1	1	23	-24	1	2	1	26	25	9	3	1	21	21
10	2	0	36	-35	4	5	0	15	14	-9	1	1	23	25	2	2	1	31	30	10	3	1	40	-39
11	2	0	13	-12	5	5	0	13	-13	-8	1	1	9	11	3	2	1	37	35	12	3	1	5	5
12	2	0	9	9	6	5	0	10	-9	-7	1	1	15	11	4	2	1	48	-49	13	3	1	12	-11

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	3	1	6	6	-9	5	1	16	-17	4	6	1	25	25	2	8	1	12	-13	-11	1	2	7	9
-14	4	1	10	10	-8	5	1	16	16	5	6	1	4	3	3	8	1	12	-13	-10	1	2	6	-6
-13	4	1	4	3	-7	5	1	18	17	6	6	1	9	-10	4	8	1	6	8	-9	1	2	11	-11
-12	4	1	7	-6	-5	5	1	5	4	7	6	1	36	-36	5	8	1	7	7	-8	1	2	41	40
-11	4	1	15	-15	-4	5	1	40	-40	8	6	1	10	-10	7	8	1	10	-10	-7	1	2	44	-43
-10	4	1	20	20	-3	5	1	21	21	9	6	1	13	12	8	8	1	5	5	-6	1	2	32	34
-9	4	1	21	-20	-2	5	1	3	3	12	6	1	6	5	-14	0	2	21	21	-5	1	2	35	35
-8	4	1	50	-52	-1	5	1	8	5	-11	7	1	8	9	-13	0	2	20	20	-4	1	2	7	7
-7	4	1	19	-16	1	5	1	14	14	-9	7	1	25	-26	-12	0	2	23	-25	-3	1	2	59	-63
-6	4	1	37	37	2	5	1	14	-14	-8	7	1	7	8	-11	0	2	16	-16	-2	1	2	121	-127
-5	4	1	17	11	3	5	1	9	-8	-7	7	1	19	18	-10	0	2	24	25	-1	1	2	12	-12
-4	4	1	25	-24	4	5	1	6	5	-6	7	1	13	13	-9	0	2	46	47	0	1	2	31	-32
-3	4	1	18	15	5	5	1	5	6	-5	7	1	9	-9	-8	0	2	9	-4	1	1	2	96	102
-2	4	1	58	57	6	5	1	9	-10	-4	7	1	6	2	-7	0	2	5	3	2	1	2	57	58
-1	4	1	51	47	7	5	1	15	-14	-3	7	1	37	37	-6	0	2	15	-13	3	1	2	20	17
0	4	1	52	-52	8	5	1	16	-16	-2	7	1	20	-19	-5	0	2	8	8	5	1	2	8	6
1	4	1	22	-22	9	5	1	15	15	-1	7	1	9	-9	-4	0	2	42	-46	6	1	2	12	14
2	4	1	18	18	10	5	1	12	11	1	7	1	4	4	-3	0	2	97	-112	8	1	2	18	-19
3	4	1	21	22	11	5	1	15	-16	2	7	1	18	19	-2	0	2	11	11	11	1	2	11	-11
4	4	1	5	5	12	5	1	4	4	3	7	1	26	-27	2	0	2	55	58	13	1	2	20	20
5	4	1	16	-17	13	5	1	9	9	4	7	1	31	-32	3	0	2	20	20	14	1	2	4	3
6	4	1	20	19	-11	6	1	8	-8	5	7	1	15	16	4	0	2	45	-44	-14	2	2	17	-14
7	4	1	10	11	-10	6	1	11	-12	6	7	1	16	16	5	0	2	36	-36	-13	2	2	10	11
8	4	1	29	-28	-9	6	1	17	17	8	7	1	18	-19	6	0	2	9	11	-12	2	2	14	-15
9	4	1	35	-34	-8	6	1	11	12	9	7	1	7	-7	7	0	2	93	92	-11	2	2	7	6
10	4	1	18	16	-7	6	1	13	-11	10	7	1	18	10	8	0	2	29	-29	-10	2	2	10	10
11	4	1	11	11	-6	6	1	8	-8	-8	8	1	16	15	9	0	2	29	-30	-9	2	2	19	20
12	4	1	8	-8	-5	6	1	24	-25	-6	8	1	9	-8	10	0	2	39	39	-8	2	2	4	3
13	4	1	20	-20	-4	6	1	5	3	-5	8	1	13	-13	11	0	2	6	6	-7	2	2	6	-6
14	4	1	6	7	-3	6	1	18	18	-4	8	1	6	5	13	0	2	5	-7	-6	2	2	20	20
-13	5	1	10	-11	-2	6	1	9	9	-3	8	1	5	4	14	0	2	13	-13	-5	2	2	22	21
-12	5	1	8	-10	0	6	1	5	5	-2	8	1	5	-3	-14	1	2	16	19	-4	2	2	42	-42
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC
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-4	2	16	9	-10	2	3	16	16	-16	-6	1	17	7	-7										

APPENDIX D

Observed and calculated structure factors for $C_{14}H_{15}O_4P$.

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	0	7	6	10	3	0	13	13	9	0	1	15	15	0	2	1	11	-14	1	4	1	18	-19
4	0	0	38	-37	0	4	0	10	-12	11	0	1	10	-8	1	2	1	44	43	2	4	1	13	12
6	0	0	40	-38	1	4	0	20	20	-12	1	1	14	-15	2	2	1	97	96	3	4	1	12	-12
10	0	0	27	-27	3	4	0	5	6	-11	1	1	7	8	3	2	1	12	12	5	4	1	9	-6
12	0	0	7	-7	4	4	0	5	4	-9	1	1	19	-21	4	2	1	23	-23	6	4	1	24	-24
1	1	0	92	-99	5	4	0	7	-7	-8	1	1	61	63	5	2	1	36	-35	7	4	1	30	31
2	1	0	54	54	6	4	0	22	20	-7	1	1	37	-37	6	2	1	18	-19	8	4	1	6	-3
3	1	0	109	111	7	4	0	29	29	-6	1	1	49	-49	8	2	1	10	-9	10	4	1	22	23
4	1	0	26	27	10	4	0	9	-5	-5	1	1	53	-53	10	2	1	12	11	-9	5	1	16	-15
6	1	0	18	17	11	4	0	13	-14	-4	1	1	9	-10	-11	3	1	10	11	-8	5	1	9	-8
7	1	0	34	-35	1	5	0	8	-7	-3	1	1	56	-60	-9	3	1	10	-10	-5	5	1	7	6
8	1	0	12	-13	2	5	0	26	-27	-2	1	1	33	37	-7	3	1	22	22	-4	5	1	17	18
9	1	0	6	8	4	5	0	11	10	-1	1	1	76	77	-6	3	1	32	-32	-3	5	1	16	-17
10	1	0	14	15	5	5	0	8	-8	0	1	1	3	-3	-5	3	1	20	19	-2	5	1	9	-9
11	1	0	9	9	6	5	0	20	-20	1	1	1	68	70	-4	3	1	14	-14	-1	5	1	22	22
12	1	0	7	5	7	5	0	15	16	2	1	1	53	-57	-3	3	1	19	-19	0	5	1	10	-11
0	2	0	34	35	8	5	0	14	-13	3	1	1	29	29	-2	3	1	40	40	1	5	1	6	7
1	2	0	33	-31	0	6	0	9	-9	4	1	1	23	22	-1	3	1	28	26	2	5	1	17	-18
2	2	0	118	-116	3	6	0	12	10	5	1	1	5	4	0	3	1	11	11	6	5	1	12	-11
3	2	0	90	-89	4	6	0	20	21	6	1	1	10	9	1	3	1	24	-24	7	5	1	16	15
4	2	0	43	-43	5	6	0	22	-23	8	1	1	25	-25	2	3	1	30	-31	9	5	1	6	-7
5	2	0	15	-15	7	6	0	11	10	9	1	1	13	-13	3	3	1	30	-29	-8	6	1	7	6
6	2	0	34	33	8	6	0	12	-12	12	1	1	11	7	4	3	1	37	36	-7	6	1	11	11
7	2	0	21	23	1	7	0	12	11	-12	2	1	8	-9	5	3	1	5	-3	-6	6	1	10	-11
8	2	0	30	31	3	7	0	14	-13	-11	2	1	8	5	7	3	1	22	23	-5	6	1	11	-12
9	2	0	15	17	4	7	0	19	18	-10	2	1	12	11	8	3	1	10	10	-4	6	1	18	19
11	2	0	16	-16	-11	0	1	24	24	-9	2	1	17	-17	9	3	1	16	-15	-2	6	1	7	-6
1	3	0	10	-11	-9	0	1	39	-38	-8	2	1	7	-7	-10	4	1	20	19	-1	6	1	29	29
2	3	0	7	-6	-7	0	1	7	6	-6	2	1	13	-14	-7	4	1	14	-13	0	6	1	21	-22
3	3	0	39	40	-5	0	1	62	61	-5	2	1	53	53	-6	4	1	19	-20	1	6	1	7	-9
4	3	0	15	15	-3	0	1	61	-63	-4	2	1	22	-20	-5	4	1	17	15	3	6	1	13	-13
5	3	0	10	-10	3	0	1	47	45	-3	2	1	55	-55	-3	4	1	17	-17	4	6	1	23	24
7	3	0	12	-10	5	0	1	13	-14	-2	2	1	70	69	-1	4	1	19	21	-5	7	1	13	12
8	3	0	18	-16	7	0	1	5	2	-1	2	1	33	-34	0	4	1	26	-26	-4	7	1	23	23

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
-3	7	1	15	-15	7	1	2	34	33	-1	3	2	11	12	-2	5	2	20	-21	-1	0	3	98	99
-2	7	1	13	-12	8	1	2	19	20	0	3	2	22	21	-1	5	2	25	25	1	0	3	34	-33
0	7	1	6	-5	9	1	2	18	-18	2	3	2	61	59	0	5	2	12	-11	3	0	3	27	-27
2	7	1	12	10	11	1	2	9	-8	3	3	2	30	30	1	5	2	8	-8	5	0	3	11	10
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-12	0	2	12	-12	-10	2	2	17	16	5	3	2	8	10	3	5	2	11	-11	9	0	3	16	-16
-10	0	2	22	23	-9	2	2	15	16	6	3	2	25	-26	4	5	2	12	-11	11	0	3	18	18
-8	0	2	5	-5	-8	2	2	15	-14	7	3	2	26	27	5	5	2	19	-20	-12	1	3	11	11
-6	0	2	10	11	-7	2	2	7	-5	10	3	2	6	-5	6	5	2	6	6	-11	1	3	12	-12
-4	0	2	47	48	-6	2	2	25	-24	11	3	2	11	-8	7	5	2	10	-11	-9	1	3	12	13
-2	0	2	24	-25	-4	2	2	28	28	-11	4	2	9	-10	8	5	2	9	6	-8	1	3	29	-32
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6	0	2	13	13	-1	2	2	47	47	-5	4	2	36	-38	-5	6	2	22	-22	-5	1	3	31	31
8	0	2	9	-9	0	2	2	28	29	-4	4	2	27	26	-4	6	2	15	-16	-4	1	3	27	30
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-11	1	2	13	-11	2	2	2	11	12	-2	4	2	30	-31	-2	6	2	17	-16	-2	1	3	19	-21
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-7	1	2	49	49	6	2	2	12	-12	3	4	2	10	-9	6	6	2	7	6	2	1	3	26	27
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-3	1	2	18	-20	10	2	2	14	14	7	4	2	7	7	-1	7	2	6	-8	7	1	3	21	-23
-2	1	2	45	-46	11	2	2	7	5	9	4	2	9	-7	0	7	2	12	-12	8	1	3	25	25
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1	1	2	73	-73	-7	3	2	8	-9	-9	5	2	11	12	4	7	2	10	-8	-10	2	3	23	-22
2	1	2	45	-43	-6	3	2	26	27	-8	5	2	31	-33	-11	0	3	15	-16	-9	2	3	9	10
3	1	2	5	-5	-5	3	2	54	-52	-7	5	2	8	-9	-9	0	3	29	25	-7	2	3	10	11
4	1	2	9	-10	-4	3	2	4	-5	-5	5	2	6	-9	-7	0	3	45	-44	-6	2	3	14	15
5	1	2	29	-28	-3	3	2	29	-29	-4	5	2	13	14	-5	0	3	48	-47	-5	2	3	14	14
6	1	2	15	-15	-2	3	2	27	-27	-3	5	2	25	25	-3	0	3	83	-82	-4	2	3	35	34

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
-3	2	3	22	21	-10	4	3	17	-19	0	6	3	16	16	6	1	4	9	9	-1	3	4	15	15
-1	2	3	58	58	-9	4	3	17	-18	2	6	3	19	21	7	1	4	12	-12	0	3	4	12	-11
0	2	3	21	21	-7	4	3	10	9	3	6	3	10	11	8	1	4	22	-22	1	3	4	34	-35
1	2	3	62	-61	-6	4	3	18	18	4	6	3	22	-24	9	1	4	14	15	2	3	4	50	-48
2	2	3	54	-54	-4	4	3	17	-17	-6	7	3	10	-9	-11	2	4	24	25	3	3	4	12	13
3	2	3	23	-22	-2	4	3	20	-20	-5	7	3	14	-16	-10	2	4	22	-21	4	3	4	6	5
4	2	3	8	-9	-1	4	3	10	-10	-4	7	3	11	-11	-9	2	4	19	-18	5	3	4	21	-21
5	2	3	12	12	0	4	3	8	-7	-3	7	3	10	9	-7	2	4	21	20	6	3	4	36	36
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8	2	3	10	9	4	4	3	10	-11	0	7	3	10	9	-4	2	4	12	11	9	3	4	10	10
9	2	3	14	-13	5	4	3	12	11	2	7	3	10	-10	-3	2	4	6	8	-10	4	4	6	7
10	2	3	9	-9	6	4	3	27	26	-12	0	4	26	26	-2	2	4	10	-11	-9	4	4	17	-18
11	2	3	10	9	7	4	3	11	-12	-10	0	4	12	-13	-1	2	4	67	-65	-8	4	4	6	-6
-13	3	3	15	-16	9	4	3	13	-13	-4	0	4	24	-24	0	2	4	22	21	-7	4	4	8	-8
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-9	3	3	16	15	-9	5	3	7	8	0	0	4	55	54	2	2	4	28	26	-4	4	4	13	-12
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-4	3	3	6	5	-4	5	3	21	-22	-13	1	4	12	-13	6	2	4	19	19	0	4	4	22	-21
-3	3	3	17	17	-3	5	3	17	19	-11	1	4	8	7	7	2	4	16	17	1	4	4	50	48
-1	3	3	29	-29	1	5	3	19	-20	-9	1	4	25	26	8	2	4	17	-18	3	4	4	9	10
0	3	3	24	22	3	5	3	9	8	-8	1	4	6	7	9	2	4	28	28	4	4	4	12	-10
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4	3	3	25	-25	-7	6	3	7	-6	-3	1	4	36	36	-9	3	4	6	4	9	4	4	11	10
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6	3	3	12	-12	-5	6	3	17	16	0	1	4	6	-3	-6	3	4	16	-17	-9	5	4	14	-14
7	3	3	17	-17	-4	6	3	17	-16	1	1	4	17	-19	-5	3	4	16	16	-8	5	4	15	15
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-12	4	3	14	14	-1	6	3	23	24	4	1	4	6	-7	-2	3	4	45	44	-5	5	4	22	22

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	5	4	21	-21	5	0	5	10	-9	-4	2	5	17	15	0	4	5	36	-36	0	7	5	15	-13
-3	5	4	15	-14	7	0	5	12	10	-3	2	5	5	5	1	4	5	24	-23	-12	0	6	35	-35
-2	5	4	20	19	-14	1	5	10	11	-2	2	5	49	47	2	4	5	8	-9	-8	0	6	18	18
-1	5	4	13	-13	-12	1	5	10	-12	0	2	5	46	-44	3	4	5	12	-13	-6	0	6	7	-7
0	5	4	13	14	-11	1	5	17	17	1	2	5	20	18	4	4	5	27	27	-4	0	6	16	18
1	5	4	5	-5	-10	1	5	26	-26	2	2	5	12	12	6	4	5	11	-11	-2	0	6	42	39
2	5	4	22	-22	-9	1	5	7	6	3	2	5	7	-4	7	4	5	7	7	0	0	6	22	-23
3	5	4	19	20	-8	1	5	27	27	4	2	5	17	16	-9	5	5	10	-7	2	0	6	28	27
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5	5	4	7	-3	-6	1	5	19	19	6	2	5	7	-7	-7	5	5	17	17	6	0	6	8	-8
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-1	6	4	23	-24	2	1	5	34	31	-3	3	5	55	-54	2	5	5	6	6	-2	1	6	45	-44
0	6	4	10	-9	3	1	5	10	-9	-2	3	5	8	8	3	5	5	31	-30	-1	1	6	8	-9
2	6	4	16	-16	4	1	5	14	14	-1	3	5	33	32	4	5	5	6	-4	1	1	6	23	-22
3	6	4	18	18	5	1	5	12	-12	0	3	5	30	-27	7	5	5	11	9	2	1	6	29	29
-4	7	4	15	-13	6	1	5	9	8	1	3	5	55	54	-6	6	5	19	-19	3	1	6	9	-9
-3	7	4	17	-16	7	1	5	13	12	2	3	5	18	-19	-5	6	5	13	-12	4	1	6	22	22
0	7	4	9	9	8	1	5	26	-26	3	3	5	15	-15	-4	6	5	16	14	7	1	6	11	10
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-13	0	5	13	-13	-13	2	5	15	-18	-10	4	5	22	23	-1	6	5	21	[illegible]	-10	2	6	13	11
-11	0	5	38	40	-11	2	5	19	17	-8	4	5	6	6	0	6	5	15	-15	-9	2	6	21	21
-9	0	5	21	-21	-10	2	5	15	14	-7	4	5	10	-10	3	6	5	6	6	-8	2	6	19	19
-7	0	5	21	-22	-9	2	5	7	6	-6	4	5	25	-25	4	6	5	23	22	-7	2	6	9	-11
-5	0	5	51	-50	-8	2	5	23	-23	-5	4	5	27	27	5	6	5	7	6	-6	2	6	30	-29
-3	0	5	35	34	-7	2	5	7	-6	-4	4	5	23	23	-5	7	5	14	15	-5	2	6	18	-17
-1	0	5	14	-14	-6	2	5	36	-36	-3	4	5	15	-15	-4	7	5	13	12	-4	2	6	12	-11
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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	2	6	8	7	5	4	6	15	15	-11	1	7	23	-24	-11	3	7	7	6	-6	6	7	11	13
-1	2	6	54	51	-11	5	6	8	7	-10	1	7	7	9	-10	3	7	19	20	-4	6	7	16	-16
0	2	6	21	-20	-10	5	6	7	5	-8	1	7	24	-24	-9	3	7	21	20	0	6	7	6	6
1	2	6	7	-7	-9	5	6	13	12	-6	1	7	23	-22	-8	3	7	8	-9	-12	0	8	66	65
3	2	6	[illegible]	-5	-8	5	6	19	-18	-5	1	7	39	37	-7	3	7	20	-20	-10	0	8	6	5
5	2	6	12	12	-7	5	6	6	-4	-4	1	7	67	67	-6	3	7	11	-10	-8	0	8	18	17
7	2	6	6	-5	-6	5	6	17	16	-3	1	7	56	53	-4	3	7	6	-6	-4	0	8	35	-33
9	2	6	6	-5	-5	5	6	8	-8	-2	1	7	6	4	-3	3	7	23	21	-2	0	8	24	-24
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-3	3	6	[illegible]	-8	-5	6	6	27	-27	8	1	7	7	8	-8	4	7	9	6	-11	1	8	11	-13
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1	3	6	33	33	-1	6	6	10	9	-12	2	7	9	9	-6	4	7	21	22	-9	1	8	34	34
2	3	6	33	32	0	6	6	14	14	-11	2	7	27	-27	-5	4	7	14	-16	-8	1	8	16	16
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6	3	6	16	-17	4	6	6	8	-10	-9	2	7	8	-8	-3	4	7	5	-5	-6	1	8	10	11
7	3	6	10	-9	-3	7	6	6	8	-8	2	7	7	7	-2	4	7	13	-14	-5	1	8	10	-9
8	3	6	6	[illegible]	-2	7	6	8	-7	-7	2	7	17	17	0	4	7	20	20	-4	1	8	17	-16
-11	4	6	11	-12	-13	0	7	16	16	-6	2	7	20	20	1	4	7	10	11	-3	1	8	9	9
-10	4	6	8	-7	-11	0	7	29	-28	-5	2	7	12	-12	4	4	7	10	-9	-2	1	8	16	16
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-7	4	6	24	25	-3	0	7	35	-34	0	2	7	24	23	-3	5	7	13	13	1	1	8	6	4
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1	4	6	26	-27	-13	1	7	14	-14	8	2	7	10	5	4	5	7	7	3	-13	2	8	8	9
3	4	6	13	-9	-12	1	7	16	16	-12	3	7	9	10	-6	6	7	8	8	-12	2	8	9	6

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	2	8	13	12	-4	4	8	7	7	-10	2	9	37	37	-2	4	9	25	27	-2	2	10	21	22
-10	2	8	37	-37	-1	4	8	19	-20	-9	2	9	6	4	-1	4	9	6	6	-1	2	10	6	4
-9	2	8	35	-36	3	4	8	8	10	-8	2	9	6	6	4	4	9	9	9	0	2	10	17	-16
-8	2	8	17	-17	5	4	8	7	-6	-7	2	9	9	-9	-9	5	9	12	-11	2	2	10	14	-15
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-6	2	8	13	12	-7	5	8	8	-7	-5	2	9	6	8	-3	5	9	8	-6	5	2	10	7	6
-5	2	8	15	15	-6	5	8	17	-19	-4	2	9	15	-15	1	5	9	7	8	-12	3	10	7	5
-3	2	8	31	33	-4	5	8	20	-20	-3	2	9	18	-19	3	5	9	8	-10	-11	3	10	7	-4
-1	2	8	12	-12	0	5	8	9	12	-2	2	9	14	14	0	6	9	9	-10	-10	3	10	22	21
0	2	8	20	20	-8	6	8	6	3	-1	2	9	18	-17	-12	0	10	26	-24	-7	3	10	11	13
2	2	8	[illegible]	10	-5	6	8	9	10	0	2	9	8	-8	-10	0	10	13	13	-6	3	10	6	-6
3	2	8	10	10	-4	6	8	8	-9	2	2	9	13	-12	-8	0	10	10	-11	-5	3	10	17	18
4	2	8	8	-8	-3	6	8	7	-9	3	2	9	9	10	-2	0	10	21	21	-4	3	10	11	9
5	2	8	7	-8	0	6	8	6	-9	-13	3	9	13	12	0	0	10	15	-15	-3	3	10	7	-4
-13	3	8	7	-7	-9	0	9	6	-7	-10	3	9	7	-6	4	0	10	21	21	-2	3	10	12	-13
-12	3	8	14	-12	-7	0	9	7	6	-9	3	9	17	-18	-13	1	10	16	15	-1	3	10	9	-10
-9	3	8	19	19	-5	0	9	19	18	-8	3	9	14	16	-12	1	10	6	-8	0	3	10	7	-7
-8	3	8	14	13	-1	0	9	15	-16	-7	3	9	7	6	-11	1	10	14	-13	1	3	10	9	11
-7	3	8	15	-16	1	0	9	17	18	-5	3	9	13	14	-10	1	10	12	-13	2	3	10	8	9
-4	3	8	16	-16	3	0	9	17	17	-4	3	9	7	3	-9	1	10	14	-13	3	3	10	8	-10
-3	3	8	8	8	5	0	9	14	-15	-3	3	9	20	-21	-8	1	10	12	-11	-11	4	10	19	-18
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-1	3	8	11	12	-12	1	9	10	-11	0	3	9	9	11	-5	1	10	17	16	-7	4	10	16	15
1	3	8	13	-14	-11	1	9	10	9	1	3	9	15	17	-4	1	10	12	13	-6	4	10	10	-10
2	3	8	18	-19	-8	1	9	10	9	2	3	9	6	-7	-3	1	10	23	-24	-4	4	10	11	-13
4	3	8	11	-14	-7	1	9	12	11	-12	4	9	14	-13	1	1	10	14	16	-1	4	10	9	9
6	3	8	8	9	-5	1	9	10	12	-11	4	9	9	-6	2	1	10	7	8	-8	5	10	14	-14
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-9	4	8	6	-5	2	1	9	11	-11	-6	4	9	24	-23	-9	2	10	12	11	0	5	10	6	-7
-7	4	8	8	-8	6	1	9	14	14	-5	4	9	21	24	-7	2	10	14	14	1	5	10	6	6
-6	4	8	27	29	-12	2	9	10	-10	-4	4	9	3	-8	-5	2	10	9	-9	-11	0	11	9	-8
-5	4	8	24	24	-11	2	9	15	15	-3	4	9	11	14	-3	2	10	23	-25	-7	0	11	6	7

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	0	11	13	-14	-1	2	11	15	15	2	0	12	7	5	1	3	12	6	1	-9	4	13	9	-6
-1	0	11	32	33	1	2	11	6	-6	-9	1	12	11	11	-7	4	12	17	-17	-6	4	13	7	-7
1	0	11	7	-7	3	2	11	10	-9	-7	1	12	9	-9	-6	4	12	10	9	-12	0	14	8	-7
3	0	11	13	-13	-11	3	11	6	-7	-6	1	12	9	9	-2	4	12	7	3	-10	0	14	13	13
5	0	11	8	10	-10	3	11	14	14	-4	1	12	10	-10	-4	5	12	6	-5	-8	0	14	9	7
-9	1	11	7	7	-9	3	11	9	7	-3	1	12	24	26	-11	0	13	18	[illegible]	-4	0	14	10	-10
-8	1	11	14	-13	-8	3	11	12	-14	-1	1	12	12	-13	-3	0	13	8	[illegible]	-9	1	14	10	-10
-5	1	11	20	-20	-5	3	11	8	-9	1	1	12	8	-8	-1	0	13	17	-19	-8	1	14	11	12
-4	1	11	26	28	-4	3	11	7	-7	2	1	12	6	-1	-12	1	13	9	-7	-5	1	14	8	9
-3	1	11	11	-11	-3	3	11	21	21	-12	2	12	10	6	[illegible]	1	13	7	-5	-2	1	14	7	-9
-2	1	11	12	-12	2	3	11	10	14	-11	2	12	8	7	-8	1	13	11	12	-1	1	14	7	-6
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0	1	11	10	-11	-6	4	11	18	19	-7	2	12	15	-15	-2	1	13	7	6	-10	2	14	6	-3
2	1	11	21	11	-2	4	11	14	-14	-6	2	12	17	18	1	1	13	6	0	-7	2	14	6	3
-13	2	11	10	9	-9	5	11	11	10	-5	2	12	8	8	-12	2	13	12	-10	-2	2	14	7	8
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-8	2	11	12	-11	0	5	11	7	-4	-10	3	12	18	-19	-5	2	13	7	7	-3	0	15	8	-4
-7	2	11	9	7	-12	0	12	8	7	-7	3	12	11	-12	-4	2	13	[illegible]	-3	-6	1	15	10	-10
-6	2	11	11	9	-10	0	12	17	-17	-6	3	12	13	12	-3	2	13	6	6	-4	1	15	10	10
-5	2	11	9	-11	-6	0	12	11	10	-5	3	12	7	-8	-11	3	13	7	9	-7	2	15	9	8
-4	2	11	9	9	-4	0	12	17	-19	-4	3	12	11	-10	-4	3	13	7	3	-8	0	16	8	-6
-2	2	11	6	-6	0	0	12	25	26	0	3	12	8	4	-3	3	13	7	-9	-6	0	16	10	6

APPENDIX E

Observed and calculated structure factors for $C_{16}H_{14}O_2$.

H	K	L	FO	FC
2	0	0	152	152
4	0	0	61	62
6	0	0	24	24
2	1	0	108	-111
4	1	0	23	23
8	1	0	18	-19
2	2	0	280	-289
4	2	0	21	-18
2	3	0	195	-196
8	3	0	14	7
0	4	0	47	-49
2	4	0	127	-126
4	4	0	41	41
6	4	0	20	-23
2	5	0	12	12
4	5	0	90	91
0	6	0	93	91
2	6	0	46	45
4	6	0	92	95
2	7	0	14	-16
6	7	0	33	-37
0	8	0	50	-50
2	8	0	25	-25
6	6	0	35	-37
2	9	0	22	22
4	9	0	16	-12
6	9	0	14	-13
0	10	0	47	44
6	10	0	17	-17
2	11	0	19	21
6	11	0	16	13
2	12	0	20	-23
2	13	0	33	-37
4	13	0	19	-29
0	14	0	20	17
4	14	0	18	17
2	16	0	16	-14
2	1	1	107	109
4	1	1	10	-12
5	1	1	25	27
1	2	1	43	-44
2	2	1	20	-16
4	2	1	35	-36
1	3	1	43	-43
2	3	1	20	-22
3	3	1	13	-10
4	3	1	24	-21
5	3	1	10	-20
7	3	1	14	-14
0	4	1	81	81
1	4	1	42	43
2	4	1	88	-92
3	4	1	46	47
4	4	1	41	-42
5	4	1	17	18
1	5	1	22	22
2	5	1	82	-83
4	5	1	19	16
6	5	1	21	18
0	6	1	92	92
1	6	1	41	-40
2	6	1	29	30
3	6	1	50	-49
4	6	1	54	57
6	6	1	27	29
2	7	1	40	-37
3	7	1	12	16
4	7	1	28	30
5	7	1	13	-12
0	8	1	79	-77
1	8	1	16	13
2	8	1	51	-53
6	8	1	20	-19
1	9	1	37	-38
4	9	1	20	20
6	9	1	17	-15
1	10	1	23	22
6	10	1	15	-17
1	11	1	13	12
2	11	1	14	14
0	12	1	43	40
1	12	1	14	10
2	12	1	24	25
2	14	1	18	-16
3	14	1	12	-1
1	0	2	19	-20
2	0	2	52	-50
3	0	2	63	62
4	0	2	25	-23
6	0	2	13	11
7	0	2	22	19
1	1	2	41	42
2	1	2	35	-34
3	1	2	30	31
4	1	2	11	-6
5	1	2	29	32
0	2	2	15	15
1	2	2	61	-61
2	2	2	97	96
3	2	2	11	-17
4	2	2	16	16
5	2	2	38	-42
1	3	2	13	-15
2	3	2	69	68
3	3	2	28	-31
5	3	2	11	7
0	4	2	28	-27
1	4	2	46	-46
3	4	2	47	48
4	4	2	36	-34
6	4	2	12	9
1	5	2	28	-26
2	5	2	13	-11
3	5	2	25	-25
4	5	2	20	-20
1	6	2	38	-36
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3	6	2	62	59
4	6	2	45	-46
5	6	2	19	20
1	7	2	48	47
2	7	2	36	-37
3	7	2	16	19
4	7	2	12	16
0	8	2	16	-12
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5	8	2	19	-18
6	8	2	16	19
4	9	2	23	22
0	10	2	37	-35
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1	11	2	30	-29
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3	12	2	18	17
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3	16	2	13	-7
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2	1	3	35	36
3	1	3	54	56
4	1	3	16	-15
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6	1	3	12	13
0	2	3	63	60
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6	2	3	15	-10
1	3	3	136	-134
2	3	3	25	25
3	3	3	11	-6
4	3	3	27	-27
5	3	3	15	-17
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1	4	3	27	26
2	4	3	30	-33
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1	5	3	46	47
3	5	3	19	-16
0	6	3	27	26
1	6	3	39	37
2	6	3	17	-16
3	6	3	45	45
4	6	3	13	-9
5	6	3	24	26
2	7	3	12	8
5	7	3	19	22
7	7	3	23	24
0	8	3	13	13
1	8	3	28	-29
3	8	3	72	-26
6	8	3	23	26
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5	9	3	26	-31
6	9	3	13	-15
4	10	3	17	-16
4	11	3	24	29
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2	14	3	14	20
3	14	3	20	13
0	16	3	17	-16
0	0	4	20	-18
2	0	4	32	34
3	0	4	18	-20
4	0	4	45	47
5	0	4	23	24
6	0	4	39	41
1	1	4	25	-25
0	2	4	47	-46
2	2	4	18	17
3	2	4	16	-16
6	2	4	25	-26
1	3	4	18	-14
2	3	4	61	65
4	3	4	12	5
0	4	4	29	-26
1	4	4	18	20
2	4	4	10	-5
4	4	4	16	-16
6	4	4	12	-14
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1	6	4	13	13
4	6	4	13	-5
3	7	4	16	14
6	7	4	18	23
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1	9	4	12	-14
2	9	4	15	16
3	9	4	18	-20
5	9	4	15	-24
5	10	4	25	22
5	11	4	13	-11
2	12	4	12	-19
3	12	4	23	-25
4	12	4	13	-13
1	13	4	12	3
3	13	4	26	27
4	13	4	18	17
1	14	4	15	14
2	14	4	14	11
1	15	4	29	-31
0	2	5	44	-45
1	2	5	13	-11
2	2	5	34	-33
4	2	5	20	16
5	2	5	12	11
6	2	5	15	9
2	3	5	11	10
3	3	5	26	25
4	3	5	21	-24
0	4	5	48	48
1	4	5	42	43
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SOLUTION EQUILIBRIA OF THE METHYLDOPA-COPPER(II) SYSTEM AND THE CRYSTAL AND MOLECULAR STRUCTURES OF SELECTED COMPOUNDS

A thesis submitted to
THE UNIVERSITY OF CAPE TOWN
in fulfilment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

by

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August, 1979

SOLUTION EQUILIBRIA OF THE METHYLDOPA-COPPER(II) SYSTEM

ABSTRACT

The system copper(II) ions in aqueous solution in the presence of L-3-(3',4'-dihydroxyphenyl)-2-methylalanine (methyldopa), at 25°C and I = 0,150 mol dm^{-3} $Na^+ClO_4^-$ has been characterised using glass electrode potentiometry. Both mononuclear and oligonuclear complexes were found to occur, the former including a series of successively deprotonated species in the higher ligand to metal ratio titrations, the latter including a cyclic dimer in the 1:1 ligand to metal solutions. Interpretation of the results was facilitated by (i) ultraviolet/visible spectrophotometry of solutions containing copper(II), methyldopa or alanine or catechol at various pH's, (ii) ^{1}H NMR measurements of methyldopa in ^2H_2O solutions, (iii) glass electrode potentiometric measurements on alanine and catechol in the presence of copper(II) ions. Formation constants are given for 3 proton - and 11 copper(II) - complexes of methyldopa, 2 proton and 2 copper(II) complexes of alanine and 1 proton and 2 copper(II) complexes of catechol.

PACKING PATTERNS IN LANTHANIDE-EDTA COMPLEXES: CRYSTAL AND MOLECULAR STRUCTURES OF SODIUM TRIAQUOETHYLENEDIAMINETETRAACETATODYSPROSIUM(III) PENTAHYDRATE AND CAESIUM DIAQUOETHYLENEDIAMINETETRAACETATOYTTERBIUM(III) TRIHYDRATE

ABSTRACT

$Na^+[DyEDTA(3H_2O)]^-.5H_2O$ crystallises in the space group *Fdd*2 with a = 19,34(1), b = 35,40(2), c = 12,116(6) Å, z = 16. $Cs^+[YbEDTA(2H_2O)]^-.3H_2O$ crystallises in the space group $P2_1/c$ with a = 12,935(6), b = 8,997(5), c = 17,22(1) Å, β = 106,7(2)°, z = 4. The structures were determined by Patterson and Fourier methods and refined by full-matrix least-squares to a final R of 0,045 and 0,050 respectively. The decrease in ionic radius from Dy^{3+} to Yb^{3+} results in a change in coordination number of the Ln^{3+} ion from 9 to 8 with concomitant loss of a water molecule. The changed geometry of the lanthanide complex gives rise to a different space group.

THE CRYSTAL STRUCTURES OF A PENTA-COORDINATE PHOSPHORUS COMPOUND: 3,4,8,9-DIBENZ-5,7-DIMETHYL-1-PHENYL-2,6,10,11-TETRAOXATRICYCLO[5,3,1,$0^{1,5}$] PHOSPHA-UNDECANE AND ITS HYDROLYSIS PRODUCT: PHENYL-1-HYDROXY-1-(2'-HYDROXYPHENYL)-ETHLYLIDYNYL PHOSPHINIC ACID

ABSTRACT

Reaction of $PhPCl_2$ with o-$HOC_6H_4COCH_3$ gives an unusual tricyclic tetraoxaphospha-undecane. Crystals of this compound are monoclinic, $\underline{P}2_1/c$, with $\underline{a}$ = 13,874(7), $\underline{b}$ = 7,924(4), $\underline{c}$ = 16,572(8) Å, β = 94,5(2)°, $\underline{z}$ = 4. The geometry around the phosphorus atom is distorted trigonal bipyramidal, with the two five-membered and one six-membered rings all in apical-equatorial positions. It is postulated that permutational isomerisation in solution is unlikely for this compound due in part to its molecular rigidity. Crystals of the disubstituted phosphinic acid are monoclinic, $\underline{P}2_1/n$, with $\underline{a}$ = 13,886(7), $\underline{b}$ = 7,378(4), $\underline{c}$ = 15,280(8) Å, β = 116,9(2)°, $\underline{z}$ = 4. The phosphorus atom has the expected tetrahedral environment. O....O close contacts less than 2,76(1) Å indicate hydrogen bonding which extends throughout the lattice.

CRYSTAL STRUCTURE AND MOLECULAR CONFORMATION OF 2,3-DICYCLOPROPYL-1,4-NAPHTHOQUINONE

ABSTRACT

Crystals of the title compound are orthorhombic with *a* = 8,483(4), *b* = 18,249(9), *c* = 15,889(8) Å, space group *P*bca, *z* = 8. The quinone ring shows distinct distortions from planarity. The solution NMR spectrum of the compound at various temperatures suggest a measure of restricted rotation about the cyclopropyl - quinonoid bonds. This is partially substantiated by a conformational analysis using the method of atom pair potentials.