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SOME RECENT X-RAY STUDIES OF COORDINATION COMPOUNDS OF THE TRANSITION ELEMENTS

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CONTENTS

ABBREVIATIONS

en	ethylenediamine
NTA	nitrilotriacetate
DPM	dipivaloylmethane
diars	"diarsine", *o*-phenylenebisdimethylarsine
phen	*o*-phenanthroline

A. INTRODUCTION

The last few years have seen a considerable increase in the application of X-ray diffraction methods to the solution of structural problems in inorganic chemistry. Although the number of topics explored has been quite wide, perusal of the relevant sections in the Annual Reports of the Chemical Society of the last few years indicates that the largest portion of this effort has been concentrated in two areas; firstly, in the field of metal carbonyls and organometallic compounds, where a great variety of complex and novel structures have been elucidated and, secondly, in the field of transition element coordination compounds, where verification of stereochemistry by X-ray methods is so often required to clarify results obtained from spectroscopic and other indirect methods. It is with some of the more recent work in this latter field that the present review is concerned.

While the coordination chemist has usually been content until quite recently to use X-ray diffraction to determine solely the gross stereochemistry of molecules in which he is interested, the improvements that have taken place in experimental techniques and in methods of structure refinement, mean that individual molecular parameters can now be determined to greater accuracy, so enabling detailed considerations of bonding to be made. Obviously, with the tremendous increase of activity on the preparative side, systematic and detailed characterisations of this sort are necessary if the many factors influencing stereochemistry are to be fully understood.

From the large amount of material available, the author has selected items which probably reflect the interest of a large number of structural inorganic chemists at the present time, or will do so in the relatively near future. Thus, there is a section, (B)*, on the stereochemistry of compounds in which the metal atoms have high coordination number, *i.e.* greater than six, an area of coordination chemistry which should prove of much interest and which is overdue for the sustained application of diffraction methods, and a section, (C), on pentacoordinate transition metal complexes, a field which is undergoing rapid expansion at the present time and where some detailed considerations of bonding should soon be possible.

The two final shorter sections, (D and E), deal with coordination compounds of specific ligands. Included in D are some structural results for the new series of metal dithiolate complexes, several of which exhibit the hitherto unknown (in discrete compounds) trigonal prismatic stereochemistry, while in E the stereochemistries of β-diketone complexes, which illustrate the versatility of these ligands, are reviewed.

Space excludes discussion of more of the interesting coordination compounds which have been characterised structurally in recent years, prominent among these being complexes containing metal to metal bonds, an area in which many exciting discoveries have been made and which has owed much for its development to X-ray diffraction techniques. However, there have been several reviews of this topic during the last few years, so that this omission is remedied elsewhere.

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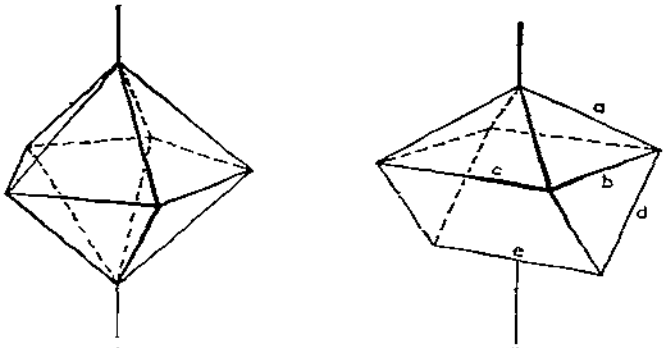
* Since the completion of this section, a comprehensive review of polyhedra with high coordination numbers has appeared: E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 21 (1967) 109.

B. STEREOCHEMISTRY OF COMPOUNDS EXHIBITING HIGH COORDINATION NUMBERS

In this section, some recent structural results on compounds in which the metal atom exhibits coordination number from seven upwards will be reviewed and discussed in terms of the anticipated configurations. Until a few years ago there was a paucity of direct structural evidence for high coordination, and what information was available was of doubtful accuracy, due to the complexity of the crystallographic problem to be solved. While the number of analyses that have been carried out to date is not large, the results obtained have been interesting and informative. It is probable that with the increasing number of investigations of compounds of the second and third transition series and the lanthanides where the greater size of the metal ions, their favourable charge, and the availability of orbitals of favourable energy make species of high coordination number more likely, more details will be revealed, and analysis of the factors affecting the stereochemistry will be made more definite. Here, attention will be confined to discrete coordination in molecules and ions (*i.e.* one metal atom involving unidentate and/or multidentate ligands). Although many examples of high coordination can be found amongst metal atom cluster compounds and in polymeric species, in the first instance it probably emphasises the wrong aspect in bonding considerations—the structure should be considered as a whole, *i.e.* on an M.O. scheme, it is difficult to analyse many of the additional factors introduced secondly.

(i) *Seven coordination*

The theoretical aspects of seven coordination have been dealt with in two recent articles[1,2] and the prediction of configuration on the basis of ligand-ligand repulsion made. Dependent upon the value of the coefficient n in the Born term in the interparticle potential, r^{-n}, there are several idealised possibilities of the highest symmetry, two of which are depicted in Fig. 1. When $n = 1$, the predicted



(i) (ii)

Fig. 1. Two of the idealised seven coordination polyhedra; (i) the pentagonal bipyramid of symmetry D_{5h} and (ii) the capped trigonal prism of symmetry C_{2v}.

stereochemistry is that of a pentagonal bipyramid with D_{5h} symmetry, while for large values of n, the coordination polyhedron has C_{3v} symmetry and can be considered as an octahedron with an additional ligand at the centre of one face (this is the configuration expected on the basis of the hard sphere approximation). For intermediate values of n, the predicted stereochemistry has C_{2v} symmetry and is derived from a trigonal prism by the substitution of a seventh ligand to one of the rectangular faces. A calculation[2] not limited to any of the three previously mentioned geometries indicates that a model with only C_2 symmetry is that with minimum energy.

While these predictions are perhaps useful when considering compounds containing identical unidentate ligands, it should be remembered that the energy differences between the predicted configurations are very small and that they will not be satisfactory when discussing chelating ligands or differing unidentate ligands. Here the constraints imposed by the chelates and the differing bonding requirements may be the controlling factors in determining the stereochemistry, not to mention intermolecular forces in the crystals. These factors have been discussed in more detail with respect to eight coordination.

Examples of all three types of stereochemistry have been found in the past, the D_{5h} arrangement in the discrete ions $UO_2F_5^{3-}$,[3] UF_7^{3-},[4] ZrF_7^{3-},[4] and HfF_7^{3-},[4] while the C_{3v} arrangement is found in $NbOF_6^{3-}$,[5] and the NbF_7^{2-} and TaF_7^{2-} [6] ions are found to possess the C_{2v} configuration. A recent refinement of the NbF_7^{2-} [7] ion, based on neutron diffraction data, confirms this result and gives the following data for the dimensions of the polyhedron averaged for C_{2v} symmetry: a = 2.45 Å, b = 2.83 Å, c = 2.53 Å, d = 2.415 Å, e = 2.357 Å. The Nb-F distances range from 1.94–1.98 Å when corrected for thermal motion, with an average of 1.96 Å. Another recently characterised complex fluoro ion of zirconium occurs in $Na_5Zr_2F_{13}$.[8] A two dimensional study revealed that the $Zr_2F_{13}^{5-}$ ion contains two ZrF_7 entities, each of "quasi" C_{2v} symmetry which share the "unique" fluorine atom. The Zr-F distances quoted fall in the range 2.00–2.10 Å.

Other recent definitive examples of seven coordination are provided by several peroxo complexes of chromium, molybdenum and tungsten, in which the peroxide ions can be considered to be acting as bidentate ligands. These compounds are all based on the pentagonal bipyramidal configuration with the peroxy groups occupying equatorial positions, and for chromium they comprise the following: (i) $Cr(O_2)_2(NH_3)_3$[9] and the ion (ii) $Cr(O_2)_2(CN_3)^{3-}$ [10] derived from it, the oxoperoxo complex (iii) $Cr(O_2)_2O$ phen.[11,12] and the aquoperoxo complex (iv) $(Cr(O_2)_2H_2O(en))\cdot H_2O$.[11,13] The coordination polyhedron in all of these has the general structure depicted in Fig. 2, where in (i) and (ii) X, Y and Z are NH_3 and CN^- respectively and in (iii) and (iv) X and Y are the nitrogen atoms of the *o*-phenanthroline and ethylenediamine chelates and Z, the remaining oxygen atom. The oxygen–oxygen distances in the peroxo groups range from 1.415-1.46 Å and the metal–oxygen distances from 1.83–1.90 Å, the average values in each molecule being as follows: (i) 1.42 (0.26) Å[*] and 1.876 (.020) Å, (ii) 1.448 (.012) Å and 1.887 (.009) Å, (iii) 1.42 (.02) Å and 1.83, (iv) 1.45 (.04) Å. These are all somewhat shorter than the O-O distance of 1.49 Å found for the peroxide ion in BaO_2. The other chromium-ligand distances have values anticipated for single bond lengths, *e.g.* Cr-N is 2.110 (.022) Å, the one exception being the Cr–N bond trans to the Cr-O bond in (iii) which is significantly longer (2.26 *vs.* 2.11 Å) than the Cr-N bond lying in the equatorial plane. In addition, the chromium atom is displaced .27 Å from the plane towards the oxygen atom.

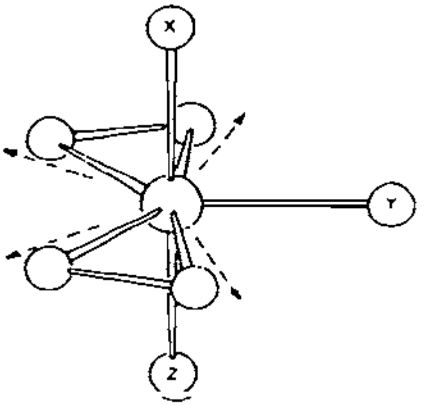


Fig. 2. The general form of the coordination polyhedron found in seven coordinate peroxo complexes of chromium and tungsten. The bonding directions for the idealised D_{5h} polyhedron are indicated by broken lines (see text).

The D_{5h} configuration is also found in the $Mo(O_2)_2OF_2^{2-}$ ion.[14] Here the axial positions are occupied by the oxygen atom and one of the fluorine atoms. No details on the molecular dimensions have been given. A detailed report of the stereochemistry of a peroxo complex containing seven coordinate tungsten has been given.[15] This contains a dinuclear complex anion and the formula is best written $K_2((W(O_2)_2OH_2O)_2O)2H_2O$. The two halves of the anion each have pentagonal bipyramidal stereochemistry and are linked by an oxygen atom (Y in Fig. 2) which lies in the equatorial planes of the two bipyramids. The equatorial planes are approximately normal to one another, the W-O-W bond angle is 139° and the mean W-O bond distance 1.925 (.03) Å. The axial positions of the two coordination polyhedra are each occupied by the remaining oxygen atom at a mean distance of 1.685 (.03) Å and a water molecule at 2.35 (.03) Å. The tungsten atom is displaced .35 Å out of the equatorial plane of five oxygen atoms towards the apical oxygen atom. The mean O-O distance observed here is larger (1.50 (.03) Å) than that found in the chromium compounds and the mean W-O (peroxy) distance is 1.93 Å.

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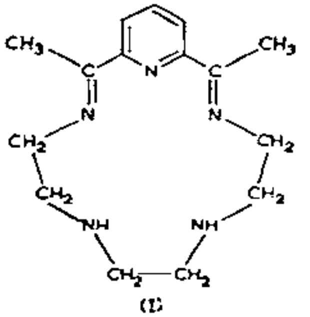
[*] Standard deviation.

The accumulation of reasonably accurate structural data on peroxo complexes lends support to the recent description of the bonding of the peroxo group.[16] In all compounds examined, the O-M-O angle is in the range 45–47°, and assuming that the normal metal hybrid orbitals used for σ bonding (in D_{5h}) lie at 72°, the O-M-O angle lies between these directions (see Fig. 2). If the σ orbitals on the oxygen atoms subtend angles of *ca.* 20° outwards from the M-O directions, then good overlap can occur and "bent" bond formation takes place. In this way, the peroxo group can be considered bidentate. This description of bonding is thought to be superior to that treating O_2^{2-} as a π donor.

In connection with peroxo complexes, some recent work on a dinuclear peroxocobalt species is worthy of mention. An initial two dimensional study of decammine μ-peroxodicobalt pentanitrate[17] suggested that the peroxo group lay normal to the Co-Co direction, so that each cobalt could be considered to be effectively seven coordinate. However, a more detailed study of the same cation in the corresponding sulphate complex indicates that the cobalt atoms are six coordinate—one oxygen only being bonded to each cobalt atom.[18] Moreover, the O-O distance is only 1.31 (.02) Å, which is indicative of a superoxide ion, O_2^-, rather than a peroxide ion.

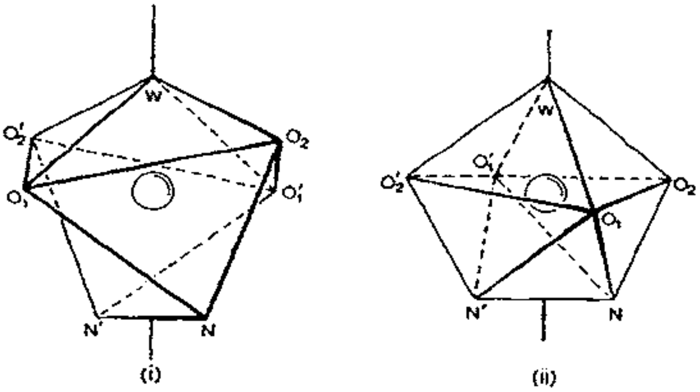
The final group of complexes in this section are manganese and iron chelates of ethylenediamine tetracetic acid (H_4Y) and 1,2-diaminocyclohexane *NN'*-tetracetic acid (H_4Z),[19,20,21] and two iron chelates with the macrocylic ligand, B.[22]



B.

(I)

The studies of the ethylenediaminetetracetate chelates of Mn and Fe by Hoard and coworkers,[19,20] have provided quite precise information on molecular parameters and details of the stereochemistry of these molecules. One of the interesting facts to emerge from this work is that the configuration adopted by the two metal ions is markedly different and does not appear to be governed by crystal forces. The coordination polyhedron of the iron chelate is of roughly pentagonal bipyramidal shape,[19] and since this basic shape is the same for both the rubidium and lithium salts which belong to different crystal systems (P2/a and Pbca), it can be assumed to be the stereochemically preferred form, whereas the polyhedron for the manganese compound[20] bears more resemblance to that of idealised C_{2v} symmetry (NbF_7^{2-} ion), or possibly that of C_2 symmetry.[2] The seven coordinate $Mn(H_2O)Y^{2-}$ ions occur in the compound $Mn_3(HY)_2 \cdot 10H_2O$ which also contains octahedrally coordinated manganese, situated at a crystallographic symmetry centre. The $Mn(H_2O)Y^{2-}$ ions are linked together by very strong hydrogen bonds (2.47 (.01) Å) *via* the carboxylate oxygens, such that they can be considered to form infinite chains of type $(Mn(H_2O)YH)_n^{n-}$, whereas the $Fe(H_2O)Y^-$ ions are discrete. Although crystallographically neither of the complex ions possesses any symmetry elements, the coordination polyhedra can each profitably be considered to possess a quasi-twofold axis and the two polyhedra with the dimensions averaged according to C_2 symmetry are illustrated in Fig. 3. (Parameters from the Li salt are of higher accuracy.)



(i) (ii)

Fig. 3. The coordination polyhedra found in the complex ions (i) $Mn(H_2O)Y^{2-}$ and (ii) $Fe(H_2O)Y^-$ idealised to C_2 symmetry. The dimensions averaged to this symmetry are as follows, the values for (i) being given first: NN': 2.90 Å, 2.79 Å, NO_1: 2.70 Å, 2.74 Å; NO_2: 2.65 Å, 2.60 Å; O_1O_1: 3.43 Å, 2.92 Å; O_1O_2': 2.96 Å, 2.98 Å, WO_1: 3.32 Å, 3.05 Å; WO_2: 2.83 Å, 2.50 Å; and for (ii) $N'O_1$: 3.04 Å. The chelate rings span edges NO_1, NO_2 and NN'.

In addition to this difference in shape of the coordination polyhedra, there is also a marked difference in the metal–oxygen bond distances, which though not easy to rationalise, is probably a consequence of the steric requirements of the two polyhedra. The Mn-O distance (average) is 2.24 Å, with a mean deviation of .017 Å and individual standard deviations of .005 Å while the Fe-O distances fall into two sets, $Fe\text{-}O_2 = 2.12$ (.009) Å and $Fe\text{-}O_1 = 1.97$ (0.3) Å. The metal–oxygen (water) distances also differ, being 2.23 Å and 2.11 Å respectively. The metal–nitrogen distances, in contrast, are virtually identical at the rather high value of 2.35 Å. Hoard, *et al.* comment that for this ligand, ring constraints are best served by seven coordinate species when bond lengths exceed 2.15 Å. Analysis of the complex $Ca(Fe(H_2O)Z)_2 9H_2O$,[21] again reveals the presence of a seven coordinate iron species, $Fe(H_2O)Z^-$. Here, the coordination polyhedron is intermediate between the two previously described, with perhaps a closer resemblance to that of C_{2v} or C_2 symmetry. Cohen and Hoard point out that in this chelate, ring constraints are best served by this geometry. The metal–ligand distances are much smaller than those observed in the manganese compound, $\text{Fe-O}_{(\text{chel})}$ 2.017 Å and 2.092 (.004) Å; $\text{Fe-O}_{(\text{H}_2\text{O})}$ 2.090 (.005) Å and Fe-N 2.290 (.004) Å.

The complex cation $\text{H}_2\text{OFe(B)OFe(B)H}_2\text{O}$ in the perchlorate salt, consists of two approximate pentagonal bipyramids linked through a linear oxygen bridge in the apical position, the macrocyclic ligand, B, forming the equatorial plane.[22] The Fe-N, Fe-O and $\text{Fe-O}_{(\text{H}_2\text{O})}$ distances are 2.2, 1.8 and 2.15 Å. A similar configuration is found for the monomeric cation in $(\text{FeB(NCS)}_2)\text{ClO}_4$.[22]

(ii) *Eight coordination*

This is the most common of the higher coordination numbers and three basic types of polyhedra have been found. These are the square antiprism, the dodecahedron and the hexagonal bipyramid. The classic example of dodecahedral coordination is given by the $\text{Mo(CN)}_8{}^{4-}$ and $\text{W(CN)}_8{}^{4-}$ ions,[23] while the square antiprism has been found more recently in the discrete ions $\text{TaF}_8{}^{3-}$ [24] and $\text{ReF}_8{}^{2-}$.[25] Examples of the hexagonal bipyramid (and possibly the puckered hexagonal bipyramid) appear to be confined to uranyl compounds where the requirement of linearity for the $\text{UO}_2{}^{2-}$ group stabilizes this configuration. Although there are many well characterized examples of eight coordination in these compounds the structural data until recently was of low accuracy and they will not be discussed further here.

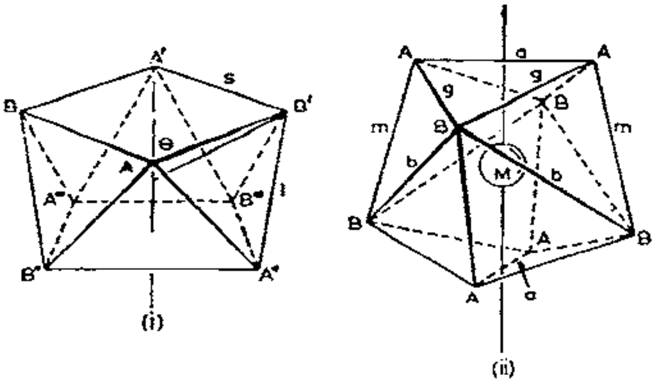


Fig. 4. Two of the idealised eight coordination polyhedra; (i) the square antiprism of symmetry D_{4d} and (ii) the dodecahedron of symmetry D_{2d}. The angles θ_A and θ_B define the inclination of the bonds M-A and M-B to the $\bar{4}$ axis.

While the cube can be considered as the natural extension of the puckered hexagonal bipyramid, non-bonding repulsions would be at a maximum in this configuration and there are too few orbitals of the proper symmetry for bonding (unless f-orbitals are considered). No examples of a coordination polyhedron of this shape have been characterized in discrete species.

A detailed consideration of the relative energies of the dodecahedron and the square antiprism, which are illustrated in Fig. 4, has been made by Hoard and Silverton[26] and by Kepert.[27] Both workers have concluded that the energetics of the direct bonding interactions differ so little for the two configurations, that the stereochemistry is controlled by other factors. These are (a) ligand–ligand repulsions, (b) ligand constraints, (c) the charge (if any) carried by the species, and (d) non-bonding d electrons. Consideration of (a) leads to significant deviations away from the hard sphere models (H.S.M.) for both, and for a value of 6 for n, in the interparticle potential, r^{-n}, both configurations are equally favourable when equivalent unidentate ligands are considered. (When $n = 7$ the antiprism is slightly favoured, although there is now more effective shielding in the dodecahedron.) The deviations are such that in the antiprism, θ is decreased by $\sim 2°$ (H.S.M.θ = 59.4), while in the dodecahedron, θ_A is decreased slightly, and θ_B increased by a larger amount from the H.S.M. values listed in Table I. The calculated values are in good agreement with those predicted from the two hybridisation schemes.[28,29]

TABLE I

DIMENSIONS OF DODECAHEDRAL COORDINATION POLYHEDRA AVERAGED TO D_{2d} SYMMETRY

Compound or ion	*a*	*b*	*m*	*g*	*M–A*	*M–B*	θ_A	θ_B	*Refs.*
$Mo(CN)_8^{4-}$[a]	2.45	3.14	2.54	2.63	2.15	2.15	36.0	71.8	23
ZrF_8^{4-}	2.94	3.14	2.46	2.48	2.16	2.05	43.0	65.5	40
$Zr(C_2O_4)_4^{4-}$[b]	2.570	3.19	2.563	2.735	2.230	2.168	35.2	73.5	39
$Zr(NTA)_2^{2-}$[b]	2.68		2.62	2.785	2.25(O) 2.44 (N)	2.124			41
$TiCl_4(diars)_2$[c]	3.21	3.64	3.02[e]	3.2[e]	2.71	2.46	36.3	72.5	42
$Ti(NO_3)_4$	2.51	2.95	2.13	2.73	2.07	2.06	37.0[e]	81.0[e]	49
$Co(NO_3)_4^{2-}$	2.99	3.54	2.04	3.02	2.07	2.45	46.5	80.5	47
$Cr(O_2)_4^{3-}$	2.57	2.79	1.47[d]	2.67	1.87	1.97	43.4	93.0	45, 43, 44
H.S.M. Model	1.2	1.5	1.2	1.2	1	1	36.85	69.46	27, 26
Hoard and Silverton Model	1.17	1.49	1.17	1.24	1.03	1	35.2	75.5	27, 26
d^4sp^3 hybrids							34.6	72.8	29

[a] $Mo(CN)_8^{4-}$ is isomorphous with $W(CN)_8^{4-}$.

[b] The corresponding hafnium chelates are isomorphous.

[c] The diarsine ligand chelates along the a edges.

[d] The peroxy bond length given in ref. 45 and based on a refinement of the data of ref. 43 is 1.41 Å, and there are consequent minor changes in the other dimensions.

[e] Estimated by the author.

If, however, the ratio of the lengths of the two types of bond M-A and M-B in the dodecahedron are allowed to vary, *i.e.* considering species of type ML_4L_4' with non-equivalent ligands, then this configuration is stabilised relative to the antiprism when M-A > M-B. The relevant values are given in Table I. Although this conclusion is confirmed by the structural data available, the d^4sp^3 hybrid set of orbitals which might be used for bonding have greater "d" character for the

M-A σ bonds which as a consequence might be expected to be shorter, it would appear that the non-bonding repulsions are more important. The dodecahedron can therefore be considered as the important configuration for ligand arrangements which are able to take advantage of the distinction in the bonding in the A and B positions, such as ligands differing electronically or in their steric requirements, and for polarisable ligands, such as the cyanide ion.[30]

Factor (b) was considered in detail by Hoard and Silverton[26] and it will suffice to say here that the main requirement for a bidentate ligand is that the ring span matches the edge of the polyhedron as closely as possible in order to minimise ring strain. Overriding both (a) and (b) is the situation when the complex species carries a resultant charge and contains bidentate ligands. It appears that this factor becomes predominant in determining the configuration and that minimisation of coulombic repulsions is best served by the dodecahedron. The data presented in Table I concur with this and all the species concerned have idealized D_{2d} geometry, *i.e.* with ligands bridging m edges.

The only square antiprismatic structures for which accurate three dimensional results have been recorded are zirconium tetrakisacetylacetonate,[31] Zr(acac)$_4$ and yttrium trisacetylacetonate dihydrate in Y(acac)$_3$ · 3H$_2$O.[32] The Zr(acac)$_4$ molecule which is crystallographically required to possess only a C_2 axis in the crystal passing through the mid points of sides AA″ and A′A‴, comes very close to having D_2 symmetry with the bidentate ligands chelating square edges (s). The dimensions of the polyhedron averaged to this symmetry are (in Å) (see Fig. 4) A-B (ring span) 2.674 (.013); A-B′ 2.590 (.012); A-A″ 2.689 (.017); B-B″ 2.812 (.012) and A-B″, 2.722 (.013). The rectangular face is folded slightly about the line BB′, this distance being 3.66 and AA′, 3.78, so that the resulting distortion from the antiprismatic configuration is towards a dodecahedral configuration with the ligands spanning the g type edges. The value of θ, 57.3°, is less than that for the H.S.M. (59.4°), but agrees exactly with that calculated by Hoard and Silverton,[26] and well with the value of 57.6° for d^4sp^3 hybrid orbitals.[28] The average Zr-O distance is 2.198 (.009) Å. The hafnium compound Hf(acac)$_4$ is isomorphous with Zr(acac)$_4$.

The yttrium atom in Y(acac)$_3$ · 3H$_2$O is surrounded by two of the water molecules and a distorted square antiprismatic array of oxygen atoms provided by the three acetylacetonate ligands, which bridge square edges[32]. The Y-O distances range from 2.30 to 2.47 (.013) Å and the edges of the polyhedron from 2.72 to 2.98 (.02) Å (s edges) and from 2.83 to 3.23 (.02) Å (l edges). The authors point out that the average parameters for the polyhedron agree well with those of the Hoard and Silverton model—θ_{av} being 57.1°.

Two dimensional structure analyses of tetrakisacetylacetonates of cerium and thorium have been reported and there are reputed to be two isomorphous series of these compounds, α and β,[33-35] the aforementioned zirconium and hafnium compounds being members of the latter series. The β modification of the thorium chelate yields an average Th-O distance of 2.41 Å[33] and average polyhedron distances of 2.74 Å (ring bite) and 3.07 Å, while the corresponding distances in the cerium chelate which belong to the α series,[34] are 2.40 Å, 2.81 Å and 2.96 Å respectively. However, too much reliability should not be placed on results based on two dimensional data for molecules of this complexity, due to possible ambiguous interpretation of electron density projections.

The only discrete species with unidentate ligands for which structural data are available are the octafluorometallate ions, the TaF_8^{3-}[24] and ReF_8^{2-}[25] ions mentioned earlier and the recently described ZrF_8^{4-} ion found in $Cu_2ZrF_8 \cdot 12H_2O$,[36] and a series of lanthanide chlorides of type MCl_36H_2O. All these results are based on two dimensional analyses. The average metal–fluorine bond lengths in the three octafluoro anions average 1.98 Å and 2.09 Å respectively and the value of θ in TaF_8^{3-} is given as 59°. Analysis of $Eu(H_2O)_6Cl_3$[37] and $Gd(H_2O)_6Cl_3$[38], shows these to be composed of Cl^- ions and distorted square antiprismatic ions $M(H_2O)_6Cl_2^+$, in which the chlorine atoms are situated across one of the square faces. The average bond lengths are 2.77 Å for M-Cl and 2.41 Å for M-O.

The pertinent dimensions of the coordination polyhedra in several species with the dodecahedral configuration are given in Table 1, together with the values for the hard-sphere model and the most favourable polyhedron parameters. All values are obtained by averaging to D_{2d} symmetry where necessary, the bidentate ligands in the M(chelate)$_4$ species spanning the m edges of the polyhedron.

Dealing with the complexes individually, it is seen that the relative values for the M-A and M-B bond distances as found for the tetrakisoxalatozirconate ion (in $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$),[39] the octafluorozirconate ion (in $Li_6BeF_4ZrF_8$)[40] and the bisnitrilotriacetate zirconate ion (in $K_2Zr(NTA)_2 \cdot H_2O$)[41] and for $TiCl_4$-(diars)$_2$[42] are in accord with prediction. In the case of the latter, an allowance has to be made for the difference in covalent bond radii of chlorine and arsenic, which when included still leaves the M-A distance larger by .06 Å. [26] Isomorphous, and presumably isostructural, with $TiCl_4$ (diars)$_2$[42] are the corresponding Zr, V, Nb and Hf species and also the series of complexes with the tetrabromides of the same metals. While the ZrF_8^{4-} ion[42] is crystallographically required to possess D_{2d} ($\bar{4}2$ m) symmetry, the dodceahedron is considerably compressed along the $\bar{4}$ axis relative to its "ideal" configuration. This, the authors believe, is due to the close proximity of the Li^+ ions.

The other two zirconium species both possess a two-fold axis in the crystal and for the $Zr(NTA)_2^{2-}$ ion[43] this bisects two of the b edges, the tetradentate ligand spanning the a, m and g edges, while for the $Zr(C_2O_4)_4^{4-}$ ion,[39] it is coincident with the "quasi" $\bar{4}$ axis. As might be anticipated for the former, with the large disparity in Zr-N and Zr-O_A distances, there is considerable distortion of the dodecahedron, and averaging the M-A distances to D_{2d} is not very meaningful. The length of the Zr-N bond is not easily accounted for. Some of the deviations away from the idealised D_{2d} symmetry in the $Zr(C_2O_4)^{4-}$ ion are significant in a statistical sense, but from a chemical viewpoint can probably be ignored. The most striking deviation is that each oxalate group, while remaining planar and containing the metal atom, is twisted about an axis midway between the two metal oxygen bonds, such that there is a small resulting dihedral angle (~4°) between the mean trapezoidal plane through Zr, O_A, O_B, O_A' and O_B', and the plane of the oxalate group. The deviation is such that O_A and O_B' are .11 Å above the mean plane, while O_A' and O_B are .11 Å below.

The remaining species listed in Table 1 contain the compact nitrate and peroxo ligands and here the M-B bonds are longer than or equal to the M-A bonds, the latter situation also obtaining in the $Mo(CN)_8^{4-}$ ion.[23] In the case of the chromium complex ion,[43-45] there is obviously a large deviation from the "ideal" shape, due to the restrictions imposed by the O-O separation on the side m. However, if the bonding for this species is considered in the same way as mentioned earlier for the other peroxo complexes, then the O-Cr-O angle lies approximately between the "normal" directions for M-A and M-B bonds. The compounds $K_3Nb(O_2)_4$, $K_3V(O_2)_4$ and $K_3Ta(O_2)_4$ are isomorphous with the chromium complex.[46]

The structure of the $Co(NO_3)_4^{2-}$ ion is of interest in connection with its electronic absorption spectrum and magnetic moment.[48,47] Both of these are indicative of regular tetrahedral coordination for the metal ion, which fact can be satisfactorily explained if the nitrate groups are considered as unidentate ligands. Their effective mid points, from a ligand field viewpoint, describe an almost regular tetrahedron about the metal atom. In the crystal the ion has only C_{2v} symmetry, the Co-O_A distances being 2.03 (.02) Å and 2.11 (.02) Å, and the Co-O_B distances, 2.36 (.02) Å and 2.54 (.02) Å.

The $Ti(NO_3)_4$[49] molecule can be considered in a similar way. Here the metal oxygen bond distances are virtually identical and considering the nitrate groups as unidentate ligands, the resulting tetrahedron is considerably flattened.

Several tetrakis-β-ketoenolate complexes also apparently have a dodecahedral configuration of ligand atoms surrounding the metal.[50,51] On the basis of two dimensional results, 1,3,diphenyl,1,3,butanedione (dibenzoylmethane) forms an isomorphous series of complexes with Ce^{IV}, Th^{IV} and U^{IV}, with the ligands chelating along m edges. That this ligand gives the dodecahedron as the preferred coordination polyhedron, in contrast to acetylacetone, might be ascribed to the steric requirements of the phenyl groups. However, three dimensional results are obviously needed for a definitive description of the polyhedron. A three dimensional analysis of the tetrakisfluoroacetylacetonate yttrium ion as found in $Cs(Y(CF_3\text{-}COCHCOCF_3)_4)$ reveals the bidentate ligands to be chelating along the g edges of the dodecahedron giving an idealised D_2 configuration.[51] (N.B. the distortion of the $Zr(acac)_4$ molecule was toward this arrangement.) The average metal oxygen bond distance is given as 2.33 (.04) Å with $\theta_A = 40°$ and $\theta_B = 67.5°$.

(iii) *Nine and ten coordination*

While coordination number nine occurs quite commonly in some of the extended structures of compounds of the rare earths and actinides, it has been characterised in only a few discrete complex ions. The aquated neodymium ion $Nd(H_2O)_9^{3+}$ in $Nd(BrO_3)_3 \cdot 9H_2O$ was found early to be nine coordinate,[52] and to possess the one possible regular arrangement for this coordination number. This is derived from a trigonal prism, by placing three additional ligands outside the three rectangular faces; the resulting symmetry remaining at D_{3h}. The six "outer" Nd-O bond lengths are 2.47 Å and the three equatorial ones 2.51 Å. An almost similar arrangement has also been found in a series of aquated lanthanide ethyl sulphate complexes, $M(C_2H_5SO_4)_3 \cdot 9H_2O$.[53] In the erbium and yttrium compounds, the three equatorial bond distances were found to average 2.54 Å and the six "outer" bonds, 2.37 Å.

Essentially this arrangement is found in the rhenium hydride ion, ReH_9^{2-},[54] and presumably the isostructural TcH_9^{2-} ion.[55] There are two crystallographically independent anions in the hexagonal unit cell and although the spread in the four Re-H distances is .11 Å, the authors do not consider this significant and use the average value of 1.68 Å. The mean angle between the Re-H (prism) bonds is 93.6 ± .6, which gives an angle of 43.2° for the inclination of the bond to the three fold axis. This is a little larger (~2°) than that calculated using the hard sphere model, assuming a prism-equatorial bond length ratio of unity.[26]

A different arrangement is found in the complex ion $Nd(COOCH_2OCH_2COO)_3^{3-}$ as it occurs in the sodium salt.[56] Here the neodymium atom lies on a three fold axis in the crystal and the diglycolate ligand is tridentate, the coordinated carboxyl oxygens forming a distorted octahedral array about the metal, rather than a trigonal prism. The three remaining coordination sites are occupied by the ethereal oxygens and are situated midway along the edges of the octahedron. As these atoms are located on two-fold axes, the complex ion possesses rigorous D_3 symmetry. The two metal oxygen distances are 2.4 Å and 2.5 Å.

The remaining nine coordinate species is the ion $La(H_2O)_3Y^-$ (a) (H_4Y = E.D.T.A.) found in the compound $KLaY \cdot 8H_2O$.[57] (Isomorphous with this species are several other alkali metal and ammonium salts of the La, Nd, Tb, Gd and Er chelates.) This can be considered along with $La(H_2O)_4HY \cdot 3H_2O$ (b) which contains ten coordinate lanthanum.[58] Both of these species can be related to the dodecahedral configuration (the ligand constraints prevent an approximation to the D_{3h} structure in the case of (a)) and are illustrated in an idealized fashion in Fig. 5. In each, the four chelate oxygen atoms define one of the trapezoidal planes of the dodecahedron, the metal atoms being displaced away from the nitrogen atoms by .6 Å in (a) and .77 Å in (b), while the second trapezoidal plane (which, as regards the coordination polyhedron, is a "quasi" mirror plane) is defined by the two nitrogen atoms and the water molecules. The dodecahedral site B, in (a), is "shared" by two molecules, and in (b) occurs at the mean position of three water molecules.

The relevant average molecular parameters, which were determined to high accuracy, are: for (a) La-O, 2.507 (.006) Å; La-H_2O, 2.580 Å and La-N, 2.755 (.006) Å; for (b) La-O, 2.537 Å (three values) and 2.609 Å (the free carboxyl oxygen of this group is assumed to carry the hydrogen atom); La-H_2O, 2.592 Å and La-N, 2.865 Å, S.D.s. 007 Å. Comparison of these values indicates that loss of the hydrogen leads to a tightening of the chelate around the metal and the consequent ejection of a water molecule.

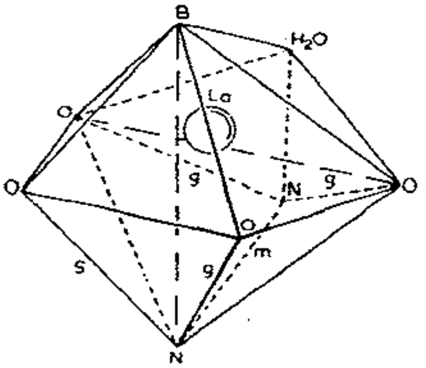


Fig. 5. The coordination polyhedron in $La(H_2O)_3Y^-$ (a) and in $La(H_2O)_4HY$ (b) related to a dodecahedron. The position B, of the dodecahedron is "shared" by two water molecules in (a) and occurs at the mean position of three water molecules in (b) (see text). The chelate rings span edges g and m.

(iv) *Eleven and twelve coordination*

These coordination numbers are found in nitrate complexes of thorium and cerium, and it is highly probable that they will be limited to species containing similar "compact" bidentate ligands. In both of the compounds $Mg(H_2O)_6Th(NO_3)_6 \cdot 2H_2O$[59] and $(Mg(H_2O)_6)_3(Ce(NO_3)_6)_2 \cdot 6H_2O$[60] the complex anions are twelve coordinate species containing bidentate nitrate groups, the resulting coordination polyhedron being an irregular icosahedron in each case. While the $Ce(NO_3)_6^{3-}$ ion, from the crystal site symmetry, is only required to have a $3(C_3)$ axis, the symmetry of the polyhedron in fact closely approaches $\bar{3}(S_6)$. A similar situation also obtains for the $Th(NO_3)_6^{2-}$ ion, which possesses only a centre of symmetry; although there is a wide variation in the lengths of the polyhedron edges, within the large standard deviations (results from a two dimensional analysis) of the determination, the approximation to $\bar{3}(S_6)$ symmetry holds. The idealized coordination polyhedron is illustrated in Fig. 6 and the distances for $Th(NO_3)_6^{2-}$, averaged for $\bar{3}(S_6)$ symmetry are given. The averaged metal–oxygen distances for both species are 2.63 Å. If the nitrate ions are considered as unidentate ligands, then the coordination closely approximates to octahedral.

Analysis of the thorium nitrate pentahydrate, $Th(NO_3)_4 \cdot 5H_2O$, by both X-ray and neutron diffraction,[61] reveals the presence of eleven coordinate thorium. The coordination polyhedron, which possesses a crystallographic two-fold axis, as might be anticipated, is irregular and is best viewed by considering the nitrate ions as unidentate ligands, when the coordination number reduces to seven and the resulting polyhedron approximates readily to the C_{2v} (NbF_7^{2-}) arrangement illustrated earlier. The Th-O bond distances average 2.57 Å for the nitrate oxygens and 2.46 Å for the water molecules.

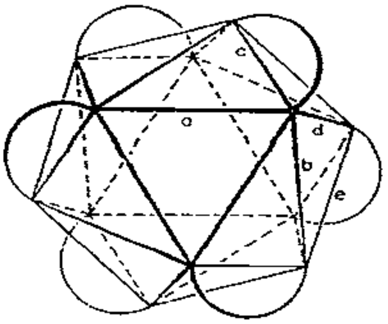


Fig. 6. The idealised polyhedron (of S_6 symmetry) found in $Th(NO_3)_6^{2-}$ and $Ce(NO_3)_6^{3-}$. The chelating nitrates are indicated by curved lines and the dimensions of the polyhedron averaged to S_6 symmetry are: a, 2.91 Å; b, 2.83 Å; c, 2.10 Å; d, 3.09 Å and e, 3.00 Å.

C. PENTACOORDINATE TRANSITION METAL COMPLEXES

The subject of pentacoordination in general has been treated very extensively in an excellent review by Muetterties and Schunn,[62] and a short review of the molecular structures of five coordinate transition metal complexes determined by X-ray diffraction has also appeared.[63] However, since the latter review, there has been considerable activity in this field and the recent results prove to be of interest.

As is well known, there are only two idealised geometries for the coordination polyhedron which are of importance here; namely, the trigonal bipyramid of D_{3h} symmetry and the tetragonal (or square) pyramid of C_{4v} symmetry. These are illustrated in Fig. 7, together with a commonly observed distorted form of the tetragonal pyramid. The energy level difference for the two configurations is believed to be small[64] and will, in all probability, often be less than packing forces in the solid state and energies of solvation in the liquid state. Discussions on structural features of a given species should therefore be referred to the physical state for which the determination is made, since, due to the potentially easy re-arrangement process, it may well be different for other states where the "external" factors differ.

With transition metal complexes, there is the additional complicating factor of the effect of the unfilled d configurations upon stereochemistry. In discussing this factor, Gillespie has suggested, on the basis of electron repulsion considerations,[65] that where the interaction between the non-bonding d electrons and the ligand electron pairs is less than the ligand electron pair repulsions, the trigonal bipyramid will be the anticipated configuration, while the tetragonal pyramidal structure will be expected for the reverse situation. Therefore, for molecules with d^{6-9} configurations, one might anticipate the latter. In addition, Gillespie predicted that for the tetragonal pyramid, the apical bond would be longer than the basal bonds, while in the trigonal bipyramid, axial and equatorial bonds would be virtually the same.

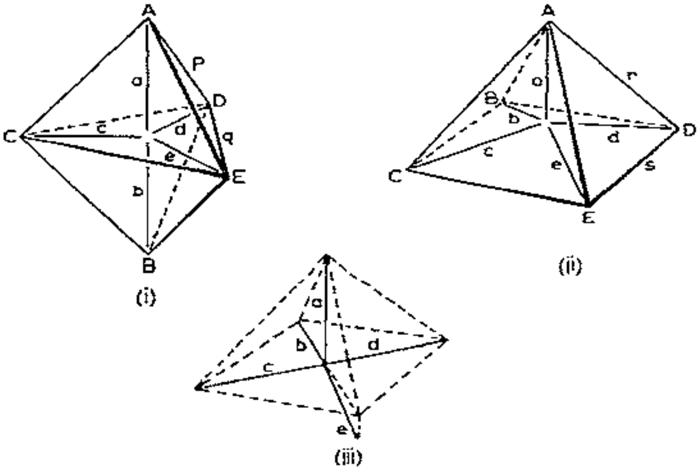


Fig. 7. The idealised five coordination polyhedra: (i) the trigonal bipyramid of symmetry D_{3h} and (ii) the tetragonal pyramid of symmetry C_{4v}. (iii) A commonly observed distorted form of the tetragonal pyramid with one of the ligands depressed below the basal plane.

A survey of the available structural data indicates that these suggestions are not very closely followed in practice even if one confines oneself to compounds containing solely monodentate ligands, where the complicating factor of the steric requirements of chelating ligands is absent. The trigonal bipyramid seems a particularly stable configuration for the d^8 configuration when all ligands are identical, while minimisation of ground state energy for species with four identical ligands is achieved for the tetragonal pyramid, regardless of the d electronic configuration.

In the majority of cases, the stereochemistry appears to be intermediate between the two idealised configurations and it is often a matter of taste whether the polyhedron is referred to as a distorted trigonal bipyramid, or a distorted tetragonal pyramid. Although it must be admitted that the latter approach does have a pictorial usefulness when discussing structural results, in actual fact in many instances, the polyhedron will be very sensitive to non-bonding repulsions when bulky ligands are involved, to steric requirements of the ligands when these are multidentate and will also presumably be a function of the differing bonding requirement of the ligands, so that such descriptions are not very meaningful. Examination of the available data indicates roughly equal numbers of structures attaining or approximating to the two idealised polyhedra, while, for chelating ligands and especially terdentate ligands, the tetragonal pyramidal configurations denoted by structures (ii) and (iii) in Fig. 7 are preferred.

While the distinction between polyhedra outlined above can be made on the basis of the purely stereochemical influences of the ligands, or on the stoichiometry of the compounds, at the present time the effect of the varying d electronic configuration is scarcely known, although recent detailed structural, spectroscopic and magnetic studies on a series of isomorphous molecules of titanium,[66,68] vanadium,[68] and chromium[67] have enabled progress to be made in this direction. Very little work has been reported on M.O. descriptions of the bonding in pentacoordinate molecules.[69]

STRUCTURAL RESULTS

(i) *Species containing monodentate ligands*

In this group we have compounds ranging from those in which the ligands are all equivalent, *i.e.* ML_5 species, to those of stoichiometry $ML_2L'L''L'''$. Of this group only the ML_5 and ML_3L_2' species are capable of possessing the idealised D_{3h} symmetry, while only ML_5 and ML_4L' are capable of possessing C_{4v} symmetry.

On the very limited evidence available, it appears that the ML_5 species prefer the trigonal bipyramidal stereochemistry and this has been found for four compounds or complex ions, $Fe(CO)_5$,[70] $Co(CNCH_3)_5^+$,[71] $Pt(SnCl_3)_5^{3-}$,[72] and $CuCl_5^{3-}$.[73] Three of these have the metal atom with a d^8 configuration. In the pentakismethylisonitrile Co^I ion, $Co(CNCH_3)_5^+$, the deviations of the bond angles within the equatorial plane, from 120°, can be attributed to crystal packing forces. For all of the species, the axial and equatorial bonds are equal to within the determined standard deviations: for $Fe(CO)_5$, the average bond distance is 1.79 Å, for $Co(CNCH_3)_5^+$, 1.87 (.015) Å, for $CuCl_5^{3+}$, 2.34 (.03) Å and for $Pt(SnCl_3)_5^{3-}$, 2.54 Å.

Considering the ML_3L_2' species for which X-ray data are available, namely $(TiCl_2(OC_6H_5)_2)_2$,[74] $PdBr_2$tris,2-phenylisophosphindoline,[75] two phosphine complexes, $CoBr_2((C_6H_5)_2PH)_3$,[76] and $RuCl_2((C_6H_5)_3P)_3$,[79] and $MX_3 \cdot 2N(CH_3)_3$,[66–68] only in the case of the latter do we find a close or an exact approximation to the idealised D_{3h} configuration. For this series of compounds, when M = Ti, V or Cr and X = Cl or Br, the X-ray data indicate that they are isomorphous and virtually isostructural. In the case of $TiBr_3 2N(CH_3)_3$ (A)[66] and $CrCl_3 \cdot 2N(CH_3)_3$ (B)[67] for which complete analyses have been carried out, there are significant deviations, especially in the chromium compound, in the bond angles of the MX_3 group of atoms from the idealised values of 120°, such that the polyhedra only possess C_{2v} symmetry. The X-M-X angles are for (A) 117.5° and 121.25° and for (B) 111.5° and 124.25° and the metal-bromine and metal-chlorine bond distances average 2.42 (.008) Å and 2.23 (.008) Å respectively. These deviations can be rationalised in terms of the electronic structures of the molecules and a detailed analysis of the spectra and magnetic properties indicates that these are in accord with the observed configuration. In particular, the low value for the crystal field strength arising from the axial trimethylamine ligands in these molecules can be correlated with the rather long metal–nitrogen bonds, which in (A) average 2.29 (.04) Å and in (B) 2.19 (.02) Å. In addition, the magnetic properties of the vanadium analogues indicate that these do not deviate from the idealised symmetry[68] and the structure is currently being determined.

The dichlorodiphenoxytitanium(IV)[74] complex is dimeric, the two titanium atoms being linked by oxygen bridges, such that each is pentacoordinate, the resulting polyhedra being distorted trigonal bipyramids sharing an edge of type p. The two chlorine atoms at an average distance of 2.216 (.006)Å and one of the bridging oxygen atoms at 1.910 (.009) Å, form the equatorial plane. The axial bond lengths a and b are vastly different at 2.122 (.009) Å and 1.744 (.010) Å respectively, the former being the bridge bond.

The other molecules in this group which contain various phosphines as ligands, can be considered to be basically square pyramidal. For one of these, $CoBr_2((C_6H_5)_2PH)_3$,[76] the authors prefer to describe the coordination polyhedron as a distorted trigonal bipyramid, with phosphine groups in the axial positions. However, it appears to this reviewer that a distorted tetragonal pyramid of type Fig. 7. (iii) is a better description in view of the difference between the two cobalt–bromine bond lengths and the P-Co-Br bond angles (98.1° and 136.3°). One of the Co-Br bond distances (a) at 2.54 (.01) Å is much larger than the other (b) at 2.33 (.01) Å and is in keeping with the anticipated long apical bond. This difference is even more pronounced in the isostructural $NiI_2((C_6H_5)_2PH)_3$.[76] An analogous ruthenium complex, $RuCl_2((C_6H_5)_3P)_3$,[77] conforms closely to the tetragonal pyramidal structure of type Fig. 7 (ii). The basal plane is defined by the two chlorine atoms at a distance of 2.388 (.007) Å (bonds c and d) and two of the phosphorus atoms at distances of 2.374 Å and 2.412 (.006) Å (bonds b and e) respectively. The apical Ru-P bond length at 2.230 (.008) Å is significantly shorter than the basal bonds, contrary to usual observation. The ruthenium atom is .456 Å above the mean plane and the sixth octahedral position is effectively blocked by the hydrogen atom on one of the phenyl groups.

In the palladium dibromide phosphine complex,[75] the metal atom and the three phosphorus atoms define the basal plane at M′CBD (structure Fig. 7 (iii)), the Pd-P bond lengths being 2.19 Å (b) and 2.29 Å (c and d), while the bromine atom E (e = 2.52 Å) is depressed below the plane. The apical bond length, a, is 2.93 Å.

The copper atoms in the μ_4-oxo-hexa-μ-chloro-tetrakis-(triphenylphosphine oxide)Cu^{II} complex, $Cu_4Cl_6((C_6H_5)_3PO)_4O$, are five coordinate and in trigonal bipyramidal environments[78] (strictly C_{3v}). Each unit can be formulated as $CuCl_3$-$OPO(C_6H_5)_3$ and can be considered as ML_3L_2' complexes, the Cu-O bond lengths, a and b, being equivalent at an average value of 1.897 Å. The Cu-Cl bond distance is 2.38 (.01) Å and the copper atom is displaced .23 Å from the plane toward the oxygen of phosphine oxide.

In contrast to the ML_3L_2' species, those with formula ML_4L' conform quite closely to the tetragonal pyramidal configuration, the four equivalent ligands forming the basal plane and the metal atom being displaced appreciably from the plane. This arrangement occurs in a variety of oxo complexes. In the salts $((C_2H_5)_4N)(ReBr_4O(H_2O))$[79] and $((C_6H_5)_4As)(ReBr_4O(CH_3CN))$[80] the $ReBr_4O$ group has C_{4v} symmetry within experimental error, with an average Re-Br distance of 2.49 (.02) Å and an apical rhenium–oxygen bond distance of 1.72 (.05) Å. The rhenium atom is displaced .33 Å above the plane. Although the solvent molecule H_2O or CH_3CN is located at the sixth position, the bond distance is considered to be long and the solvent molecule weakly bonded. The solvent free salts would expect to have the tetragonal pyramidal geometry. A similar situation occurs in the $VO(NCS)_4^{2-}$ ion,[81] where the sixth position is occupied by a water molecule. The thiocyanates are nitrogen bonded at a distance of 2.04 (.03) Å, and the vanadium oxygen terminal bond is 1.62 Å. In $VO(OCH_3)_3$, the same arrangement is found,[82] although with considerable deviations from C_{4v} symmetry in the dimeric $(VO(OCH_3)_3)_2$ unit, which is composed of two square pyramids sharing an edge of type s. The terminal bonds have an average length of 1.54 Å, the bridge bonds, 2.02 Å and the other terminal bonds defining the basal plane, 1.79 Å. Bridging to the sixth position results in the molecules forming a linear polymer in the crystal.

The final example of ML_4L' species is provided by the isomorphous series of complexes formed by the metal(II) perchlorates of manganese, iron, cobalt, nickel, copper and zinc with diphenylmethylarsine oxide.[83] From the single crystal analysis of the cobalt complex, the metal atom is found to lie on a fourfold axis and hence all metal oxygen distances in the basal plane are equal at 2.02 Å. The cobalt atom is .32 Å above the plane formed by the four oxygen atoms. The perchlorate ion is disordered about the fourfold axis and the oxygen, coordinated to the metal at a distance of 2.10 Å, lies some .72 Å from the axis.

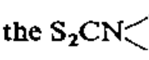
Of the remaining complexes with monodentate ligands, two are of formulation $ML_2L_2'L''$, *viz.* $ReNCl_2((C_6H_5)_3P)_3$ and $VOCl_2 \cdot 2NMe_3$.[84] The latter, which is isomorphous with the $MX_3 \cdot 2NMe_3$ complexes discussed earlier, approximates very closely to a trigonal bipyramidal configuration. The rhenium complex, for which a very accurate analysis has been reported,[85] is crystallographically required to possess C_2 symmetry, but the coordination polyhedron comes very close to C_{2v} symmetry. This can be viewed either as a distorted trigonal bipyramid, with axial triphenylphosphine groups, or a distorted tetragonal pyramid. The rhenium phosphorus distance is 2.448 (.002) Å, Re-Cl 2.377 (.002) Å and the Re-N distance 1.602 (.009) Å. The latter is significantly shorter than that of 1.788 (.011) Å found in an analogous octahedral complex, $ReNCl_2(P(C_6H_5)_3)_3$.[86]

Finally, there are three triphenylphosphine complexes of rhodium and iridium which are pentacoordinate. These are all carbonyl species, $RhH(CO)((C_6H_5)_3P)_3$,[87] $IrO_2Cl(CO)(P(C_6H_5)_3)_2$[88] and $IrSO_2Cl(CO)(P(C_6H_5)_3)_2$.[89] The first two can be viewed as possessing distorted trigonal bipyramidal coordination polyhedra, while the last is square pyramidal, with the SO_2 molecule bonded through sulphur in the apical position.

(ii) *Species containing bidentate ligands*

Several of the complexes in this group conform quite closely to the tetragonal pyramidal structure Fig. 7 (ii) and have the general formula ML_2L', the bidentate ligands forming the basal plane of the polyhedron. This configuration is also achieved by dimerisation, in several complexes of formula ML_2, such that in these species, the two polyhedra share an edge of type r. This situation is particularly evident for copper.

The best known of the tetragonal pyramidal structures is vanadyl bisacetylacetonate,[90] $VO(CH_3COCHCOCH_3)_2$, which has an apical V-O bond length of 1.57 (.01) Å and an average basal bond length of 1.97 (.01) Å—the vanadium atom being .56 Å above the basal plane and roughly at the centre of gravity of the polyhedron. An almost identical arrangement has been found in the vanadyl bisbenzoylacetonate complex, $(VO(C_6H_5COCHCOCH_3)_2)$*cis*-$VO(bzac)_2$.[91] Here, however, the symmetry of the polyhedron deviates significantly from the C_{2v} symmetry found in $VO(acac)_2$, the non-bonded distances between the two pairs of oxygen atoms in the basal plane being 2.56 Å for the atoms of the C-O bonds adjacent to the phenyl group and 2.70 Å for the other pair. This distance averages 2.625 Å in $VO(acac)_2$ and the "bite" of the chelate is the same in both complexes. The difference between the non-bonded distances is rationalised by the authors as arising from the conjugation between the phenyl and chelate rings which leads to a lowering of double bond character in the C-O bond adjacent to the phenyl group and the consequent redistribution of electron density from the lone pair σ orbitals on the oxygen.

The same tetragonal pyramidal geometry, actually C_{2v}, is found in the bisdiethylthiocarbamate iron(III) chloride complex, $Fe(S_2CN(C_2H_5)_2)Cl$,[92] which is one member of a series of five coordinate Fe(III) complexes having a quartet ground state ($S={}^3/_2$). The Fe-S and Fe-Cl bond lengths are 2.32 Å and 2.27 Å respectively, with the four sulphur atoms being coplanar and the iron atom .63 Å above the plane. In contrast to $VO(acac)_2$, the metal atom in this molecule is coplanar with the  $S_2CN{<}^{C}_{C}$ skeleton, and, as a result, the dihedral angle between the two planes is 50°. The bis-diethylthiocarbamate iron(II) nitrosyl complex has a similar structure,[93] with the nitric oxide coordinated through nitrogen and almost colinear with the Fe-N bond. The Fe-S bond distances average 2.28 (.01) Å and the iron atom is .63 Å above the plane, with the Fe-N bond 1.69 Å. An earlier determination of the structure of a cobalt analogue, $Co(S_2CN(CH_3)_2)_2NO$,[94] indicates a different mode of coordination for the nitrosyl ligand. However, these results are from a two dimensional analysis.

Formation of tetragonal pyramidal coordination by dimerisation is exhibited by bis(*cis*-1,2-bis(trifluoromethyl)-ethylene-1,2-dithiolate cobalt(II) complex, $Co((CF_3)CS \cdot CS(CF_3))_2$,[95] bisdiethyldithiocarbamate copper(II), $Cu(S_2CN(C_2H_5)_2)_2$,[96] and the corresponding *n*-propyl complex, $Cu(S_2CN(C_3H_7)_2)_2$,[97] copper 8-hydroxyquinolate,[98] and the γ form of bis *N*-methylsalicylaldimine copper, $Cu(C_6H_4O \cdot CHNH(CH_3))_2$.[99] In the cobalt complex,[95] the four basal Co-S bond distances average 2.161 (.016) Å, the ring S-Co-S angles 89.8 (.4)° and the apical Co-S distance is 2.382 (.004) Å. The cobalt atom is displaced from the mean basal plane by .37 Å and the Co-Co distance of 2.68 Å implies that there is an appreciable interaction between the metal atoms. The compound is diamagnetic.

In the two copper-dithiocarbamate complexes,[96,97] the four basal bonds lie in the range 2.30–2.34 Å, while the apical Cu-S bond is 2.85 Å in the ethyl derivative and 2.71 Å in the *n*-propyl derivative. In the crystals of both of these molecules and also of the cobalt complex, the two halves of the dimeric unit, are related by a centre of symmetry. The coordination of the metal atom in $Cu(S_2CN(C_2H_5)_2)_2$[96] is alternatively considered by the authors to be octahedral, since the sixth position is occupied by a hydrogen atom of an ethyl group of a neighbouring molecule, at 2.86 Å, although the metal is displaced by .26 Å toward the apical sulphur atom. In the 8-hydroxyquinolate complex,[98] the Cu-O and Cu-N distances are 1.93 Å and 1.97 Å respectively and the apical Cu-O distance is 2.83 Å, while in the salicylaldimine complex,[99] these dimensions average 1.89 (.015) Å, 1.92 (.015) Å and 2.45 Å respectively.

The other molecules in this group deviate markedly from either idealised configuration. While the metal atoms in the bis *N*-methylsalicylaldimine complexes of manganese, cobalt and zinc achieve five coordination by dimerisation,[100] here, in contrast to the copper complex mentioned above, the resulting polyhedron is best described as distorted trigonal bipyramidal. These three compounds are isomorphous and the analysis was carried out on the zinc complex. The two polyhedra share an edge of type p and are related by a centre of symmetry in the crystal.

The two ligands chelate along edges p, with the nitrogen atoms in the equatorial positions (non-shared) at an average distance of 2.057 (.005) Å. The two apical Zn-O distances are 2.096 (.003) Å for the shared oxygen, and 1.965 (.003) Å, and the equatorial Zn-O distance is 1.994 (.003) Å. The metal atom is displaced from the equatorial plane by .17 Å and the O-Zn-O bond angle is 172.5°.

A distorted trigonal bipyramidal arrangement is also found for two of the metal atoms in the bis-acetylacetonate zinc trimer, $(Zn(acac)_2)_3$.[101] This molecule, in contrast with the analogous nickel complex, indicates the preference of zinc for five coordination. The average angular deviation from the trigonal bipyramidal geometry is 5°. The mono-aquo bis(acetylacetonate)zinc is also five coordinate with an intermediate configuration. All Zn-O bonds lie in the range 2.0–2.02 Å.[102,102a]

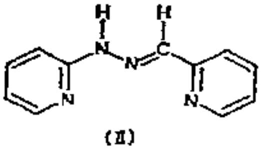
Analysis of bis(dimethyldithiocarbamate)monopyridine zinc, $Zn(S_2CN(CH_3)_2)_2 \cdot C_5H_5N$,[103] shows the coordination polyhedron in this molecule to possess C_2 symmetry within the standard deviations. The chelates span the p edges of a distorted trigonal bipyramid and their mean planes are normal to the equatorial plane of the polyhedron. The apical Zn-S distances are 2.605 (.004) Å and the equatorial distances 2.327 (.004) Å. The Zn-N bond length is 2.08. The angles within the equatorial plane are N-Zn-S, 116.5° and S-Zn-S, 127.1°.

In bis(diethylthiocarbamate)zinc, pentacoordination is achieved by dimerisation as for the copper compound.[104] However, the mode of linking the two halves differs markedly from the latter, and the molecule is probably best considered as analogous to the *N*-methylsalicylaldimine complex, although the departure of the polyhedron from D_{3h} symmetry is far more marked, so that the approximation is very poor. The three formally equatorial Zn-S bond distances average 2.356 Å, while distance to the apical sulphur (non-bridging) is 2.433 (.03) Å and to apical sulphur (bridging), 2.815 (.02) Å.

The iridium atom in iridium bis(1,2-bisdiphenylphosphine ethane) carbonyl chloride, $IrCO((C_6H_5)_2P \cdot CH_2CH_2P \cdot (C_6H_5)_2)_2Cl$ is five coordinate, the coordination polyhedron being intermediate between the two idealised forms.[105] The Ir-P bond distances are all 2.37 (.02) Å and the Ir-C bond length 1.82 (0.02) Å.

(iii) *Species containing terdentate ligands*

The first complex of this type to be structurally characterised was terpyridyldichlorozinc, which was described[106] initially as a distorted trigonal bipyramid (with approximate C_{2v} symmetry), the chlorine atoms being in equatorial positions. However, recent refinement[107] and comparison with the complex Co(PAPHY)Cl_2,

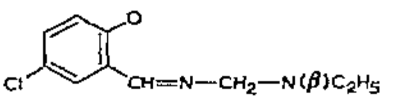


(II)

(PAPHY (II) = Pyridine-2-aldehyde-2-pyridylhydrazone) on the basis of its near isomorphism, has lead to the suggestion that square pyramid of type Fig. 7 (iii) is a better description. In the latter complex,[108] the terdentate ligand is planar, bonds b, c and d being 2.08 (.009) Å, 2.150 (.015) Å and 2.114 (.014) Å respectively. The 'basal' chlorine atom is .17 Å below the plane with e = 2.275 (.004) Å and the cobalt atom. 39 Å above the plane. The apical metal–chlorine bond distance, a, is 2.330 (.004) Å. The author notes that there is "sufficient room" for the cobalt atom within the plane of the ligand, but suggests that its preference for the position above the plane is evidence for the stability of the tetragonal pyramidal configuration. The manganese, cobalt, iron and zinc terpyridyl complexes are all isomorphous.[109]

Tetragonal pyramidal coordination of type Fig. 7. (iii) is found in the methyl bis-(3-dimethylarsinopropyl)-arsine nickel dibromide complex, $NiBr_2 \cdot CH_3$-$As((CH_2)_3As(CH_3)_2)_2$.[110] The metal atom is coplanar with the three arsenic atoms, the Ni-As distances being 2.27 Å. The apical Ni-Br bond distance, (a) is 2.69 Å and the "basal" Ni-Br distance, (e), 2.37 Å.

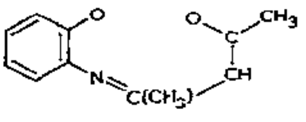
The potentially terdentate Schiff-base ligand, *N*-β-diethylaminoethyl-5- chlorosalicylaldimine (III) forms isomorphous compounds with cobalt and nickel, in which one ligand is bidentate and one tridentate.[111] From an analysis of the nickel complex, it has been found that the coordination polyhedron approximates to type Fig. 7 (ii), with the terdentate



(III)

ligand spanning edges s, and the oxygen atom of the second ligand completing the basal plane. The metal ligand distances in the basal plane, range from 2.20 (.02) Å to 1.93 (.016) Å, with the nickel atom .36 Å above the mean plane. The apical Ni-N distance is 1.98 (.017) Å.

The copper complex derived from acetylacetone-mono (*o*-hydroxyanilate) (IV) is essentially tetrameric with two



(IV)

of the metal atoms in tetragonal pyramidal coordination.[112] The molecule consists of two planar dimeric units, formed by sharing of the phenolic oxygen atoms, which are further associated by sharing of the phenolic oxygen atoms, so that two metal atoms are four coordinate and two are five coordinate. The bond lengths within the basal plane range from 1.90 Å to 2.02 Å, while the apical bond distance is 2.68 Å.

The final group of compounds in this category is derived from terdentate amines. With the metal dihalides, MX_2, M = Mn ... Zn, X = Cl, Br, I, bis-(dimethylaminoethyl)methylamine, $((CH_3)_2NCH_2CH_2)_2NCH_3$, ($Me_5$dien), forms an isomorphous series of pentacoordinate molecules.[113] Analysis of the cobalt complex, Co(Me_5dien)Cl_2, indicates a configuration intermediate between the two idealised polyhedra, with an average Co-Cl bond distance of 2.305 Å and Co-N distances of 2.11 Å, 2.15 Å and 2.30 Å. Bis(diethylaminoethyl)amine, $((C_2H_5)_2NCH_2CH_2)_2NH$, forms a similar complex, Co(Et_4dien)Cl_2, with average Co-Cl bond distances of 2.34 Å and 2.19 Å respectively.[114] In contrast, Ni(Et_4dien)Cl_2 is square planar.

(iv) *Species containing tetradentate ligands*

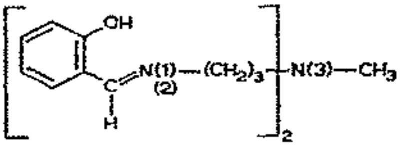
The molecules in this category conform closely to the idealised geometries, primarily as a result of the stereochemical requirements of the ligands. With the tertiary amine, tris(2-dimethylaminoethyl)amine, $N(CH_2CH_2N(CH_3)_2)_3$, (Me_6-tren), the divalent metals, chromium to zinc, form an isomorphous series of complexes of formulation (M(Me_6tren)X)X, where X = Cl, Br, I, ClO_4.[115] Detailed analysis of the cobalt complex (Co(Me_6tren)Br)Br[115] shows the presence of a pentacoordinate cation which, in the crystal, possesses rigorous C_3 symmetry, the axis passing through the apical bromine, metal and tertiary nitrogen atoms. The Co-N (apical) distance is 2.15 (.02) Å and the equatorial bond distance, 2.08 (.018) Å. The cobalt atom is displaced .32 Å from the equatorial plane toward the bromine atom and the Co-Br bond distance is 2.431 (.004) Å.

Essentially, this same arrangement is found in the tris-(*o*-diphenylarsinophenyl)arsine platinum iodide ion,[116] $Pt(As(\text{-}C_6H_5As(C_6H_5)_2)_3)I$, and in a somewhat distorted form for the cation in (Cu(tren) (NCS))SCN.[117] In the latter, the five metal nitrogen distances (NCS coordinated through nitrogen) range from 1.95 Å to 2.16 Å, while two of the angles in the equatorial plane average 113.5° and the third is 130°.

In the second category, the tetradentate ligand closely approaches planarity and the overall structure is of type Fig. 7. (ii). This arrangement is found in the monohydrates of the copper[118] and zinc[119] complexes of *NN'*-disalicylidene ethylenediamine and by means of dimerisation, in the anhydrous copper complex of the same ligand.[120] A similar arrangement is also found in the bis(acetylacetonatoethylenediamine) copper monohydrate,[121] $Cu(H_2O)$ $(CH_3COCH(CH_3)CNCH_2CH_2NC(CH_3)CHCOCH_3)$. Here, the basal bond lengths are in the range 1.85–20.5 Å and the apical bond length is 2.30 Å.

A recent re-examination of the X-ray data of an iron complex of tetraphenylporphine, (TTP), originally formulated as Fe(TTP)$H_2O(OH)$,[122] has shown it to be, in fact, a chloro complex of formula FeCl(TTP).[123a] The iron atom is pentacoordinate with the basal plane of the tetragonal pyramid defined by four nitrogen atoms at a distance of 2.05 (.009) Å. The apical Fe-Cl distance is 2.192 (.012) Å and the iron atom is .38 Å out of the ligand plane. A similar situation exists in the monoaquo zinc complex of the same ligand, $Zn(H_2O)$ (TTP). Here, the metal-nitrogen distance is 2.05 (.01) Å and the $Zn-O(H_2O)$ distance, 2.20 (.06) Å, with the metal .20Å above the ligand plane.[123b] The methoxyiron(III)-mesoporphyrin(IX)dimethyl ester possesses a similar arrangement, with the iron atom .49 Å above the ligand plane and a short iron–oxygen apical bond length of 1.84 Å. The iron–nitrogen distances average 2.073 (.006) Å.[124]

A single structurally characterised example of a pentadentate ligand producing a pentacoordinate complex, is provided by the nickel chelate of the ligand bis(salicylidene-iminopropyl)methylamine(V), Ni(SALMeDPT).[125]

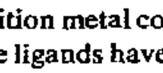


(V)

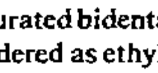
The axial positions of a distorted trigonal bipyramid are occupied by the nitrogen atoms 1 and 2 at a distance of 1.99 Å, while the equatorial Ni-N(3) and Ni-O distances are 2.07 Å and 1.95 Å respectively. The O-Ni-O bond angle at 142° indicates that the coordination polyhedron is really intermediate between the two idealised forms.

D. COORDINATION COMPOUNDS CONTAINING ORGANO-SULPHUR LIGANDS

While there have been several structure analyses of complexes containing dithiocarbamate and xanthate ligands, some of which have been mentioned in the previous section, one of the more exciting discoveries in coordination chemistry in recent years has been the novel trigonal prismatic stereochemistry found in several transition metal complexes of certain unsaturated bidentate organo-sulphur ligands. These ligands have alternatively been considered as ethylene *cis* dithiolate dianions,

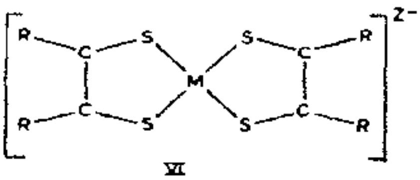


or as dithioketones,



or as intermediate between these extremes and controversy exists as to their exact nature when complexed to the metal atom.

In addition to the formation of the tris complexes for several of which this new stereochemistry has been found, this series of ligands also forms bis complexes with most transition metals, and in those which have been structurally characterised to date, the square planar geometry is stabilised. Compounds in this series which may be formulated:



VI

where R = CN, CF_3, CH_3, C_6H_5, H and z = 0, 1 or 2, readily undergo electron transfer reactions without change in the coordination geometry and for some metals, all three complexes with a given ligand have been isolated,[126] thus making it possible to study similar complexes in a series of *formal* and unusual oxidation states.

The tetracoordinate species whose structures have been elucidated and for which a nearly square planar array of bonds about the transition metal atom occurs, are five of those listed in Table 2. Four of these involve the maleonitriledithiolate ligand (MNT), *i.e.* when R = CN. The sixth species is a neutral cobalt complex, and as mentioned in the previous section, this is a dimeric, diamagnetic molecule in which the metal atom is pentacoordinate.[95]

TABLE 2

AVERAGED DIMENSIONS OF THE CHELATE RINGS IN BIS-DITHIOLATE METAL COMPLEXES (DISTANCES IN Å)

Compound or Anion	*M-S*	*S-C*	*C-C*	*S-M-S*	*Ref.*
$\{Co(S_2C_2(CF_3)_2)_2\}_2$	2.161 (.016)	1.694 (.016)	1.393 (.020)	89.8°	95
$Ni(S_2C_2(C_6H_5)_2)_2$	2.101 (.002)	1.705 (.010)	1.37 (.014)	90.2°	129
$Cu(S_2C_2(CN)_2)_2^-$	2.170 (.004)	1.72 (.01)	1.315 (.020)	92.3°	130
$Ni(S_2C_2(CN)_2)_2^-$	2.146 (.003)	1.714 (.006)	1.356 (.010)	92.2°	131
$Co(S_2C_2(CN)_2)_2^{2-}$	2.161 (.003)	1.723 (.007)	1.34 (.01)	91.4°	128
$Ni(S_2C_2(CN)_2)_2^{2-}$	2.165 (.006)	1.750 (.015)	1.33 (.02)	91.5°	127

Crystallographically, the $Ni(MNT)_2^{2-}$ ion in the tetramethylammonium salt,[127] the $Co(MNT)_2^{2-}$ ion in the tetra-*n*-butylammonium salt,[128] and the neutral bis(*cis*-diphenylethylenedithiolate)nickel,[129] are all required to possess a centre of symmetry, but (apart from the phenyl groups in the latter) in fact the deviations from the idealised D_{2h} symmetry of these anions are very small and chemically insignificant. The other two examples, *viz.* the $Cu(MNT)_2^-$ ion in the tetra-*n*-butylammonium salt,[130] and the $Ni(MNT)_2^-$ ion in the methyltriphenylphosphonium salt,[131] are not required to possess any symmetry elements, but, in the case of the former, the small deviations of the atoms from coplanarity are not thought to be chemically significant, so that the ion again approximates to D_{2h} symmetry.

Approximate coplanarity is also achieved in $Ni(MNT)_2^-$ but here, in addition, it is suggested that weak dimerisation occurs between neighbouring anions.

This is of the same type as that in $(Co(S_2C_2(CF_3)_2)_2)_2$,[95] *i.e.* the anions are stacked in a similar manner in the crystal, but the relevant metal–sulphur distance here is 3.59 Å. Stronger evidence for such an interaction between neighbouring anions is given by the observed low value of the magnetic moment and its temperature dependence. Such an interaction also apparently occurs in the $Fe(MNT)_2^-$ ion, which is pentacoordinate, with an apical Fe-S distance only slightly greater than those in the basal plane.[132]

Comparison of the dimensions of the chelate rings for the six species (listed in Table 2) reveals the essential constancy of the ligand geometry and its apparent independence of the charge on the species, for although it may be argued that the structural data do indicate a tendency for longer C-C and shorter C-S distances in the neutral complexes, and hence a greater degree of delocalisation, it appears that more data are needed to substantiate this. The gross structure of the nickel complex strongly indicates that these ligands should not be considered as dithiodiketones, as the then zerovalent metal would be expected to show a tetrahedral disposition of bonds. In the dianions, in fact, the C-C distance very closely approaches the accepted ethylenic double bond value, so that here the ligands can be considered as dithiolate dianions, and the metal atoms as M^{2+}.

The surprising trigonal prismatic stereochemistry initially found in the tris(*cis*)-diphenylethenedithiolate)rhenium complex,[133] has since been definitively characterised in the corresponding vanadium complex,[134] and the analogous molybdenum complex, $Mo(S_2C_2H_2)_3$.[135] From comparison of powder data, it also apparently occurs in the tungsten, molybdenum and chromium analogues of the rhenium complex.

While the rhenium complex has no symmetry requirements and the vanadium complex has only twofold symmetry, the molybdenum atom in $Mo(S_2C_2H_2)_3$ lies on a threefold axis in the crystal and the coordination polyhedron possesses rigorous D_{3h} symmetry, being, within the standard deviations, a perfect trigonal prism with side of length 3.105 Å.[135] Inclusion of the remainder of the chelate ring reduces the symmetry of the molecule to C_{3h}, there being a dihedral angle of 18° between the plane of the ligand and that defined by the metal and sulphur atoms. The Mo-S distance is 2.33 Å. The idealised polyhedron is illustrated in Fig. 8.

The coordination polyhedron in the rhenium complex is likewise an essentially perfect trigonal prism,[133] the average S-S distance being 3.043 Å, the rhenium–sulphur distance is 2.325 (.01) Å, and the angle subtended at the metal atom, 81.5°. Although there is an appreciable and irregular variation in the C-S distances (1.62 Å–1.75 Å) the molecule possesses roughly C_3 symmetry. In the analogous vanadium complex, the polyhedron is bisected by a crystallographic twofold axis passing through one chelate ring, and there are some deviations away from the idealised symmetry, perhaps due to crystal packing.[134] However, the average intraligand, (d), and interligand, (a), (b) and (c), sulphur–sulphur distances of 3.058 Å and 3.064 Å respectively and the metal–sulphur distance of 2.338 (.004) Å are essentially the same as in the molybdenum and rhenium complexes. In both the rhenium and vanadium complexes, the five membered chelate rings are essentially planar.

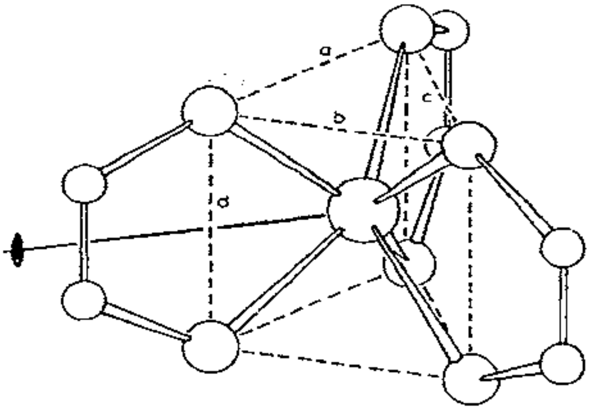
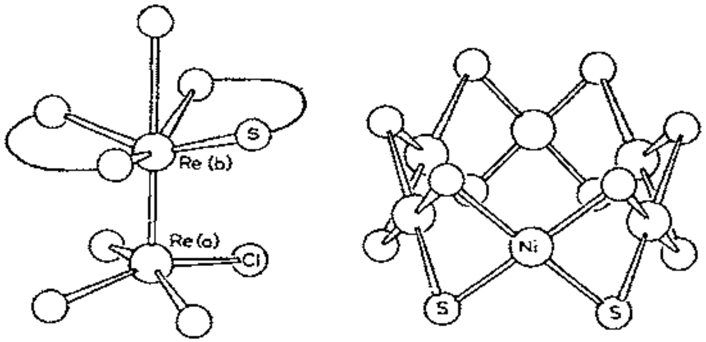


Fig. 8. The idealised arrangement (D_{3h}) of chelate rings in the trigonal prismatic, dithiolate complexes. The crystallographic twofold axis for the $V(MNT)_3^{2-}$ ion is indicated and the interligand distances a, b and c are 3.43 Å, 2.98 Å and 3.18 Å respectively.

The constancy of the formally non-bonded interligand and intraligand sulphur–sulphur distances, irrespective of the nature of the metal atom, led Gray *et al.* to suggest that there are considerable bonding interactions between neighbouring sulphur atoms in these molecules, which are important for the stabilisation of this stereochemistry.[134] Evidence to support this is provided by the structure of the $V(MNT)_3^{2-}$ ion, in which the coordination polyhedron (having C_2 symmetry) is intermediate between an octahedron (strictly D_{3d}) and a trigonal prism.[136] Here, the three independent interligand S-S distances are 2.98 Å, 3.18 Å and 3.43 Å, and it is suggested that the shorter distances are indicative of residual sulphur–sulphur bonding of the type stabilising the trigonal prism. In addition, the intraligand S-S distances are marginally longer (average 3.13 Å) than in the neutral complexes. (The vanadium sulphur distances average 2.36 (.01) Å. An indication of the intermediate character of the polyhedron is provided by the angles subtended at the metal atom by the pair of donor atoms furthest apart. In the neutral complexes this is 136° ± 1, while in the $V(MNT)_3^{2-}$ ion, the average value is 158.6° and in the D_{3d} polyhedron, 173°. This configuration is not a result of crystal packing forces and the authors suggest that for the series of tris chelates, the more highly reduced species will tend toward an "octahedral" array of ligands, while the D_{3h} arrangement will be favoured in the neutral complexes.

Two molecules containing the thioether, 2-5,dithiahexane, $CH_3SCH_2CH_2SCH_3$, (DTH), have been structurally characterised, namely, a cobalt complex, $Co(DTH)_2(ClO_4)_2$,[137] and a species of formulation $Re_2Cl_5(DTH)_2$, obtained by reaction of the octachlorodirhenate ion with dithiahexane.[138] The first molecule, which was believed, on the basis of magnetic data, to contain square planar cobalt, in fact contains coordinated perchlorate, being the first structurally authenticated example of this situation. The two dithiahexane ligands are *trans* with Co-S distances of 2.29 Å and the perchlorate oxygens complete a distorted octahedron at the rather long Co-O distances of 2.34 Å.

The rhenium complex, which is best written $ReCl_4$-$ReCl(DTH)_2$, has the structure shown in Fig. 9(i). It can be seen that the metal–metal bond of the $Re_2Cl_8{}^{2-}$ ion is retained, but that rather than having the eclipsed configuration found in this ion and which is stabilised by the formation of a δ bond,[139] the ReS_4 group is staggered with respect to the $ReCl_4$ group. The authors suggest that the destabilisation of the eclipsed configuration relative to the staggered one found in the crystal, is due to the presence of the extra electron, and that here the two metal atoms are in different oxidation states (Re(a) being III and Re(b), II) and are connected by a triple bond. The Re-Re distance is 2.29 (.01) Å, compared with 2.22 (.01) Å found for the *formally* quadruple bond in $Re_2Cl_8{}^{2-}$,[139] Re(a)-Cl is 2.33 (.03) Å, Re(b)-S, 2.44 (.02) Å and Re(b)-Cl, 2.51 (.03) Å.



(i) (ii)

Fig. 9. (i) The structure of $Re_2Cl_5(DTH)_2$. The chelate rings are denoted by the curved lines. (ii) The hexagonal nickel-sulphur skeleton found in $(Ni(SC_2H_5)_2)_6$.

Several stereochemically interesting compounds have been prepared containing metal–sulphur bridging systems and one of these, which has been structurally characterised, is bis(ethylthio)nickel(II), $Ni(SC_2H_5)_2$.[140] This has been shown to be a hexameric molecule and is depicted in Fig. 9(ii). Each nickel atom exhibits square planar coordination, with Ni-S, 2.20 (.02) Å and Ni-Ni, 2.92 Å. The nickel sulphur system has D_{6h} symmetry within the standard deviations, while the overall molecule just has symmetry C_i. The axial cavity in the centre of the molecule is large enough to accept electronically "rich" linear molecules, such as CO.

Dithiocarbamate complexes whose structures have been determined recently (in addition to those described in section C) include two nickel complexes which have square planar coordination, $Zn(S_2CN(CH_3)_2)_2$, $CuS_2CN(C_2H_5)_2$, and two ruthenium compounds, $Ru(S_2CN(C_2H_5)_2)_3$ and $Ru(S_2CN(C_2H_5)_2)_3NO$. The nickel–sulphur bond lengths in $Ni(S_2CN(C_2H_5)_2)_2$[141] and $Ni(S_2CNH_2)_2$,[142] average 2.20 Å and 2.21 Å respectively, and are much shorter than the corresponding distances found in paramagnetic complexes, *e.g.*, $Ni(SC(NH_2)_2)_4Cl_2$, where Ni-S is 2.46 Å.[143] Bis(dimethyldithiocarbamate)zinc,[144] like the diethyl compound is dimeric, but, in contrast to the latter, which is pentacoordinate, the metal here is tetrahedral and is surrounded by the two sulphurs of one ligand and one sulphur from each of two shared ligands. The central portion of the dimer (which has twofold symmetry in the crystal) is thus an eight membered ring. The average Zn-S bond distance is 2.38 Å.

Diethylthiocarbamate copper(I) is tetrameric,[145] the four metal atoms being at the corners of a tetrahedron, with Cu-Cu distances of 2.66 Å and 2.76 Å and the four ligands bonded through the faces of the tetrahedron. The two ruthenium chelates each contain octahedrally coordinated metal atoms, one of dithiocarbamate ligands in $Ru(S_2CN(C_2H_5)_2)_3NO$ functioning as a unidentate ligand. In $Ru(S_2CN(C_2H_5)_2)_3$, the metal–sulphur distances average 2.382 Å, while in the nitrosyl complex, the average is 2.402 Å and Ru-N, 1.72 Å.[146]

Xanthate complexes have rarely been studied and for the simple metal chelates, data is available only for the bis(diethylxanthate) compounds of nickel[147] and zinc.[148] The former is a centrosymmetric molecule, with square planar coordination and Ni-S distance of 2.235 Å, while the zinc atom is tetrahedrally coordinated by four sulphur atoms, all from different ligands, these latter therefore all being bridging. The Zn-S distance is 2.36 Å.

The most interesting molecule containing ethyl xanthate as ligands is a binuclear, diamagnetic oxo complex of molybdenum(V), $O(MoO(S_2COC_2H_5)_2)_2$. This molecule can be described as consisting of two distorted octahedra, sharing an oxygen atom, to give a linear Mo-O-Mo bridging group.[149] In each octahedron, the xanthate groups are *cis*, so that the terminal oxygen atoms are *cis* to the bridging one. When viewed down the Mo-O-Mo axis, these terminal Mo-O bonds are nearly superimposed, and it is suggested, on the basis of a Hückel calculation, that it is the relative orientation of these bonds which governs the magnetic properties of the molecule. The Mo-O terminal bonds are very short, having a mean value of 1.65 (.02) Å, which is indicative of a high bond order, and greater than a *formal* bond order of two, if the value of 1.737 (.005) Å found in MoO_3(dien)[150] is considered to be representative of this value. The Mo-O bridging bond, on the other hand, is considerably longer, at 1.86 (.02) Å.

The degree of multiple metal–oxygen bonding is reflected in the metal–sulphur bond lengths, the Mo-S distances *trans* to the terminal Mo-O bonds averaging 2.70 (.01) Å, and those *trans* to the bridge bonds, 2.535 (.01) Å. Taking the average value of 2.49 (.007) Å as representative of a single Mo-S distance, the weakness of bonds *trans* to bonds of high multiplicity, a point mentioned in connection with some pentacoordinate species, can be seen again. A similar trend in metal–oxygen bond lengths has also been found in $K_2(MoO_2(C_2O_4)H_2O)_2O$.[151]

E. STEREOCHEMISTRY OF β-KETOENOLATE COMPLEXES

Acetylacetone and related β-diketones are amongst the most versatile ligands in coordination chemistry, and a large amount of structural data has been accumulated on complexes involving these ligands during the last decade. The results of some of the more accurate determinations have been reviewed recently and the dimensions of the chelate rings compared.[152] In addition, a more general review of the chemistry of these compounds has been made.[153]

The compounds containing solely β-diketone ligands can be divided up according to whether the metal ligand ratio is 2, 3 or 4 and the latter group has been discussed in section B. While the tris complexes are "straightforward" octahedral species, the bis complexes exhibit a variety of stereochemistries, for, in addition to square planar and tetrahedral coordination, there is the additional possibility of molecular association, leading to five and six coordination for the metal atom.

These latter complications have been characterised for the bis(acetylacetonate)cobalt, nickel and zinc complexes, and the coordination polyhedra for these three species are illustrated in Fig. 10. While the metal atoms achieve six coordination in the tetrameric cobalt[154] and trimeric nickel chelates,[155] two of the metal atoms in the zinc chelate are five coordinate, and the third six coordinate.[101] The latter molecule possesses a twofold axis which passes through the central octahe-

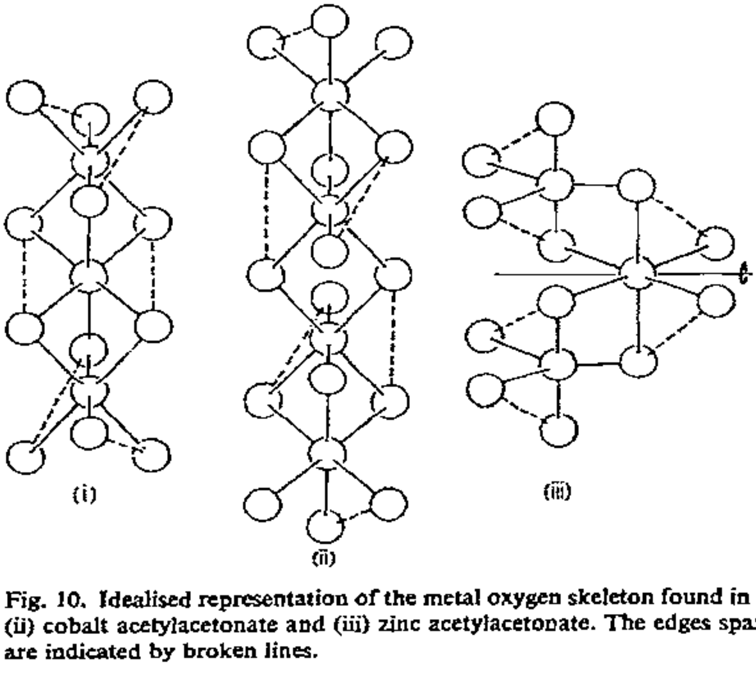


Fig. 10. Idealised representation of the metal oxygen skeleton found in (i) nickel acetylacetonate, (ii) cobalt acetylacetonate and (iii) zinc acetylacetonate. The edges spanned by the chelate rings are indicated by broken lines.

dron, the octahedron being linked to the trigonal bipyramids by common edges. In the cobalt and nickel chelates, the modes of linking the "metal" octahedra in the two molecules differ. In the nickel complex, the three octahedra share faces, the molecule possessing an approximate centre of symmetry, while the cobalt complex is best considered as being composed of two fragments which are joined along an edge common to two octahedra, each of the fragments consisting of two octahedra with a common face. The two halves of the molecule are related by a centre of symmetry, and the overall structure can be represented as *ddll*, *i.e.* in all four octahedra the two chelating ligands are *cis*. In the nickel complex, on the other hand, the ligands in the central octahedron are *trans* and the overall structure can be represented as *dtl*, this being one of nine possible structures for this molecule.[154]

The metal to oxygen bonds in these molecules can be divided into three types: (a) those in which oxygen is bonded to only one metal; (b) those between a bridging oxygen and the metal atom which the particular ligand chelates, and (c) the second type of bridging bond, *i.e.* that to the metal atom not chelated by the ligand. While this distinction can be drawn, the values observed have quite large standard deviations. However, as might be anticipated, in both molecules, the bonds in which oxygen is bonded to only one metal atom are, on average, significantly shorter than those involving oxygen as a bridging atom. Classifying the distances as above, these (average values) are for the cobalt complex: (a) 2.02 (.03) Å, (b) 2.09 (.03) Å and (c) 2.24 (.03) Å, and for the nickel complex: (a) 2.01 (.05) Å, (b) 2.11 (.05) Å and (c) 2.14 (.05) Å. Distances of type (a) and (b) are comparable with the metal–oxygen bond distances in the dihydrates.[156]

Inspection of scale models of these polymeric molecules indicates that replacement of the methyl groups on the chelate rings by more bulky substituents, should prevent molecular association occurring, due to steric repulsions between the groups, and should lead to monomeric molecules. This has been shown to be the case when the ligand is dipivaloylmethane (DPM), the substituents being *tert*-butyl groups. The nickel complex, $Ni(DPM)_2$ has square planar geometry,[157] and the cobalt atom in $Co(DPM)_2$ is tetrahedrally coordinated. The actual structure analysis which was carried out on the isomorphous (and presumably isostructural) zinc complex,[158] showed the metal atoms in these molecules to lie on fourfold inversion centres in the crystal and there to be an appreciable distortion away from the idealised tetrahedral angle—to 94.7° and 113.2°—so that the coordination polyhedron possesses D_{2d} symmetry. It is thought that these deviations are responsible for the anomalous features of the electronic spectrum of this molecule, which is unlike those found for "typical" tetrahedral cobalt complexes. The metal–oxygen bond lengths in these molecules are for $Zn(DPM)_2$, 1.962 (.007) Å and for $Ni(DPM)_2$, 1.836 (.005) Å. The low value of the latter bond length compared with the nickel–oxygen bond lengths in $(Ni(acac)_2)_3$ and in the dihydrate,[156] is consistent with the shorter bond distances generally found in square planar diamagnetic nickel complexes, as compared with those found in octahedral species.

For example, octahedral and square planar nickel complexes, with *meso*-stilbenediamine, yield values of 2.05 and 1.89 Å respectively for the metal–nitrogen bond distances.[159]

In addition to the simple octahedral dihydrates[156] $M(acac)_2 \cdot 2H_2O$, which are known for both cobalt and nickel and the X-ray structures of which have both been determined, a monohydrate has also been isolated from concentrated solutions of anhydrous cobalt acetylacetonate, and has been characterised crystallographically as a dimeric molecule with formula $(Co(acac)_2 \cdot H_2O)_2$.[160] This centrosymmetric dimer corresponds to the two central octahedra of the tetrameric $(Co(acac)_2)_4$ molecule, (*i.e.* the octahedra with a common edge) with the two positions which were filled by bridges from the terminal units now occupied by water molecules. The bond lengths in this molecule are comparable with the corresponding values for the tetramer, apart from the Co-Co separation, which is 3.27 Å, as against 3.57 Å in the tetramer. The average of (a) and (b) type bonds is 2.02 (.03) Å and of type (c), 2.16 (.03) Å, while the cobalt water–oxygen distance is 2.20 (.03) Å. It is of interest to note that this species is of the same stoichiometry as the zinc complex, which is pentacoordinate and monomeric. As in the anhydrous complex, the preference of zinc for this stereochemistry is demonstrated here.

Other molecules containing two *β*-diketoenolate metal rings include three tetracoordinate copper(II) complexes, all of which have square planar geometry and the pentacoordinate vanadium(IV) species, mentioned in section C, *viz.* $VO(acac)_2$[90] and *cis* $VO(bzac)_2$.[91] The three copper chelates are the "parent" compound $Cu(acac)_2$,[161] *trans* $Cu(bzac)_2$[162] and bis (3-phenylacetylacetonato)-copper.[163] The last two compounds have been studied in connection with the elucidation of their single crystal spectra and they also provide useful data for studying the variation of chelate ring dimensions with substituent. In connection with the latter point, it appears that in the case of benzoylacetone chelates, the carbon–oxygen bond adjacent to the methyl group has more double bond character than the one adjacent to the phenyl group, a point which was discussed in connection with the vanadyl chelates (see page 422) and which has been further confirmed by the analysis of the corresponding *trans*-$Pd(bzac)_2$ complex.[164]

The tris complexes for which accurate structure analyses have been reported are the acetylacetonates of chromium,[165] manganese,[166] and iron,[167] all of which are octahedral. For manganese(III) the regular octahedral configuration should be subject to a Jahn–Teller distortion, as the ground state is $^5E_g(d^4)$. Although idealised octahedral symmetry is unattainable, due to ligand constraints, the coordination polyhedron for this chelate deviates much more markedly from a regular octahedron, than it does for the iron and chromium chelates. The "symmetry" is destroyed by considerable variation in the bond angles at the metal and in the oxygen–oxygen distances, there being two distinct sets of the latter, the ring "bite" averaging 2.81 Å and the inter-ring distances averaging 2.60 Å. The consequence of this is that the point symmetry of the polyhedron is D_3, not the idealised D_{3d}.

These two sets of distances in the chromium complex are, by contrast, 2.786 Å and 2.751 Å. The average metal oxygen distances are 1.952 (.007) Å, 1.872 (.008) Å and 1.992 Å respectively for the Cr, Mn and Fe chelates.

One feature of the geometry of the chelate rings in many metal complexes with β-ketoenolates, is that the plane through the metal and oxygen atoms is canted to the mean plane of the ligand atoms, the dihedral angle being in the range 160°–170°. While this is a common feature, it is not necessary and for the square planar and tetrahedral species,[157] the chelate rings closely approach planarity; It might be due to intramolecular interactions in the more highly coordinated species.

In addition to the normal behaviour of β-ketoenolates as bidentate ligands, several complexes of platinum also illustrate their ability to coordinate to the metal through the "active" methylene carbon atoms of the ring. This feature is exemplified in trimethylplatinum 4–6 nonanedione, which is a dimeric, centrosymmetric molecule containing octahedral platinum.[168] The metal is surrounded by three (mutually *cis*) methyl groups (Pt-C, 2.02 Å), two oxygens of one ligand (Pt-O, 2.15 Å) and the methylene carbon atom of the other ligand (Pt-C, 2.39 Å). A consequence of the dimerisation, is that the platinum carbon bond is approximately normal to the plane of the chelate ring.

Reaction of the corresponding $(Pt(CH_3)_3acac)_2$ with dipyridyl causes the cleavage of the dimer at the platinum oxygen bonds, so that the acetylacetone remains coordinated through the methylene carbon atom, (Pt-C, 2.36 Å) the dipyridyl molecule occupying the other two positions,[169] while reaction with ethylenediamine causes cleavage of the Pt-C bond, giving a molecule in which two $Pt(CH_3)_3acac$ units are linked by the diamine (Pt-N, 2.31 Å).[170]

The square planar complex ion, $Pt(acac)_2Cl^-$, contains one ligand acting as a bidentate chelate, and one coordinated through the methylene carbon atom with Pt-O (two values) and Pt-C distances of 2.09 Å, 1.97 Å and 2.13 Å respectively.[171]

The final example of this mode of coordination is provided by the complex $Ag \cdot Ni(acac)_3 \cdot 2AgNO_3 \cdot H_2O$,[172] which contains nickel, octahedrally coordinated by the three bidentate ligands (Ni-O, 2.04 (.06) Å) with the silver ion "interacting" with the methylene carbon atom of one of the chelate rings (Ag-C, 2.34 Å).

The final molecule in this section is di μ-diphenylphosphinatoacetylacetonato chromium(III), which is the first member of a series of polymers containing the $Cr(acac)_2(OP(C_6H_5)_2O)_2$ unit. The two octahedra, in which the acac groups are *cis*, are linked by two diphenylphosphinate groups, such that the bridging system is a puckered eight membered ring. The twelve metal–oxygen distances all lie in the range 1.946–1.968 (.009) Å, and the coordination polyhedra are very little distorted.[173]

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