Coordination Chemistry Reviews, 24 (1977) 179—275

STRUCTURES OF HIGH COORDINATION COMPLEXES

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(Received 13 July 1977)

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ABBREVIATIONS *

ac	acetate
acac	acetylacetonate =pentane-2,4-dione
atp	antipyrine
bipy	2,2′-bipyridyl
butac	isobutylacetonate
bzac	benzoylacetonate
dedtc	diethyldithiocarbamate
demtc	diethylmonothiocarbamate
diars	*o*-phenylenebis(dimethylarsine)
dip	1,2-di(4-pyridyl)ethane
dipic	pyridine-2,6-dicarboxylate
dmdtc	dimethyldithiocarbamate
dmdtp	dimethyldithiophosphine
dmf	*N*,*N*-dimethylformamide
dmso	dimethylsulphoxide
dpdm	dibenzoylmethane
dpm	2,2,6,6-tetramethylheptane-3,5-dione
edta	ethylenediaminetetraacetate
etc	ethylcarbamate
facim	3-trifluoroacetyl-d-camphor
fod	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione
hac	hydroxyacetate
hfac	hexafluoroacetylacetonate
HSM	hard sphere model
imda	iminodiacetate
isonic	isonicotinate = *p*-pyridinecarboxylate
L	ligand
M	metal
MFP	most favourable polyhedron
mtc	4-morpholinecarbodithioate
naph	1,8-naphthyridine
Netsal	*N*-ethylsalicylaldimine
nic	nicotinate = *m*-pyridinecarboxylate
nta	nitrilotriacetate
ox	oxalate
oxyd	oxydiacetate

* Abbreviations for each polyhedron are given in the text.

paie	1,2-bis(pyridine-2-aldimine)
paphy	pyridine-2-carbaldehyde-2-pyridylhydrazone
pc	phthalocyaninate
phen	1,10-phenanthroline
py	pyridine
pyno	pyridine-*N*-oxide
8quin	8-quinolinol
8quinBr	5-Bromo-8-quinolinol
sal	salicylic acid
salen	*N,N'*-ethylenebis(salicylideneimine)
tfac	5,5,5-trifluoropentane-2,4-dione
thac	thiodiacetate
thacox	tetrahydrazinecarboxylate
tmu	tetramethylurea
topo	tri-n-octylphosphineoxide
tpao	triphenylarsineoxide
tptp	tetraparatolylporphyrin
tppo	triphenylphosphineoxide
trop	tropolone
γtrop	γ-isopropyltropolone
ttbd	4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione
z	normalised bite

A. INTRODUCTION

There have been a number of reviews on the structure of high coordination complexes. In 1967, Muetterties and Wright [1] discussed the structures of complexes with coordination number from 7 to 12 and this review set the ground for future work. In 1967 Lippard described eight coordinate chemistry [2]. In the ten or so years since these reviews were written, the crystal structures of well over 200 such complexes have been determined. However the large amount of new available material is not the sole justification for this present review. It has become evident that crystallographic data can provide information about the geometric features of reaction paths. This has been shown by Burgi et al. [3—6] for a whole series of inter- and intra-molecular reactions and by Muetterties and Guggenberger [7] and Drew [8] for intramolecular rearrangements in ML_5 and ML_7 molecules respectively. This has brought about changes in the way chemists look at structures. The previous emphasis on bond lengths and a qualitative description of the geometry in terms of ideal polyhedra have been replaced by a much more detailed analysis of shape characteristics.

This review reflects these changes and a critical analysis is provided of the available material *. In particular, the published coordinates for each com-

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* Two recent reviews on structures of lanthanide and actinide compounds [9,10] accept uncritically descriptions of geometry from the original references.

plex have been used to calculate the geometry of the coordination sphere which has then been analysed and tabulated in terms of polyhedra and their shape characteristics. In this way possible reaction paths between the various polytopes can be readily observed. These analyses also provide a way of checking upon the various predictions that have been made of the geometries of such complexes by the method of minimising intramolecular repulsions. The various tables of structures can also be used to predict the geometries of related molecules.

In this review the structures of complexes in which the metal atom is surrounded by between 8 and 14 atoms are described. In view of a detailed review on seven coordination published in 1977 [8], this coordination number while usually considered to be 'high', has been omitted. The structures of monomeric complexes are strongly emphasized in this review because their geometry is most often due to the interaction of the metal and its donor atoms rather than intermolecular forces. Therefore although some polymers are included, their structures are given less emphasis. This is particularly so for structures including polymeric chains whose geometric requirements may well be a dominant factor in the choice of polyhedra. Structures in which edges or faces of the coordination polyhedra are shared with other metals are usually omitted, as are organometallic compounds, molecules containing metal—metal bonds and ionic complexes of Groups I and II. There are a number of complexes whose coordination number is ambiguous containing n bonds of expected lengths and 1 or 2 more about 0.5 Å longer. Such compounds, invariably polymeric, are given only brief mention. In view of the method of analysing structures complexes whose coordinates remain unpublished could not be included in detail but are listed in the Tables with the author's choice of geometry noted.

B. ASPECTS OF MOLECULAR GEOMETRY

A brief perusal of the literature suggests that there are almost as many ways of looking at the geometry of a molecule as there are chemists. Some authors are just concerned with the coordination number and which atoms are mutually *cis* and *trans*. Thus there are a number of papers published even in 1977 in which the geometry of a molecule is found to be distorted between two ideal polyhedra and yet the author does not consider a discussion of this to be worthwhile. Others analyse M—L bond lengths, L—M—L angles or L···L distances or even packing effects to the exclusion of other dimensions. This is not a complaint as there is room for all points of view. But the bias of this review and reviewer needs stating.

Our main interest is the geometry of the ML_n core of the molecule, that is the geometry of the metal coordination sphere. Most chemists would require for this purpose a list of bond lengths and angles. For complexes with low coordination number such dimensions are often adequate to distinguish the molecular geometry. Most authors attempt to describe molecular geome-

try in terms of an ideal polyhedron. This obviously satisfies a psychological need but in most cases (with the possible exception of coordination numbers of 10 and above) is also chemically worthwhile because the ideal geometries often lie at energy minima and distortions from them are thus indicative of special electronic or steric features of the molecule. In addition this shift from an ideal polyhedron is usually along a reaction pathway. This comparison with the ideal is not as simple a process as it might appear particularly for the higher coordination numbers where the ideal polyhedron can have a wide range of L—M—L angles.

The most useful procedure in our view is to attempt to fit a set of ML_n coordinates to those of an ideal polyhedron of the requisite symmetry. The method used here is based on that of Dollase [11]; other workers [12,13] have suggested a slightly different approach. The Dollase method has already been used to analyse a number of seven coordinate polyhedra [8,14]. The root mean square difference between the coordinates observed in a ML_n coordination sphere and those of an ideal polyhedron is minimised by the method of least squares. Variables are the orientation of the coordination sphere and also isotropic and/or anisotropic dilation where appropriate to the symmetry of the polyhedron. For comparison the ideal molecule is given a radius of 1 Å. This method has the particular merit in that just one value, the r.m.s. difference gives the amount of distortion from a particular symmetry and can therefore be compared for several molecules. And in addition unlike some other methods the shape of the ideal polyhedron is allowed to vary within the limits of the ideal symmetry. The root mean square separation (Δ) is given by

$$\Delta = \sum_{i=1}^{i=n} d_i^2/n \qquad (1)$$

where n is the number of atoms around the metal in the coordination sphere and d_i is the distance between comparable points in the observed and ideal polyhedra.

In our use of the program no attempt is made to allow for the differing number of parameters in the various ideal polyhedra nor have weights been used. As Fritchie [12] has shown, it is possible by using statistical tables to estimate the confidence level at which various models can be preferred over others. However this has not been done because our primary interest is in observing the type of distortion from ideal symmetry and whether it follows specific reaction paths. The program, which was written to apply the Dollase method, using guidelines for each ideal polyhedron automatically fits a set of coordinates to all the ideal polyhedra for that coordination number. Thus it can be seen whether a molecular structure can be adequately described in terms of one polyhedron or two or even three and hence whether its structure is on the reaction pathway from one ideal polyhedron to another. The most serious difficulty about this method is that it requires a non-trivial

computer program to calculate the r.m.s. separation.

A different method has been proposed by Porai-Koshits and Aslanov [15] for eight coordinate molecules and expanded by Muetterties and Guggenberger [7,16] for four to nine coordination. They proposed that a comprehensive and quantitative measure of shape can be readily obtained from the dihedral angles formed by the normals to adjacent polytopal faces. These so called δ and ϕ angles are specific for a particular coordination number and will be discussed in detail in the appropriate sections. We have found these angles to be extremely useful for analysing eight coordinate polyhedra but to be of only limited use for seven and nine coordination and of no use at all for 10—14 coordinate polyhedra. The major problem with such angles is that there are several sets that can be chosen; one set may be characteristic of one particular polyhedron and another set of another polyhedron.

A number of authors [8,13,17] have considered the correct procedure to be adopted when the ligands around the central metal atom are different and this leads to major variations in M—L bond lengths. These differences can be avoided by normalisation of M—L bond lengths to 1.0 Å before analysing the geometry. This procedure is equivalent to analysing the L—M—L bond angles of a molecule to the exclusion of M—L bond lengths. There is considerable debate as to whether this is justified. Clearly differences in bond length are an important feature of the geometry of a molecule and to exclude them from a description of the geometry cannot be totally justified. However an attempt to compare Δ values or δ angles of two molecules with different bond lengths is complicated and can lead to unreasonable results if this is not done. In this review bond lengths are normalised but major differences found in the molecule will be noted. Values of edges quoted here are also taken from the normalised polyhedron.

Bond lengths are not of prime interest in this review but it is obvious that the coordination number is dependent upon the relative (and absolute) size of the metal and donor atoms. Day and Hoard [18] quote values for (M—L)/(L···L) of 0.83, 0.87, 0.93 for 8, 9, 10 coordination respectively but these will vary not only for different polyhedra of the same coordination number but over different edges in the same polyhedron. Only metals with particularly large radii can achieve such ratios and then only with the smaller ligands. With transition metals the maximum coordination number is 8 (the exception that proves the rule being $[ReH_9]^{2-}$) and this is only achieved with relatively small donor ligands such as S, N, O, C and F. The maximum number of large halogens, Cl, Br or I that can be fitted into an eight coordinate (or for that matter a seven coordinate) complex is four. Thus 9—12 coordination is restricted to lanthanides and actinides and to achieve 14 coordination the very large uranium and very small hydrogen atoms are required. Most high coordinate complexes contain ligands which are polydentate rather than monodentate. These ligands provide small L···L distances without adding to the sum of L···L repulsions. This is particularly important for coordination numbers 10—12 and bidentate nitrate and carbonate predominate in the coordination

sphere. However even with the presence of polydentate ligands, the ligand packing diameter is often much smaller than the sum of van der Waals radii. The importance of this is hard to assess because such radii may well be overestimated. However it is often found in such complexes that the observed distortion from ideal does increase the shortest L···L contacts. As a compensation, the metal radius is increased in high coordinate complexes and this has been analysed [19,20] in surveys of oxides and fluorides for a number of metals.

The importance of packing effects on molecular geometry is notoriously difficult to estimate. A surprisingly high percentage of molecules considered here have imposed crystallographic symmetry where packing effects may well have tipped the balance towards one geometry rather than another. Individual cases are described in the later sections.

We have not attempted to allow for standard deviations of atomic coordinates in our calculations, though they should be born in mind particularly for the earlier structures of actinide complexes where the predominance of scattering by the heavy metal led to large deviations in the positions of the lighter atoms. Bond lengths are always quoted to 0.01 Å and angles to 0.1°. This may be unfair to some recent structures but as no theory of high coordination geometry is adequate to account for differences of 0.05 Å in bond length let alone 0.005 Å such truncation is justified.

As each coordination number presents its own problems in analysis, 8, 9 and 10 coordinate complexes are considered in turn. A further section describes briefly the few 11, 12 and 14 coordinate structures. The molecules are categorised via ligand type which has been found to be the most important factor in the choice of geometry.

C. EIGHT-COORDINATION

Eight coordination has been well reviewed in the past [1,2] and in addition many structural papers have included good analyses of molecular geometry. (Unfortunately this is not true for 9 and 10 coordinate complexes). The basic analyses of the two most frequently observed 8 coordinate polyhedra, the dodecahedron (Dod) and the square antiprism (SAP) produced by Hoard and Silverton [21] have needed no modification over the years. Indeed their familiar diagrams of the two polyhedra are redrawn here as well as in scores of other publications.

Calculations of L···L repulsive energies for eight monodentate ligands [21—23] show just two minima representing the Dod and SAP stereochemistries. Blight and Kepert [24] also calculated potential energy surfaces for $M(L—L)_4$ and $ML_4(L—L)_2$ molecules and again these two predominate. Indeed the vast majority of 8 coordinate complexes can be described in terms of one or both of these geometries. Three other geometries are found in a few 8 coordinate structures. The cube is observed in one $M(L—L)_4$ and two ML_8 complexes, all three containing an actinide metal. The hexagonal bipyra-

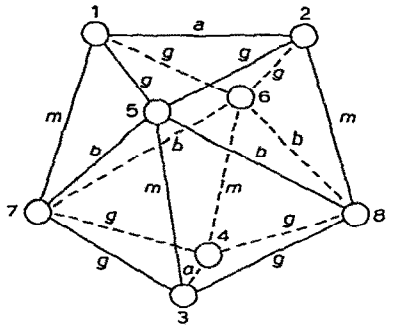

Fig. 1. The dodecahedron (D_{2d}).

mid (HP) is more common though observed only in complexes containing the unique uranyl ligand in axial sites. Whether the bicapped trigonal prism (BCTP) exists as a separate geometry is a matter of some debate but a few molecules can be adequately described in terms of it. A sixth geometry mentioned by Lippard [2] is the puckered hexagonal bipyramid but it is omitted since all the monomeric complexes in this review can be adequately described without recourse to it.

These five geometries are of course not distinct entities and conversion from one to another is a relatively trivial process. Thus a geometry not obviously comparable to one of the ideal polyhedra can be described in terms of many of them. There is an additional point to be emphasised; none of these geometries should be considered as intermediate between two others. There are distinct reaction paths between pairs of them but these do not encompass any of the others.

(i) Characteristics of ideal polyhedra

(a) Dodecahedron. The Dod (symmetry D_{2d}, $\bar{4}2m$) contains two types of ligand site called A and B (Fig. 1). The A sites (1, 2, 3, 4) form a flattened tetrahedron and the B sites (5, 6, 7, 8) an elongated one. Sites 1, 2, 7, 8 and 3, 4, 5, 6 each form trapezoids which lie in mutually orthogonal mirror planes and interlock in agreement with the $\bar{4}$ axis. The shape characteristics are the M—A and M—B bond lengths and the angles between these bonds and the $\bar{4}$ axes which are called θ_A and θ_B. There are 18 edges $2*a$, $4*b$, $4*m$ and $8*g$. The dodecahedron is one of the fundamental polyhedra in which all faces are triangular.

In the hard sphere model (HSM) with M—A = M—B = 1.00, shape characteristics are $\theta_A = 36.9$, $\theta_B = 69.5°$ with edges $a = m = g = 1.20$ and $b = 1.50$. Hoard and Silverton [21] also quote values for the most favourable polyhedron (MFP) which are $\theta_A = 35.2$, $\theta_B = 73.5°$ (M—A)/(M—B) = 1.03 with edges $a = m = 1.17$, $g = 1.24$, $b = 1.49$. To obtain these values, the total repulsive energy for a discrete complex was assumed to be given by eq. (2)

$$E = \sum_{i \neq j} r_{ij}^{-n} \qquad (2)$$

where r_{ij} is the distance between ligands i and j : n is an integer. Then the shape characteristics of the particular polyhedron (in this case the Dod) were varied and a minimum for E was obtained. It is not clear exactly what shape characteristics were allowed to vary in the calculation of E and it may even be that the MFP values were taken directly from observed values in $Zr(acac)_4$ and slightly idealised. However despite their somewhat obscure derivation the MFP values have achieved wide prominance and are largely valid for molecules with monodentate ligands and/or polydentate ligands with no unusual characteristics. However it should be noted at the outset that the Dod of D_{2d}, $\bar{4}2m$ symmetry encompasses a very wide range of shapes; for example θ_A and θ_B range between 48.6—34.3 and 88.2—73.7° in $M(L—L)_4$ complexes (Table 10).

δ angles for the Dod are calculated over the 4 b edges and are written as 1(57)3, 2(68)4, 1(67)4 and 2(58)3. 1(57)3 is an abbreviation for the angle between the normals to faces 157 and 573. δ angles are always quoted here in this particular order so that the first two angles are calculated using all eight atoms. This is particularly important when the pathway to the SAP is considered. A further set of angles called ϕ which assess the planarity of each trapezoid have been found useful. These are the angles between planes of atoms 7, 8, {1,2} and 1,2, {7,8} and between planes 5, 6, {3,4} and 3,4, {5,6} where {nm} signifies the mid-point of the edge between atoms n and m. δ angles in the HSM are all 29.5° although by definition the only requirement from symmetry is that all four are identical. Two 10 coordinate polyhedra are derived from the Dod and are described in Section E.

(b) Square antiprism. The SAP (symmetry D_{4d}, $\bar{8}2m$) contains only one type of ligand site (Fig. 2). There are two sets of 8 edges, s between sites in the same square and l between sites in different squares. The most often quoted shape characteristics are the l/s ratio and θ the angle between the bonds and the $\bar{8}$ axis but these are not independent as l/s increases as θ decreases. The two independent shape characteristics are M—L the bond length and θ. In the HSM in which edges are equivalent $\theta = 59.2°$ and $l = s = 1.21$. Hoard and

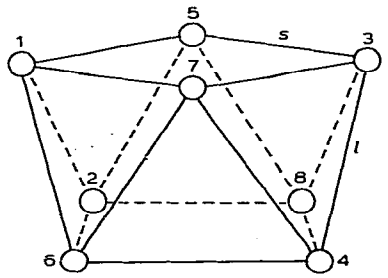

Fig. 2. The square antiprism (D_{4d}).

Silverton [21] allowed the l/s ratio to vary and found a minimum for E (in eqn. 2) at $n = 7$ with $l = 1.258$, $s = 1.190$, $l/s = 1.057$ and $\theta = 57.3°$. With $n = 1$, the minimum shifts to $l/s = 1.111$. Unlike the Dod, the shape characteristics in the SAP are not very different for wide ranges of structures.

δ angles are calculated over two diagonals of the squares and over 2 l edges and values for the angles in the HSM are 0.0, 0.0, 52.4 and 52.4° respectively for 1(57)3, 2(68)4, 1(67)4 and 2(58)3, although the only requirement from symmetry is that the first two are zero and the other two are equivalent. Of course with all four zero, an octagonal plane is formed.

The SAP is related to 9 and 10 coordinate polyhedra in which one or two of the square faces are capped. These are discussed in the appropriate sections.

(c) Cube. In the cube (symmetry O_h) the only shape characteristic is the M—L bond length. The δ angles are 0 or 90° dependent upon whether those over face diagonals or over edges are chosen. However as the cube is such a distinct polyhedron (and also so rare) this ambiguity does not matter. The cube is made up of square faces unlike any of the other 8 coordinate polyhedra and this profligacy, such an inefficient way of packing ligands around a metal, leads to high L···L repulsion.

(d) Hexagonal bipyramid. The HP (symmetry D_{6h}) has two types of site, axial and equatorial and the only shape characteristics are the two types of bond lengths. The only examples known are uranyl complexes which have strong bonds in axial sites. Calculations of δ angles are not very useful because there is such a wide choice.

(e) Bicapped trigonal prism. The BCTP (Fig. 3) has proved to be useful in describing the geometry of some 8 coordinate complexes *. It is derived either from the trigonal prism by capping two quadrilateral faces or more relevantly by removing a capping atom from the tricapped trigonal prism. The maximum symmetry of the BCTP is therefore only C_{2v}, there are three distinct types of site and six edges. However Muetterties and Guggenberger [7] have kept the D_{3h} symmetry of the TCTP and their HSM has values $v_1 = v_2 = 1.49$; $h_1 = h_2 = c_1 = c_2 = 1.155$ with δ angles of 1(57)3 21.8, 2(68)4 0.0, 1(67)4 and 2(58)3 48.2°. This restriction to the higher symmetry is clearly unreasonable as the effect of removing a capping atom from the 2648 face would surely be to make $h_2 < h_1$ and $v_2 < v_1$. However if the restriction on symmetry is lowered to just C_{2v} then a good fit can be obtained with nearly all 8 coordinate molecules. This is even true if the only restriction lifted is that of v_1 with respect to v_2 because then atoms 1357 can become planar and

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* We have changed the names of edges in the BCTP to conform with those commonly accepted for the TCTP (namely h horizontal, v vertical and c capping). Unfortunately at present h is often used for the vertical edges of the BCTP even by authors who use it for the horizontal edges in the TCTP [7,16]. Such ambiguity should be discouraged.

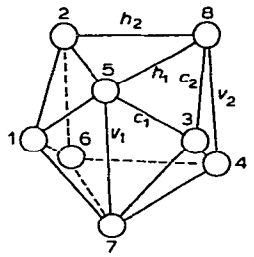

Fig. 3. The bicapped trigonal prism (C_{2v} or D_{3h}).

the SAP is formed. Therefore molecules can fit C_{2v} symmetry and yet the description 'bicapped trigonal prism' can be totally inappropriate. For these reasons we have followed ref. 7 and restricted the BCTP to D_{3h} in our refinement. However in section C(iv) the BCTP is reconsidered in the light of structural examples and MFP shape characteristics are suggested.

(ii) Reaction pathways between ideal geometries

Pairs of ideal geometries are now considered in turn and pathways between them are described. All possible pairs are not included; only those for which intermediate geometries are well established. Other pairs may well become relevant with additional structure determinations. By far the best established is the reaction cycle between the Dod, SAP and BCTP illustrated in Fig. 4. The ideal polyhedra are represented here in diagrammatic form but the numbering system is equivalent to that in the more detailed Figs. 1—3.

To proceed from the Dod to the SAP atoms 1,7,3,5 become one square face and 2,8,4,6 the other, while in the process the b edges 57 and 68 are broken. This change can easily be checked via δ angles as shown in the caption. ϕ angles are an equally good test as these vary from 0 to 24.5°. Use of these angles has superseded a test of polyhedra type formulated by Lippard and Russ [25]. They calculated the angle between the two trapezoids of the Dod. If the angle was close to 90° then the structure was thought to be a Dod and close to 79.4° a SAP. This approach has been discarded, because as Porai-Koshits and Aslanov pointed out [15], the angle in a SAP is dependent upon the l/s ratio and could be equal to 90°. This is shown by the examples in Table 2 where angles in SAP vary from 81.2 to 88.0°. An equally invalid procedure is to average edges of a polyhedron and see if they are equivalent to those of the MFP. In this way for example an ideal SAP would give the correct mean values to be characterised as a Dod or vice versa.

This pathway from the Dod to the SAP maintains D_2 symmetry. Thus there are only two independent δ angles. Values in the caption to Fig. 4 are calculated using the HSM shape characteristics but the only requirements from symmetry are that angles are equivalent to zero or are equivalent to each other. Many examples are known of geometries intermediate between the two forms and these are well distributed over the whole pathway from the Dod to the SAP (Table 20), thus confirming the existence of the low

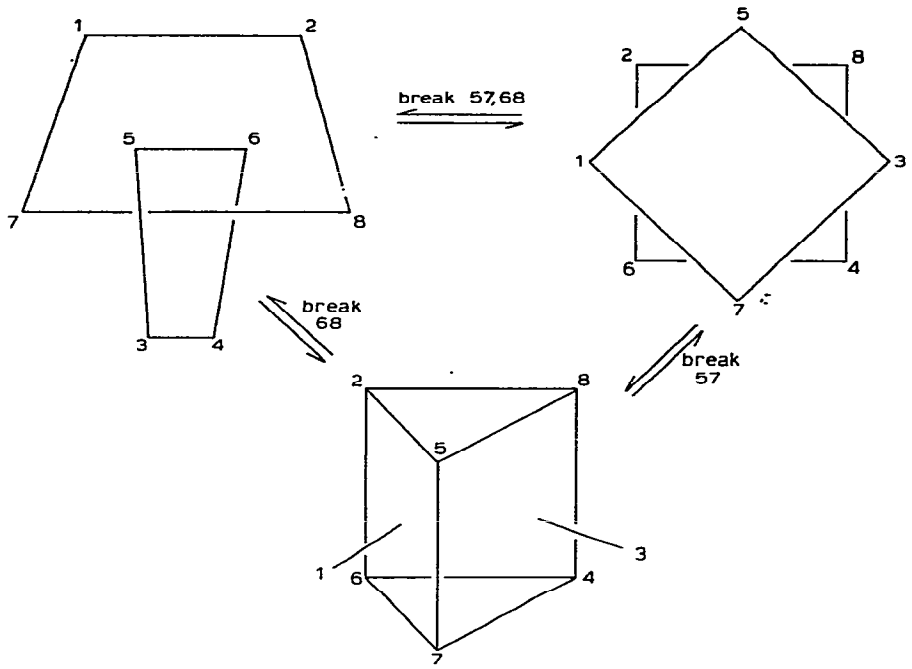

Fig. 4. Reaction paths between the Dod, SAP and BCTP.

Shape characteristics of HSM

δ angles	Values (°)		
	Dod	SAP	BCTP
1(57)3	29.5	0.0	21.8
1(67)4	29.5	0.0	0.0
2(58)3	29.5	52.4	48.2
2(68)4	29.5	52.4	48.2
ϕ	0.0	24.5	14.1

energy pathway between the two ideal polyhedra predicted by Blight and Kepert [22].

The Dod can be distorted towards two different SAP dependent upon whether 17 and 53 edges or 17 and 46 edges become one of the squares. The SAP can be distorted towards four different Dod as the unique $\bar{4}$ axis in the latter polyhedron can be obtained by bisecting the 12, 25, 58 or 83 edges in the SAP. Such niceties are particularly important for the $M(L—L)_4$ complexes where because of the chelate rings, different choices lead to different isomers.

There can be debate about whether the BCTP represents a separate minimum on the potential energy surface or is just part of a broad pathway from the Dod to the SAP. It is clear from Table 19 that there are enough molecules whose set of δ angles are close to those of the HSM of the BCTP to suggest

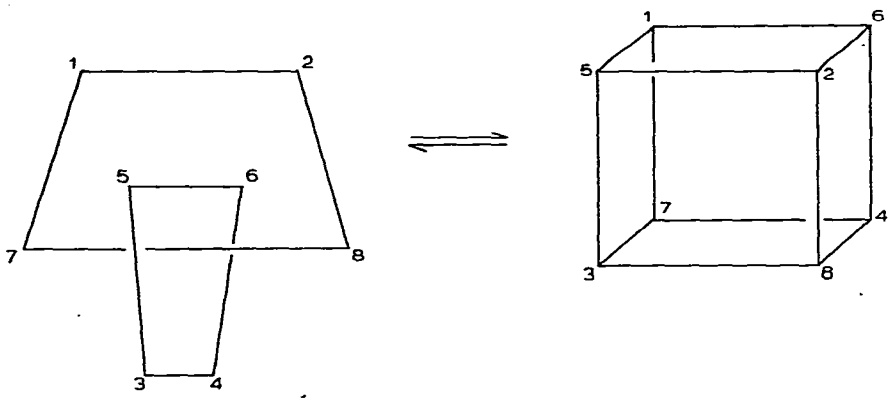

Fig. 5. Reaction path between the Dod and the cube.

that it may represent a separate geometry. To proceed from the Dod to the BCTP, two of the atoms in A sites (in this case 1 and 3) become the capping atoms in the BCTP and the 68 edge is broken. The pathway maintains C_2 symmetry.

To proceed from the SAP to the BCTP, one of the square faces in the SAP becomes slightly puckered. In Fig. 4, the 57 edge is formed but the 1357 atoms are still close to being planar, the δ angle in the HSM being only 21.8°. The pathway maintains C_{2v} symmetry. The difference between the BCTP and a midpoint on the D_2 pathway between the Dod and SAP cannot be estimated via ϕ angles because both have intermediate values of ca 14.1°. The possible existence of the BCTP is debated in more detail in section C(iv) with structural examples.

The pathway between the Dod and Cube is shown in Fig. 5. θ_A and θ_B in the Dod become closer together and when both are equal to 54.7° then the cube is formed. The best example is provided by $[ZrF_8]^{4-}$ in which δ angles are 4*20.8° intermediate between 4*29.5° in a Dod and 4*0° in a cube. For this molecule θ_A, θ_B are 43.0, 65.5° respectively. The pathway between the SAP and the cube (Fig. 6) is simply a rotation of 45° of one square face relative

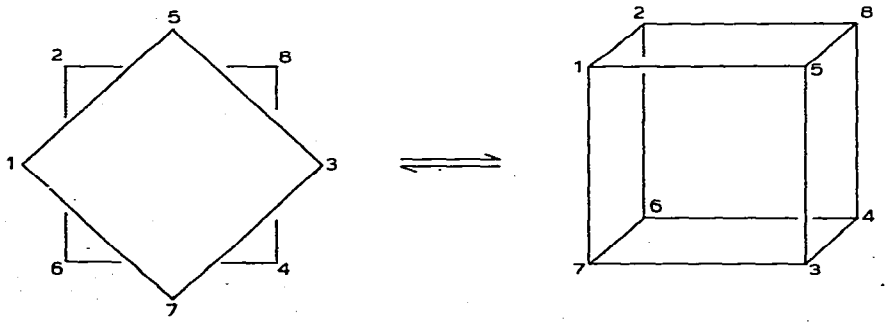

Fig. 6. Reaction path between the SAP and the cube.

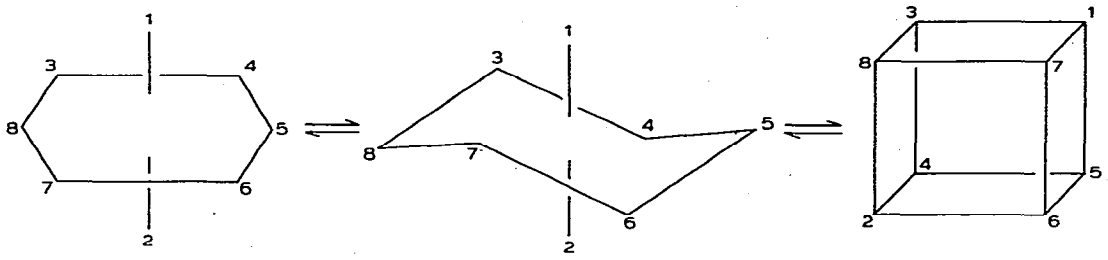

Fig. 7. Reaction path between the HP and the cube via the puckered HP.

to the parallel one. An example of this type of movement is provided by $[La(pyno)_8]^{3+}$ in which the angle of rotation is 30.8° from a cube (14.2° from a SAP) and also by $U(pc)_2$ which is 37° from a cube and 8° from a SAP. The relationship between the cube and the HP proceeds by way of the puckering of the HP girdle (Fig. 7). This is frequently found as it provides a means of relieving steric strain in the hexagonal girdle. However in only one compound of those listed in Table 17 namely $[UO_2(ox)_2]_n^{2n-}$ is the puckering sufficient to send the molecular geometry a significant way along the path to the cube.

(iii) Structures of eight-coordinate complexes

(a) ML_8 molecules with identical ligands. These molecules have several distinct geometries. There are as expected examples of the Dod and the SAP but somewhat surprisingly examples also of the cube and BCTP. These monodentate structures represent the type of molecules that are best examined in order to check the postulated structural features of each of the polyhedra and to see whether reasons are apparent for the adoption of one geometry rather than another.

Calculations [21—23] using eq. (2), while showing that the SAP and Dod

TABLE 1

ML_8 molecules with Dod geometry

Compound	Ref.	Δ (Å)			δ angles			
		Dod	SAP	BCTP				
$(NBut_4)_3[Mo(CN)_8]$	[26]	0.022	0.154	0.200	28.9	28.9	32.5	32.5
$K_4[Mo(CN)_8]$	[27]	0.023	0.165	0.193	29.7	34.4	29.7	34.4
$K_5[ThF_8]F$	[28]	0.049	0.170	0.193	27.8	35.5	27.8	35.5
$Li_6BeF_4[ZrF_8]$	[29]	0.000	0.181	0.205	20.8	20.8	20.8	20.8
$[La(pyno)_8]^{3+}$	[30]	0.080	0.130	0.148	17.0	30.7	40.3	43.9
HSM					29.5	29.5	29.5	29.5
MFP								

[a] Angle between trapezoids
[b] See text.

are more stable than any other possible geometry, were not able to predict which of the two was the most stable. It is to be expected therefore that molecules with other geometries would be abnormal in some way.

Examples with the Dod geometry are listed in Table 1 together with their shape characteristics. The first four examples have similar δ angles; the angle between the trapezoids γ is close to 90° and θ angles are close to 0°. As shown by the Δ values, the fit to the Dod is excellent. Note that $[Mo(CN)_8]^{3-}$ has a lower Δ from the SAP than $[Mo(CN)_8]^{4-}$ and $[ThF_8]^{4-}$ despite a smaller range of δ angles. This is entirely consistent as it is the first two δ angles that become zero in the SAP not the first and third as in these other two molecules. The shape characteristics of these three molecules agree well with each other and with the calculated geometries for the ML_8 polyhedra based on the HSM or MFP. It is of interest that in $[ThF_8]^{4-}$ six of the Th—F bonds are ca. 2.31 Å and the other two (in adjacent A sites) are 2.40 Å. This is thought to be due to cation···F interactions which are a well known feature of fluoride structures. Indeed as polyfluorides are always susceptible to such effects which distort the coordination sphere, their geometries must always be considered as doubtful precedents for other molecules. The other two compounds in Table 1 show considerable distortion. In $[ZrF_8]^{4-}$ θ_A is 43.0° (a = a massive 1.40) and θ_B 65.5° about 7° away from MFP values. Thus the anion is one third of the way from a Dod to a cube where both θ angles are 54.7° but of course by definition remains an ideal Dod with D_{2d} symmetry. This odd geometry could also be a result of M^+···F attractive forces.

$[Ly(pyno)_8]^{3+}$ is considerably distorted from the Dod along the BCTP pathway as shown by its δ angles, trapezoids that are significantly non-planar and a mean ϕ of 9.5°. This distortion may be a consequence of the large metal size which makes L···L repulsions in the coordination sphere of lesser importance and therefore adherence to ideal geometry less rigid.

Molecules with SAP geometries are listed in Table 2 and exhibit geometries close to the ideal with the possible exception of $[W(CN)_8]^{3-}$. This molecule is

θ_A	θ_B	a	g	m	b	$\frac{M-A}{M-B}$	γ [a]	mean ϕ
37.2	72.5	1.21	1.23	1.15	1.48	1.01	87.0	1.0
36.0	72.9	1.18	1.24	1.16	1.47	1.00	90.0	0.0
36.4	72.4	1.20	1.23	1.16	1.45	[b]	90.0	0.0
43.0	65.5	1.40	1.18	1.17	1.49	1.05	90.0	0.0
35.7	74.6	1.17	1.26	1.14	1.45	1.00	88.7	9.5
36.9	69.5	1.20	1.20	1.20	1.50	1.00		
35.2	73.5	1.17	1.24	1.17	1.49	1.03		

TABLE 2

ML_8 molecules with SAP geometry

Compound	Ref.	Δ (Å)			δ angles				γ	mean φ	l/s	θ_A
		Dod	SAP	BCTP								
$Cs_4[U(NCS)_8]$	[31]	0.148	0.017	0.181	0.0	0.0	49.2	49.2	85.6	22.9	1.08	56.7
$Na_3[W(CN)_8]$	[32]	0.135	0.043	0.166	4.0	10.3	46.8	49.4	81.2	18.9	1.011	59.1
$H_4[W(CN)_8]6H_2O$	[33]	0.147	0.023	0.167	0.0	4.3	50.2	50.3	85.4	22.6	1.069	56.5
$K_2[ReF_8]$	[34]	0.163	0.044	0.171	0.0	0.1	49.9	52.8	82.2	23.7	1.05	57.8
$H_4[W(CN)_8]4HCl, 12H_2O$	[35]	0.141	0.035	0.187	5.4	5.4	46.5	52.7	88.0	22.1	1.08	54.5, 57.6
Na_3TaF_8	[36] [a]										1.01	59.0
$Cd_2[Mo(CN)_8]2N_2H_4, 4H_2O$	[37] [a]										1.08	57.9
$[La(pyno)_8]^{3+}$	[38] [b]											55.7
HSM					0.0	0.0	52.4	52.4			1.00	59.2
MFP											1.057	57.3

[a] 2D study.
[b] Unpublished coordinates.

clearly distorted from the SAP but it is a moot point as to whether this distortion is on the D_2 pathway towards the Dod in which case the δ angles of 4.0 and 10.3° should be equivalent or along the C_{2v} pathway towards the BCTP in which case the δ angle of 4.0 should be 0.0°. There is a choice of δ angles that could be quoted for this molecule and others in this review. Therefore we always adopt the procedure of finding the Dod with the lowest Δ value and quoting δ angles calculated from its b edges. In $[W(CN)_8]^{3-}$ a further set of 4.0, 10.3, 52.3 and 54.3° correspond to the different Dod with a Δ value of 0.165 Å. Of course taking the molecule as a BCTP with C_{2v} symmetry, these δ angles 46.5, 52.7, 52.3 and 54.3° should all be equivalent. This emphasises one of the problems with δ angles in that only a set of 4 are quoted for 8 coordinate polyhedra but in a particular symmetry other δ angles should be equivalent.

As stated earlier, the angle between trapezoids ranges from 81.2 to 88.0° in these SAP, thus emphasizing that this angle is no test for this polyhedron. The ϕ angles do conform with prediction having a range around 22°. Unlike the HSM the majority of compounds have a l/s ratio above 1.0 and in some cases this is as large as 1.08. θ angles do not differ much from the calculated values in the HSM, MFP of 59.2, 57.3°.

In $[W(CN)_8]^{4-}$ [35], there are two types of W—C bond lengths, either long at 2.266 or short at 2.086 Å with associated θ of 57.6 and 54.5° respectively. A similar variation is found in $[W(CN)_8]^{4-}$ [33] with bond lengths 4*2.18, 2*2.23 and 2*2.14 Å. No explanation for these irregularities is apparent and this is salutary to those who feel that the ligand—ligand repulsions model can explain all details of molecular geometry. Of course the disparity could be due to electronic effects (d^2 metal) or packing effects particularly as the molecule has imposed crystallographic symmetry. Electronic effects were not taken into account in the calculations of HSM and MFP parameters but in high coordinate geometries it would be surprising if the electron configuration of the metal had more than marginal effect on molecular geometry. However it is clear from the shape characteristics in Table 2 that the d^0, d^1 structures are closest to the HSM and the d^2 structures to the MFP parameters though there are not enough examples for this to be taken as a general phenomenon.

The structure of $[La(pyno)_8]^{3+}$ is described as having a SAP geometry distorted towards a cube in that the projected O—La—O angles are 30.8 and

TABLE 3

The structures of other ML_8 molecules

Compound	Ref.	Structure
$(NEt_4)_4[U(NCS)_8]$	[39]	Δ = 0.005 Å from cube
$Na_3[PaF_8]$	[40]	Δ = 0.023 Å from cube
$Li_4[UF_8]$	[41]	Δ = 0.135, 0.143, 0.116 Å from Dod, SAP, BCTP respectively

59.2° rather than 45° for the SAP (0, and 90° for the cube). The structure has D_4 symmetry and the θ angle of 55.7° is rather less than that usually found in the SAP and closer to that observed in the cube (54.7°). The geometry does appear to be considerably different from the other $[La(pyno)_8]^{3+}$ structure [30].

The remaining three ML_8 structures are listed in Table 3. The first two have cubic structures with a set of δ angles of 0.0°. Both have a tetragonal distortion which is greater for $[PaF_8]^{3-}$ (edges 2.60, 2.47 Å) than for $[U(NCS)_8]^{4-}$ (2.77, 2.74 Å). A most interesting comparison can be made between the cubic $[U(NCS)_8]^{4-}$ anion [39] and the SAP $[U(NCS)_8]^{4-}$ anion [31]. In the former the cations fit into holes on the six faces of the cube thus stabilising the structure. In the SAP anion, the metal ions spurn the square faces of the SAP and fit above triangular faces. The N···N distances in the SAP are considerably longer (2.82, 2.91 Å) than those in the cube (2.77, 2.74 Å). However these latter distances are by no means excessively short and are well within the range of N···N distances acceptable in other structures. It is thus apparent that with the large actinide metals, L···L repulsions are relatively unimportant and packing effects can swing the balance from one geometry to another. It may be that it is necessary to have *f* orbitals participating in hybridisation, not possible for the transition metals, to obtain a cubic geometry.

The final example is Li_4UF_8 which is best described as a BCTP as δ angles are 0.0, 36.3, 44.6 and 45.9° and ϕ angles 11.8 and 13.6°. These eight U—F bonds are in the range 2.21—2.39 Å but there is a ninth of 3.30 Å positioned in the third capping site of the TCTP. So this unique structure, yet another example of the unpredictability of fluorides, might be best considered as 9 coordinate.

The structures of these ML_8 compounds confirm the calculations that the SAP and Dod are at energy minima although there are unexplained variations in either bond lengths or δ angles which could be due to packing or electronic effects. The compounds with different structures are either octafluorides in which cation···F interactions affect geometry, or actinides and lanthanides in which L···L repulsions in the coordination sphere are not so important. The theory also predicted, though that may be too positive a word, that there is no energy difference between the Dod and SAP and it is not unexpected, therefore, that the octacyanides are distributed in both polyhedra.

(b) ML_8 molecules with non-equivalent monodentate ligands. Molecules in this category have stoichiometry $ML_4L'_4$ or $ML_6L'_2$ and are listed in Table 4; they have a wide range of geometries. The structure of $MoH_4(PMe_2Ph)_4$ is expected, because the bulky phosphorus ligands occupy the B sites in a Dod, the least crowded sites of ideal polyhedra, and thus keep relatively far from each other. The δ angles, all of the type H(PP)H before normalisation are 67.7, 67.5, 68.7 and 66.1° a consequence of the very different size of the M—H and M—P bonds. The geometry of the MoP_4 unit is halfway between the square plane and the tetrahedron. Shape characteristics are θ_A 30.3, and

TABLE 4

Structures of ML_8 complexes with non-equivalent L

Compound	Ref.	Δ (Å)		δ angles (°)			
		Dod	SAP				
$MoH_4(PMe_2Ph)_4$	[42]	0.062	0.198	34.8	37.1	37.5	39.3
$Mo(CN)_4(CNMe)_4$	[43,44]	0.045	0.135	26.7	26.7	39.9	39.9
$[Ln(NCS)_4(OH_2)_4]^-$							
Ln = Nd	[45,46]	0.132	0.072	13.1	13.1	51.0	51.0
Ln = Eu	[45,46]	0.123	0.062	11.9	11.9	48.6	48.6
$Yb_2(SO_4)_3, 8H_2O$	[47] [a]	0.082	0.112	15.9	23.5	39.2	42.2
$Zr(SO_4)_2(OH_2)_4$	[48]	0.137	0.046	0.3	0.3	46.0	46.0
$[MCl_2(OH_2)_6]^+$							
M = Eu	[49]	0.120	0.070	12.0	12.0	43.5	49.9
M = Gd	[50]	0.117	0.075	13.3	13.3	42.0	51.3
M = Am	[51]	0.122	0.077	12.6	12.6	41.5	51.9
$[UCl_2(Me_2SO)_6]^+$	[52] [b]						

[a] See also isomorphous compounds with Nd[53], Am[54], Pr[55] and Sm[56].
[b] Unpublished coordinates.

θ_B 71.4° hardly MFP values and indeed θ_A is nearly the smallest ever value. In $Mo(CN)_4(CNMe)_4$ the A sites are occupied by —CN (Mo—C 2.177 Å) and the B sites by —CNMe (Mo—C 2.148 Å). As is apparent from the δ angles and Δ value, the geometry of the molecule is on the D_2 Dod ⇌ SAP pathway. The ϕ angles of 8.4 and 4.8° are compatible with this assessment of geometry. Shape characteristics are $\theta_A = 35.7$ and $\theta_B = 75.7°$. The distribution of —CN and —CNMe over A and B sites respectively is compatible with Orgel's rule [57] which states that in $ML_4L'_4$ Dod complexes {M being a d^n metal ($n \neq 0$)}, the better π acceptor of L and L′ will occupy the B sites where there is better overlap with the metal d_{xy} orbitals. This hypothesis is relevant to several other structures and is assessed in section C(v).

The $[Ln(NCS)_4(OH_2)_4]^-$ anions are isomorphous and have geometries intermediate between a Dod (O in A sites, N in B sites) and a SAP as shown in Fig. 8(i). They have crystallographically imposed C_2 symmetry and have geometries well on the SAP side of the D_2 pathway. Two polymeric sulphates, which contain bridging of the type M—O—S—O—M, are also included in Table 4. The isomorphous structures of $Ln_2(SO_4)_3, 8H_2O$ (Ln = Yb, Nd, Am, Pr, Sm) have all been determined and shape characteristics of the Yb coordination sphere are given in Table 4. However a recent proposal [55] that these structures are of spacegroup *Cc* rather than *C2/c* would, if true, slightly affect the geometry. Be that as it may, the structures are intermediate between the SAP and the Dod but as shown in Fig. 8(ii), the A and B sites in the Dod are shared by oxygens belonging to sulphate groups (o) and to water molecules (w). $Zr(SO_4)_2(OH_2)_4$ maintains approximate D_2 symmetry with the four sulphate oxygen atoms, which bridge to adjacent Zr atoms, sharing opposite *l* edges in the SAP. The regularity of this geometry is surprising when the rigid re-

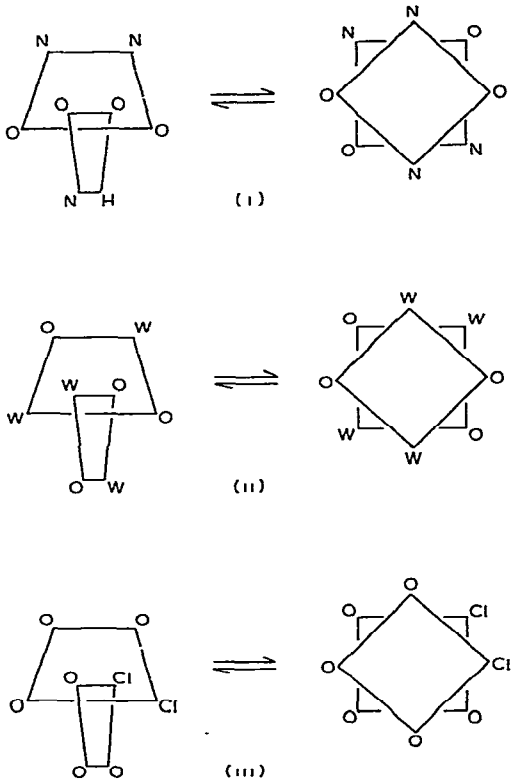

Fig. 8. Geometry of some ML_nL_{8-n} molecules. (i) $[Ln(NCS)_4(OH_2)_4]^-$ (ii) $Yb_2(SO_4)_3$, $8H_2O$ (iii) $[MCl_2(OH_2)_6]^+$.

quirements of the polymeric chains are considered.

The $[MCl_2(OH_2)_6]^+$ cations are also isomorphous and again as shown in Fig. 8(iii) on the D_2 pathway from the SAP to the Dod. The two chlorine atoms are in adjacent sites along an *l* edge in the SAP. $[UCl_2(Me_2SO)_6]^+$ is described as a distorted Dod.

It is interesting that the majority of these $ML_nL'_{8-n}$ molecules do not have an ideal geometry but one intermediate between the Dod and the SAP. This could be due to a number of factors including hydrogen bonding and imposed crystallographic symmetry, both of which occur in several examples.

(c) Molecules of the form M(unidentate)$_4$(bidentate)$_2$. Incidentally there are no monomeric structures of molecules containing just one bidentate ligand. For molecules of the $ML_4(L{-}L)_2$ type Blight and Kepert [24] calculated the potential energy surfaces using eqn. (2) but the effect of the chelate is taken into account by not including repulsions between pairs of atoms in the same chelate ring. An additional parameter is introduced, the normalised bite

TABLE 5

$M(L{-}L)_2L_4$ complexes with the *aa* Dod structure

Compound	Ref.	Δ (Å)		δ angles				M–A	M–B	θ_A	θ_B
		Dod	SAP								
$Ti(diars)_2Cl_4$	[58] [a]							2.71	2.46	36.3	72.8
$[Mo(diars)_2Cl_4]^+$	[59]	0.021	0.143	26.0	34.3	28.4	31.7	2.65	2.45	37.8	72.6
$[Ta(diars)_2Cl_4]^+$	[60]	0.010	0.163	30.5	32.7	31.2	32.4	2.76	2.41	36.3	72.9
$[Nb(diars)_2Cl_4]^+$	[60]	0.009	0.167	30.1	32.3	31.6	33.0	2.74	2.43	36.3	72.9
$[Nb(diars)_2Cl_4]^+$	[60]	0.025	0.149	27.2	31.0	33.2	33.6	2.74	2.43	36.5	73.0
$[Ta(diars)_2Br_4]^+$	[61]	0.000	0.161	(30.9)* 4				2.76	2.58	37.4	72.1
$Cd(NO_3)_2(OH_2)_4$	[62,63]	0.067	0.247	42.4	42.4	46.5	53.1	2.51	2.29	24.8	80.4

[a] Unpublished coordinates.

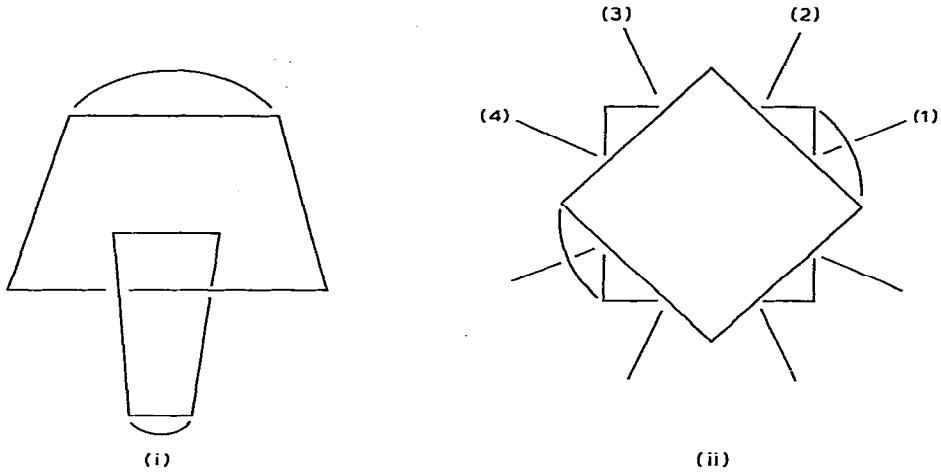

Fig. 9. Geometry of some $M(L—L)_2L_4$ molecules. (i) $Ti(diars)_2Cl_4$, the *aa* Dod (ii) $Nb(NCS)_4(bipy)_2$, the *ll* SAP. Also shown are possible positions of the $\bar{4}$ axis in the Dod. (1) → *aa* isomer (2) → *gg* isomer (3) → *bb* isomer.

(L···L)/(M—L), called z *, of the chelate. Their calculations showed that for small bites there is only one minimum on the potential energy surface, the Dod with the bidentate ligands in A sites. As z becomes > 1.0 then the D_2 SAP (bidentate ligands occupying opposite *l* edges) begins to appear as a minimum and when $z = 1.2$ becomes distinct. This calculation is consistent with the majority of $ML_4(L—L)_2$ molecules only three examples having different structures. The most common type of geometry is the *aa* Dod shown in Fig. 9(i) and examples are given in Table 5.

Most examples are if $M(diars)_2Cl_4$ with M an early transition metal and z ca. 1.20. This *a* edge is rarely occupied by bidentate ligands in other types of complex. One of the few examples is $Zr(NO_3)(acac)_3$ with the small nitrate group occupying the *a* edge of an *abmg* Dod. None of the many $M(L—L)_4$ complexes have the *a* edge occupied by a chelate. The suitability of the *aa* Dod is not just limited to the immediate coordination sphere, for this geometry also increases contacts between the chlorine atoms in B sites and the methyl groups bonded to arsenic atoms in the same trapezoid [59]. This would not happen in any other polyhedron nor in another type of Dod. The $M(diars)_2Cl_4$ compounds are so well defined that it is surprising that so much crystallographic interest has centered upon them. However separate workers were trying to prove [60] or disprove [61] the existence of 7 coordi-

* Blight and Kepert sensibly enough used *b* for the normalised bite. To adopt this nomenclature would however cause considerable confusion in a review of this type because *b* is an accepted symbol for an edge in the Dod.

nate molecules of the form $MX_5(L—L)$ [X = halogen]. Available evidence suggests that such complexes are not 7 coordinate because of the instability of molecules having five bulky halogens in the coordination sphere and can be formulated as $[MX_4(L—L)_2]MX_6$. In the Dod the X—M—X angles are >90° and thus the bulky halogen atoms are kept well away from each other. Attempts to prepare 8 coordinate cations with bulkier bidentate ligands (say —Ph for —Me in diars) or with saturated five-membered rings have not so far succeeded because of the shorter Cl···Me distances that would arise. There are minor differences in polyhedron shape for the six examples of $M(diars)_2X_4$ presumably due to variations in M—L bond lengths and packing but there is no severe distortion towards a SAP or any other polyhedron. One additional example of an *aa* Dod is $Cd(NO_3)_2(OH_2)_4$ in which the value of θ_A is much smaller than usual because of the small nitrate bite. This causes larger than usual δ angles. As is so often the case, the nitrate is bonded asymmetrically to the metal [Cd—O 2.438(9), 2.590(11) Å].

There are two examples of D_2 SAP, namely $M(NCS)_4(bipy)_2$, with M = Nb and Zr (Table 6) shown in Fig. 9(ii). These compounds are isomorphous but show different structural features. Bond lengths are Nb—NCS 2.135, Nb—N(bipy) 2.318; Zr—NCS 2.182, Zr—N(bipy) 2.412 Å and the molecules have imposed D_2 symmetry. As predicted for this isomer the bites are large (above 1.11). The ideal *ll* SAP isomer can be distorted towards a Dod in three different ways as shown in Fig. 9(ii). The unique $\bar{4}$ axis in the Dod can be chosen from the 2-fold axes in the SAP marked (1), (2), (3) and (4) in Fig. 9(ii). The Dod from (1) and (3) both maintain D_2 symmetry and have the bidentate ligands occupying A sites (*aa* isomer) and B sites (*bb* isomer) respectively. Dod (2) and (4) are equivalent; the symmetry is lowered to C_2 and the *gg* isomer is obtained in which the A and B sites are thus shared by the two types of ligand.

Δ values suggest that $Nb(NCS)_4(bipy)_2$ is distorted towards Dod (2) and $Zr(NCS)_4(bipy)_2$ towards Dod (1). However it is suggested [64] that both are distorted towards Dod (1). Even from δ angles, it is clear that this is not the case for the Nb compound. δ angles from Dod (2) are quoted in Table 6; those from Dod (1) are 3.5, 3.5, 55.1 and 55.1° a set considerably further from the ideal of four equivalent angles. However it could be argued that

TABLE 6

$M(L—L)_2L_4$ complexes with the *ll* SAP structure

Compound	Ref.	Δ (Å)				z	δ angles
		SAP	Dod(1)	Dod(2)	Dod(3)		
$Nb(NCS)_4(bipy)_2$	[64]	0.040	0.173	0.159	0.184	1.153	3.5, 3.5, 49.3, 49.3
$Zr(NCS)_4(bipy)_2$	[64]	0.063	0.143	0.162	0.209	1.119	11.2, 11.2, 52.7, 52.7

such distortions from the SAP are so small that the molecular geometry has hardly started on the reaction pathway towards the Dod. It is clear from these two molecules that interaction between the bipy hydrogen atoms and the —NCS groups would preclude a Dod structure with the bidentate ligands occupying the *a* edges as for the $M(diars)_2Cl_4$ examples. It is believed [64] that the Nb complex is closer to the SAP and further from the Dod compared to the Zr complex because the smaller M—N bond lengths make the Dod far more unlikely. This argument is posed the wrong way round, for after all the structures are SAP.

$[Er(hac)_2(OH_2)_4]^+$ (Table 7) has crystallographically imposed C_2 symmetry and is on the reaction path between the *mm* Dod (*m* edges in the same trapezoid) and *ss* SAP (*s* edges in different squares). This structure is thus reminiscent of the popular $M(L—L)_4$ geometry intermediate between the *mmmm* Dod and *ssss* SAP and indeed the counter ion $[Er(hac)_4]^-$ has exactly that structure. With a z of 1.09 there seems little reason why the structure could not adopt one of the expected categories although as we have seen 8 coordinate complexes of the larger lanthanides do not have as predictable structures as those of the transition metals. It is clear that the metal size needs to be considered as well as z in predictions of geometry as the larger the metal the less important are the L···L repulsions. In $[Eu(hac)_2(OH_2)_4]^+$, the $M—O_A$ bond lengths are shorter than the $M—O_B$ bond lengths. Thus for bidentate oxygen bond lengths are 2.30 (A) and 2.34 (B) and for water 2.28 (A) and 2.37 Å (B). $WMe_4[ON(Me)NO]_2$ (z = 1.13) is of particular interest as its geometry is neither ideal nor on any of the established pathways. Considered as a SAP, the two bidentate ligands occupy a square face with a δ angle of 6.0° but over the other face of four methyl groups the δ angle is 27.0°. This might suggest distortion towards a BCTP with two methyl groups in the capping position. However inspection of the L—M—L angles shows that this molecule does not have the C_{2v} symmetry common to both the SAP and BCTP and the reaction pathway between them. From these L—M—L angles, δ angles and a Δ value of 0.156 Å from the BCTP, it is apparent that the molecule is not well described by the latter geometry. The structure is aptly described [66] as being partly SAP (the bidentate part) and partly Dod (the monodentate part).

TABLE 7

Structures of other $M(L—L)_2L_4$ complexes

Compound	Ref.	Δ (Å)		δ angles			
		Dod	SAP				
$[Er(hac)_2(OH_2)_4]^+$	[65]	0.079	0.112	12.9	12.9	47.1	47.1
$WMe_4[ON(Me)NO]_2$	[66]	0.100	0.115	6.0	27.0	47.6	48.0
$Ca(NO_3)_2(MeOH)_4$	[67]	0.237	0.156	28.9	42.5	34.2	47.0

The $Ca(NO_3)_2(MeOH)_4$ molecule has been included because the structure can be nicely contrasted with that of the Cd salt, which is an *aa* Dod (z = 0.80). This is not the case however for the Ca salt (z = 0.85) and indeed the geometry is not close to any of the ideal polyhedra. The best fit is to a Dod in which the bidentate ligands occupy an *a* and *m* edge in opposite trapezoids. The distortion produced by such an arrangement is difficult to exaggerate. It is not clear why there should be such a difference between the Ca and Cd compounds though of course regular polyhedra are not frequently found in alkali metal salts.

(d) Molecules of the form M(unidentate)$_2$(bidentate)$_3$. Molecules of the type $M(L{-}L)_3L_2$ are listed in Table 8 and shown in Fig. 10. All examples include lanthanide metals and steric effects will be less important than usual. Not surprisingly therefore the molecules have a wide range of geometries. Structures can be divided into three groups dependent upon whether the angle between the monodentate ligands (L—M—L) is ca. 140, 115 or 75°. The first four molecules in Table 8 have L—M—L angles in the range 139—153° but have different geometries which are intermediate between two ideal forms as shown in reaction path (1) of Fig. 10, where 2 Dod and 2 SAP are connected in the usual way via *l* edges in the SAP becoming *a* edges in the Dod. The type of geometry of each molecule is listed in Table 8.

This wide variation in geometry is reminiscent of that found in $Ln(L{-}L)_3L$ complexes [8]. Perhaps the explanation for the range of these 7 and 8 coordinate structures lies in the large size of the metal which ensures that L···L distances in chelate rings are comparable to L···L distances between rings and thus positions of chelates and monodentate ligands are interchangeable. Despite this, the structures are close to ideal geometries or to ideal reaction paths.

$Ln\{S_2P(OEt)_2\}_3(tppo)_2$ has a geometry close to the *amm* Dod with C_2 symmetry even though the La—O monodentate bonds (2.44 Å) are much shorter than the La—S bidentate bonds (3.05 Å, z = 1.07). The variations in bond lengths do not fit any logical pattern and could be due to a combination of —Ph repulsions and intermolecular forces. In $Nb(ttbd)_3(tppo)_2$ for the bidentate ligand, the three Nd—O_A bonds are longer than the Nd—O_B bonds (2.49, 2.41 Å) but for the monodentate ligands the bonds are almost equivalent (2.40, 2.42 Å). In $Eu(dpm)_3py_2$ the Eu—O bond lengths range from 2.28—2.47 Å (z 1.15—1.20); but there seems to be no pattern about the variations. The Eu—N bonds are longer (2.56, 2.65 Å) and as the sites occupied by py are particularly crowded it was thought [70] that tertiary bonded nitrogen atoms could not fit into them. $Nb(ttbd)_3(dip)(OH_2)$ is also a SAP even though there are two different monodentate ligands H_2O and the bulky dip. But as can be seen from reaction path (1) both sites remain equivalent during the Dod ⇌ SAP (a) conversion. $Ho(dpm)_3(4\text{-picoline})_2$ was reported to be a SAP (type 1c) with an *l*/*s* ratio of 1.08 and square faces which intersect at 3.2°.

The majority of the remaining molecules in Table 8 contain water mole-

TABLE 8

Structures of the $M(L{-}L)_3L_2$ complexes

Compound	Ref.	Δ (Å)			Structure type	L–M–L angle	z	δ angles
		Dod	SAP	BCTP				
$Nd(ttbd)_3(tppo)_2$	[68]	0.094	0.167		(1b)	145	1.15	17.8, 38.9, 27.6, 45,8
$Nd(ttbd)_3(dip)(OH_2)$	[69]	0.137	0.071		(1a)	139	1.15	1.6, 7.9, 43.3, 48.2
$Eu(dpm)_3py_2$	[70]	0.149	0.050		(1c)	140	1.15–1.20	3.7, 5.4, 49.5, 50.6
$Ho(dpm)_3(4picoline)_2$	[71][a]				(1c)			
$Ln(S_2P(OEt)_2)_3(tppo)_2$	[72]	0.061	0.147		(1a)	153	1.07	25.2, 29.4, 41.0, 43.0
$Eu(ttbd)_3(OH_2)_2$	[73]	0.157	0.055		(2)	116	1.19	1.2, 4.9, 45.1, 53.8
$Y(acac)_3(OH_2)_2$	[74]	0.100	0.104	0.138	(3)	70	1.18	6.8, 24.6, 41.0, 41.9
$Ln(acac)_3(OH_2)_2$	[75]	0.110	0.115	0.152	(3)	76	1.12	5.7, 26.1, 38.4, 44.3
$Nd(acac)_3(OH_2)_2$	[76]	0.113	0.110	0.144	(3)	76	1.16	5.7, 26.3, 40.0, 45.8
$Ho(acac)_3(OH_2)_2$	[77]	0.049	0.134	0.176	(3)	69	1.20	22.0, 26.5, 34.9, 35.9
$Eu(acac)_3(OH_2)_2$	[78]	0.100	0.109	0.143	(3)	70	1.18	5.3, 24.8, 39.8, 42.0
$Nb(O_2CNMe_2)_5$	[79][a]				—	91		

[a] Unpublished coordinates.

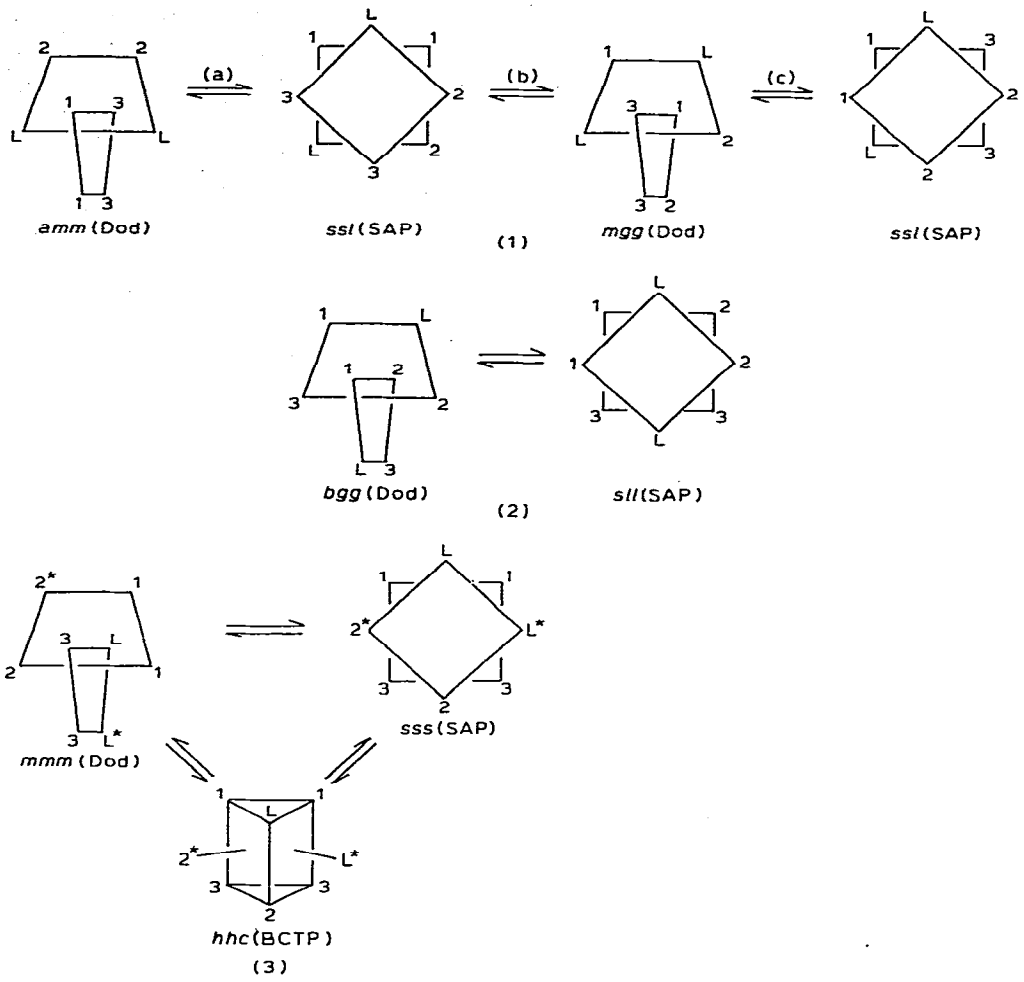

Fig. 10. Reaction paths for $M(L{-}L)_3L_2$ complexes. Monodentate ligands L, bidentate ligands (11), (22) and (33).

cules mutually *cis*. However $Eu(ttbd)_3(OH_2)_2$ is unique in that the water molecules subtend an angle of 116° at the metal atom. The best fit is to a SAP with the two water molecules on opposite sides of the same square {Fig. 10 (2)}. Thus while the molecules in reaction path (1) have bidentate ligands in *ssl* edges, this molecule in reaction path (2) has *lls* edges occupied. The *z* values are equivalent and it is hard to see the reason for $Eu(ttbd)_3(OH_2)_2$ being the odd one out. In $Nb(O_2CNMe_2)_5$ three of the five dmo ligands are bidentate. The bite is particularly small and the geometry is described as a pentagonal bipyramid in which the girdle is occupied by two bidentate ligands and a monodentate ligand and axial sites by a monodentate ligand and a bidentate ligand.

The remaining structures in Table 8 are all of the form $M(L—L)_3(OH_2)_2$ and have similar structures with the exception of M = Ho. The water molecules are mutually *cis* and subtend angles of 69—76° at the metal. Unlike the other examples the geometry does not fit the Dod or the SAP. It can best be described as distorted from three ideal polyhedra, the Dod, SAP and BCTP as shown in Fig. 10 (3).

Porai-Koshits and Aslanov [15] described the $Ln(acac)_3(OH_2)_2$ structures as distortions from the *ssss* SAP geometry of the $Ln(bzac)_4$ series. The size of z in these compounds leads to a rectangular shape in the lower quadrangular face of the antiprism containing two chelating ligands [11 and 33 in Fig. 10(3)]. Thus two of the atoms in the upper face (2* and L*) which occupy vertices opposed to the long edge of the lower rectangle can become closer to the plane of the lower base than the other two. Thus the upper face is folded about the 2*···L* line and the polyhedron becomes a BCTP of the *hhc* type. With $Ho(acac)_3(OH_2)_2$ the metal size is smaller (and z is larger, 1.20) so one might expect a more ideal *sss* geometry. However the *mmm* Dod is found, possibly because the smaller metal size increases steric problems in the SAP. This large bite would also cause crowding in the Dod were it not for the θ_B angle being reduced to 70.6° (far below any value found in *mmmm* $M(L—L)_4$ complexes) while θ_A remains reasonable at 36.9°.

However this qualitative description of $M(acac)_3(OH_2)_2$ molecules as BCTP is only superficially convincing as the chelates do not occupy edges consistent with C_{2v} symmetry and the fit is therefore far from ideal. The choice of δ angles in Table 8 may be misleading. In $Ln(acac)_3(OH_2)_2$ angles 2*(32)3 and L*(L1)1 are 38.4 and 44.3° but angles which ought to be equivalent 2*(L1)1 and L*(32)3 are 55.5 and 47.5° respectively; and for $Y(acac)_3(OH_2)_2$ these four angles (calculated over h_1 edges) are 41.0, 41.9, 52.0 and 53.9°. So the complete set of δ angles do not conform with C_{2v} symmetry.

This said, it is apparent that Porai-Koshits and Aslanov have given valid reasons why the distortions from the SAP to the Dod for the $M(acac)_3(OH_2)_2$ compounds do not follow the D_2 pathway and why the face with two bidentate ligands is puckered less than the other. This explanation is also valid for $WMe_4[ON(Me)NO]_2$ where the face of four methyls is much puckered.

(e) Molecules of the form M(bidentate)$_4$ with identical ligands. This is by far the commonest 8 coordinate stoichiometry and examples are therefore separated into geometric categories and listed in Tables 10—14. Hoard and Silverton [21] listed the six possible isomers for the Dod and the three for the SAP (Table 9) and considered that only the first three Dod and first two SAP were likely to be at all common. This calculation made in 1962 based on minimising closed shell and ring constraints has been confirmed by later structural work. To show this the number of monomeric structures determined by X-ray crystallography of each isomer is listed in Table 9. (Molecules intermediate between two geometries have been included as 1/2 in each).

In fact only the *ssss* SAP, the *mmmm* and *gggg*(D_2) Dod are at all common,

TABLE 9

$M(L—L)_4$ isomers

SAP		Dod	
Type	Symmetry	Type	Symmetry
llll	D_4-422 (2) [a]	*mmmm*	D_{2d}-$\bar{4}$2m ($35\frac{1}{2}$)
ssss	D_2-222 ($12\frac{1}{2}$)	*gggg*	S_4-4 (1)
llss	C_2-2 ($1\frac{1}{2}$)	*gggg*	D_2-222 (8)
		aabb	D_2-222 (—)
		mmgg	C_2-2 ($\frac{1}{2}$)
		abmg	C_1-1 (—)

[a] Number of structural examples of each isomer is given in parentheses.

the other isomers being only found for one or two structures. Compounds of the type $M(L—L)_n(L—L)_{4-n}$ show a little more variety and these are considered in section (f). Blight and Kepert [24] calculated the potential energy surfaces for $M(L—L)_4$ molecules by their usual method using eqn. (2) and showed that for z of 0.70—1.00, the single minimum which appeared was the *mmmm* Dod with D_{2d} symmetry. As z is increased to 1.10, a single very broad minimum appears which encompasses both this *mmmm* Dod and the *ssss* SAP isomer. On increasing z to 1.16 the minimum becomes similar to the *ssss* SAP. With z up to 1.25, separate minima occur for both the *llll* and *ssss* SAP isomers with the *gggg*(D_2) Dod at a saddle point of slightly higher energy.

These results have been supported by the vast number of crystal structures determined since that paper appeared. In Table 10, 38 structures are listed which are *mmmm* D_{2d} isomers and in which z ranges from 0.74—1.17. No $M(L—L)_4$ compound with $z < 1.05$ has any other structure. In Table 10, Δ values for the Dod and from the *ssss* SAP are listed together with δ angles and shape characteristics. It is at once apparent that the *mmmm* Dod is extremely flexible taking in a very wide range of metals and ligands. Thus $M—L_A$ lengths range from 1.87—2.97 Å and for edges, m ranges from 0.74—1.17, a from 1.13—1.50, g from 1.24—1.44 but b only from 1.42—1.47 Å. Values show the expected correlations; as $m(=z)$ increases, θ_A, θ_B, g and a decrease. On the other hand b increases but only by a very small amount. It is interesting that both HSM and MFP parameters have b larger than any known values in *mmmm* isomers. The reason why the *mmmm* Dod is not feasible for compounds with large z is that a becomes very small and interaction between donor atoms over that edge becomes excessive although this can be reduced to some extent by twisting the bidentate ligands about an axis passing through their midpoint and the central metal atom. Another factor ruling out the *mmmm* isomer is the presence of terminal groups on the donor atoms which would also give too short intermolecular contacts.

In the majority of molecules in Table 10, there is a difference in bond length between $M—L_A$ and $M—L_B$ bonds, particularly for $z > 1.0$ when $M—L_A >$

TABLE 10

$M(L—L)_4$ complexes with the *mmmm* Dod structure

Compound	Ref.	Δ (Å)		δ angles			
		Dod	SAP				
$[Nb(O_2)_4]^{3-}$	[80]	0.049	0.312	33.4	36.8	34.7	38.5
$[Cr(O_2)_4]^{3-}$	[81]	0.000	0.297		(34.9)*4		
$[Co(O_2CCF_3)_4]^{2-}$	[82]	0.012	0.271		(28.4)*4		
$[Zn(NO_3)_4]^{2-}$	[83]	0.059	0.201	21.3	21.3	34.3	34.3
$[Co(NO_3)_4]^{2-}$	[84]	0.059	0.206	22.6	22.6	29.8	29.8
$[Mn(NO_3)_4]^{2-}$	[85]	0.051	0.204	29.6	29.6	35.3	38.1
$Sn(NO_3)_4$	[86]	0.026	0.198	29.5	36.1	33.9	34.3
$Ti(NO_3)_4$	[87]	0.026	0.194	30.9	37.1	34.1	35.8
$[Fe(NO_3)_4]^-$	[88,89] [a]						
$[Cd(naph)_4]^{2+}$	[90]	0.103	0.223	27.2	35.1	34.8	29.6
$[Fe(naph)_4]^{2+}$	[91]	0.053	0.206	29.1	33.6	30.3	36.7
$[Ln(dedtc)_4]^-$	[92]	0.064	0.225	28.7	41.4	35.0	36.6
		0.043	0.211	32.7	37.5	34.3	35.4
		0.054	0.214	30.1	38.9	33.4	38.1
		0.062	0.211	32.0	35.4	34.0	38.7
$Th(hfap)_4$	[93]	0.132	0.215	26.9	36.6	39.3	43.0
$U(hfap)_4$	[93]	0.115	0.209	19.9	35.9	42.4	45.4
$Th(dedtc)_4$	[94]	0.050	0.201	30.7	34.9	42.0	42.0
$[Np(dedtc)_4]^-$	[95]	0.109	0.226	17.3	46.9	38.3	41.5
$Te(dedtc)_4$	[96]	0.053	0.191	29.8	36.6	37.9	40.5
		0.053	0.191	30.9	35.2	29.4	39.6
$Te(mtc)_4$	[97]	0.016	0.165	30.2	30.8	34.6	35.6
$Zr(dedtc)_4$	[98] [a]						
$Ti(dedtc)_4$	[99]	0.044	0.181	28.4	39.0	30.6	39.9
		0.039	0.158	27.6	31.6	40.6	41.0
$[W(dedtc)_4]^+$	[100]	0.015	0.179	32.9	35.9	36.1	36.7
$Mo(PhCS_2)_4$	[101]	0.001	0.165		(29.1)*4		
$V(PhCS_2)_4$	[102]	0.024	0.178	25.6	32.3	33.3	33.6
		0.003	0.161		(30.3)*4		
$V(S_2CMe)_4$	[103]	0.011	0.181	33.6	33.6	34.7	35.8
$Ti(demtc)_4$	[104]			26.3	26.3	34.8	34.8
$[Ta(dmdtc)_4]^+$	[105]	0.015	0.170	29.9	31.5	34.9	34.9
$[Ta(dmdtc)_4]^+$	[105]	0.045	0.168	23.8	33.9	34.1	35.7
$Zr(cupferrate)_4$	[106]	0.045	0.185	32.6	35.0	34.9	35.0
$Hf(trop)_4$	[107]	0.030	0.145	27.0	30.0	34.9	38.2
$[Zr(ox)_4]^{4-}$	[108]	0.060	0.123	24.7	24.7	41.2	41.2
$W(8quinBr)_4$	[109]	0.034	0.145	28.4	30.3	37.7	39.7

[a] Unpublished coordinates. [b] See text. [c] Ti—S_B 2.533, Ti—S_A 2.609; Ti—O_A 2.117, Ti—O_B 2.061.

M—L_B. However for a number of molecules such as the peroxides and most of the nitrates the reverse is true. The extreme example is $Co(O_2CCF_3)_4^{2-}$ in which M—O_A is 2.00 and M—O_B 3.11 Å. Whether this molecule should be considered to be 8 coordinate at all is a matter of some argument. Perhaps a better

M—A	M—B	θ_A	θ_B	m	g	a	b
2.00	2.04	43.2	86.3	0.74	1.44	1.36	1.42
1.87	1.97	43.3	88.2	0.76	1.43	1.37	1.41
2.00	3.11	48.6	87.3	0.75	1.39	1.50	1.42
2.06	2.58	45.6	82.3	0.88	1.34	1.43	1.43
2.07	2.45	46.5	80.4	0.89	1.33	1.45	1.43
2.27	2.34	43.0	83.7	0.90	1.36	1.36	1.42
2.18	2.15	38.9	81.6	0.99	1.33	1.25	1.43
2.07	2.06	37.2	80.7	1.03	1.32	1.21	1.43
2.14	2.11	38.9	80.9				
2.60	2.42	42.2	83.9	0.90	1.35	1.35	1.42
2.49	2.22	41.1	82.3	0.94	1.34	1.32	1.42
2.97	2.99	37.2	81.7	0.99	1.35	1.21	1.43
2.94	2.98	37.5	82.5	1.00	1.34	1.22	1.42
2.96	2.95	37.2	83.1	0.99	1.35	1.21	1.43
2.98	2.99	35.6	81.1	1.05	1.32	1.16	1.43
[b]	[b]	36.4	81.9	1.03	1.31	1.19	1.42
[b]	[b]	35.6	81.1	1.05	1.32	1.16	1.43
2.87	2.86	34.8	82.6	1.04	1.34	1.14	1.45
2.88	2.84	36.2	79.6	1.03	1.38	1.18	1.42
2.77	2.72	35.5	79.8	1.07	1.31	1.15	1.43
2.76	2.72	34.9	79.6	1.07	1.32	1.15	1.43
2.78	2.69	37.4	77.7	1.07	1.29	1.21	1.44
2.62	2.51	35.4	77.0	1.10	1.28	1.16	1.44
2.60	2.53	34.8	78.0	1.11	1.29	1.14	1.44
2.53	2.49	34.6	77.6	1.11	1.28	1.13	1.44
2.54	2.47	37.9	75.3	1.10	1.25	1.23	1.46
2.56	2.47	37.7	74.8	1.11	1.26	1.22	1.46
2.56	2.45	38.4	73.7	1.12	1.25	1.24	1.47
2.49	2.45	35.4	77.0	1.12	1.28	1.16	1.45
[c]	[c]						
2.59	2.52	35.0	77.4	1.11	1.28	1.15	1.45
2.59	2.51	35.5	76.6	1.12	1.28	1.15	1.45
2.17	2.21	34.3	78.4	1.10	1.30	1.13	1.44
2.19	2.18	36.0	74.4	1.14	1.25	1.17	1.46
2.23	2.17	35.2	73.9	1.16	1.24	1.15	1.46
2.06	2.20	34.3	74.1	1.17	1.24	1.13	1.46

description would be tetrahedral as θ_A at 48.6° nears half the tetrahedral angle. There are a number of other examples where the coordination number can be considered to be 4 or 8, such as $Ca[M(ac)_4]$ with M = Cu where there are four short (1.97) and four long (2.79 Å) bonds as also there are with M = Co (2.29, 2.68 Å) [110] and polymeric *o*-phthalatocuprate (II) with mean lengths in the Rb salt [1.94, 2.93] and in the Li salt (1.95, 2.90 Å) [111].

In the $M(NO_3)_4$ complexes, the differences between bond lengths in the two sites $\{(M—O_A) - (M—O_B)\}$ are —0.52 (Zn), —0.38 (Co), —0.07 (Mn), 0.04 (Fe), 0.01 (Ti) and 0.02 Å (Sn). Clearly there is no consistent theoery to cover these differences as both Zn and Ti are closed shell compounds and Mn and Fe are isoelectronic. However these differences may not be a consequence of 8 coordination as nitrates are well known for their asymmetric bonding; they seem very unlikely to be due to L···L repulsions as much more bulky ligands with bigger z can be accommodated into the Dod without such distortion and besides $M—O_A$ would be expected to be longer than $M—O_B$ in that case. The only possible explanation of the —0.52 Å difference in $[Zn(NO_3)_4]^{2-}$ is the tendency for Zn(II) compounds to have tetrahedral coordination. This is only possible with the A sites forming the tetrahedron, because if θ_B were decreased the B sites would crowd the A sites and push them closer together along the a edge. There is no problem about rationalising the small differences in Sn and Ti compounds as these metals have spherically symmetrical distributions of non-bonded d electrons (as of course does Zn). A possible electronic explanation is available for $[Co(NO)_4]^{2-}$ in that the non-bonded electron ligand repulsions will be greater near the B sites than the A sites and thus $M—O_A < M—O_B$. This explanation could hold good for $[Mn(NO_3)_4]^{2-}$ but does not explain the structure of the isoelectronic Fe^{3+} complex. An interesting feature of both the Co and Zn compounds is that they contain two independent (imposed C_2 symmetry) and different $M—O_B$ bond lengths [Co 2.36(2), 2.54(2) and Zn 2.516(12), 2.636(11) Å]. As might be expected the longest bonds have the largest θ_B angle. The tetranitrates with smaller z values show larger deviations from symmetric nitrate bonding. The δ angles of the Zn, Co and Mn ions reflect the flattening of the Dod towards the SAP. However Δ values for the SAP are high because some square edges are occupied by nitrate ($s = 0.90$) and some not ($s = 1.35$). A distortion towards tetrahedral symmetry therefore is also a distortion towards the SAP.

Many peroxide structures show variations in M—O bond lengths and the 8 coordinate examples are no exceptions with $M—O_A < M—O_B$. In these $[M(O_2)_4]^{3-}$ structures, θ_B approaches 90° and thus the four B atoms become close to planar. The structures are comparable to that of $Mo(tptp)(O_2)_2$ where the tetradentate planar macrocycle occupies the B sites and the peroxides the A sites (Table 16).

$[M(napth)_4]^{2+}$ M = Fe, Cd have similar structures with $M—N_A$ bonds longer than the $M—N_B$ bonds reflecting the greater repulsion energy experienced by the atoms at the A sites. Despite the rather bulky ligand and no doubt as a consequence of the small bite the trapezoids are relatively planar. The next series of compounds in Table 10 are lanthanide and actinide complexes in which z ranges from 1.00—1.05. Because of the large size of the metal, contacts between adjacent ligands are in excess of the van der Waals contacts. Thus in $[Np(dedtc)_4]^-$ S···S contacts are greater than 3.7 Å while in many of the other $M(dedtc)_4$ compounds (M = Mo, V, Ti, Zr, W) S···S is ca 3.2 Å. One might expect variations from the ideal to increase with these compounds

but this is not as large a factor as might be expected. Thus the four molecules of $[Ln(dedtc)_4]^-$ in the asymmetric unit have very similar geometries only slightly distorted from the Dod, Δ values being 0.043—0.064 Å. $[Np(dedtc)_4]^-$ does have a higher Δ value and also rather disparate δ angles, one being lower than the others. The molecule is not distorted towards the SAP; but in such a manner that each trapezoid is rotated about an axis perpendicular to it so as to bring one sulphur atom towards the plane of the other trapezoid. This rotation is stated [95] to bring one sulphur atom in an A site into the plane of the other trapezoid but this is far from true using the published coordinates. Taking one trapezoid, distances of atoms in the other trapezoid from it are 3.01, 2.42, —2.49 and —0.88 and vice versa 2.37, 2.96 —2.51 and —1.00 Å. The distortion is towards a planar pentagonal arrangement of five sulphur atoms with one atom above and two below the plane. This distortion keeps the angle between trapezoids at 90° and the ϕ angles at 0°, and of course maintains C_s symmetry. No reason for this from inter- or intra-molecular forces is apparent though of course having five planar atoms in a girdle is a common feature of uranyl 7 coordinate complexes. The same type of distortion is also apparent but to a smaller extent in the $[Ln(dedtc)_4]^-$ molecules and in $Th(hfap)_4$ and $U(hfap)_4$ but it is not likely to be found in the more crowded transition metal Dod. $Th(dedtc)_4$ is much closer to the ideal Dod *. The only difference between the structures of $M(hfac)_4$ with M = Th, U is the 0.05 Å change in bond length due to the lanthanide contraction. Nitrogen and oxygen donor atoms are distributed equally over A and B sites. Much of the distortion in these polyhedra arises from the differences in bond lengths for M—O (2.29, 2.23 Å) and M—N (2.64, 2.60 Å) and the greater crowding of oxygen atoms in the ligand.

In these structures containing lanthanide and actinide metals, there is very little variation between $M—L_A$ and $M—L_B$ bond lengths. However for the remaining compounds in the Table with z = 1.07—1.17, bond lengths to the A sites are longer than to B sites.

The $M(S—S)_4$ polyhedra can be divided into two types; the majority having a edges ca 1.15 and the minority 1.23 Å. In the former type, for example $Ti(dedtc)_4$, the a edges at 3.0 Å are only slightly greater than the S···S distances in the same chelate. This suggests that weak attractive forces exist between sulphur atoms. The two molecules of $Ti(dedtc)_4$ in the asymmetric unit have slightly different geometries only the second being distorted towards the SAP. The first has δ angles of 28.4, 39.0, 30.6 and 39.9°. This rather unusual distortion is caused by one trapezoid being shifted by 0.15 Å to one side of the metal atom such that of the two m edges in the other trapezoid, one is much closer to it (1.08, 2.36 Å) than the other (—1.90,

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* θ_A, θ_B are quoted [94] as 44,66° but we calculated 34.8, 82.6° which fit better to the trends of Table 10. $Th(dedtc)_4$ has been stated to be a *gggg*(D_2) isomer [24] but using the published coordinates, it is a regular *mmmm* isomer.

—2.52 Å). This second trapezoid is coplanar with the metal. This pattern of δ angles is found in a few other 8 coordinate Dod. An interesting sidelight on the possibility of S···S attractive forces is shown by $Ti(demtc)_4$ in which the four (S···O) ligands are arranged in the Dod such that the sulphur atoms are to one side of the metal occupying both A and B sites and thus there is the maximum number of short S···S contacts. The occurrence of weak attractive forces has been considered [138] as an explanation for the wide range of $M(dtc)_3$ geometries from the trigonal prism to the octahedron.

In the other type of geometry *a* is much larger but *g* is smaller and steric effects are probably no greater. However S···S over the *a* edge in $Te(mtc)_4$ is 3.39 Å compared to 3.17 Å in $Te(dedtc)_4$ and this is stated to be one reason for the greater stability of the mtc complex. The remaining examples with large *a* are the $M(S_2CPh)_4$ compounds with M = V, Mo. This contrasts with $[W(dedtc)_4]^+$ and $V(S_2CMe)_4$ which have the small *a* structure. There is no steric explanation for this as all compounds have similar S···S bites. We suggest that the presence of the phenyl ring may cause an increase in delocalisation over the ligand which may preclude the weak attractive forces between sulphur from occurring over the *a* edge and therefore *a* and *g* edges are equated. It is interesting that the $V—S_A$ distances in $V(S_2CMe)_4$ are 0.07 Å shorter than in $V(S_2CPh)_4$ despite the sites being more crowded; by contrast $V—S_B$ distances are similar.

However both types of geometry have $M—L_A > M—L_B$. In addition to the steric explanation for this it is possible that the $M—L_B$ ligand will be shortened relative to $M—L_A$ by π-electron overlap with the metal d_{xy} orbital. There is very little evidence for this but it may occur in one or two molecules.

The remaining compounds of Table 10 contain the smaller donor atoms, oxygen and nitrogen, and unlike compounds with sulphur as a donor atom, are allowed the luxury of five-membered chelate rings around the metal. $Zr(cupferrate)_4$ is the only compound with $z > 1.0$ in which $M—O_B$ is longer than $M—O_A$. There seems no explanation for this as the most crowded part of the ligand occupies the A sites but it could be due to the bonding pattern of the unsaturated ligand or caused by a few short intermolecular distances in the unit cell. In $[Zr(ox)_4]^{4-}$ the distortions are quite severe; each oxalate group being inclined at about 5° to the mean trapezoidal plane so that each oxygen atom is 0.11 Å from that plane. A similar geometry is found in $Hf(trop)_4$. In $W(8quinBr)_4$, the W—O bonds in A sites are considered to be stronger than the W—N bonds in B sites (2.06, 2.20 Å). This is an example of the distribution of ligands in the Dod being fixed by L···L repulsions as there is no way in which the oxygen atoms can occupy adjacent A sites. These last three compounds have large bites (z = 1.14, 1.16, 1.17 respectively) and as a consequence are distorted towards the SAP via the D_2 reaction path, as illustrated by the δ angles and the Δ values. Brief reports of $Ce(dbm)_4$ [139—141] and $[Ho(trop)_4]^-$ [142] show that these molecules have the *mmmm* geometry.

Molecules with the *ssss* SAP geometry are listed in Table 11. Taking into account that several are isomorphous, there are not many of them. As ex-

TABLE 11

$M(L{-}L)_4$ complexes with the *ssss* SAP structure

Compound	Ref.	Δ (Å)		δ angles	s_1 (= z)	s_2 (≠ z)	l_1	l_2	l_3	θ_A
		SAP	Dod							
$\beta U(acac)_4$	[112]	0.046	0.133	(5.9, 48.2)*2	1.16	1.21	1.26	1.26	1.29	56.7
$\beta Np(acac)_4$	[113]	0.022	0.142	(3.4, 49.3)*2	1.17	1.23	1.26	1.25	1.27	57.4
$\beta Ce(acac)_4$	[114]	0.035	0.127	(5.3, 46.7)*2	1.16	1.20	1.26	1.25	1.30	56.9
$Zr(acac)_4$	[115]	0.024	0.147	(3.2, 49.6)*2	1.22	1.18	1.21	1.14	1.29	57.9
$[Eu(bzac)_4]^-$	[116]	0.057	0.121	(7.9, 46.0)*2	1.15	1.20	1.24, 1.30	1.20, 1.29	1.30	57.0
$[Eu(bzac)_4]^-$	[116]	0.027	0.157 [a]	1.0, 1.5, 50.1, 52.4	1.18	1.20	1.26	1.26	1.25	57.4
$[Gd(bzac)_4]^-$	[117]	0.062	0.111	(9.9, 44.6)*2	1.15	1.20	1.24, 1.29	1.27, 1.34	1.26	56.2
$Sr(biuret)_4$	[118]	0.123	0.175	(3.6, 60.3)*2	1.08	1.23	1.25	1.41	1.22	54.7
$U(butac)_4$	[119] [b]									

[a] *mmgg* Dod. [b] Unpublished coordinates.

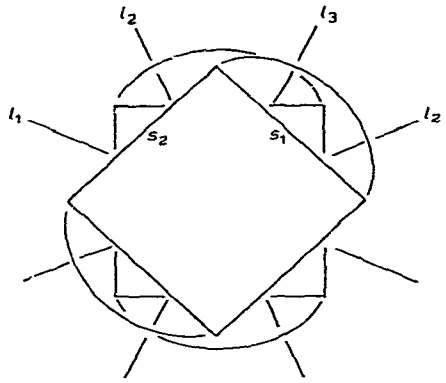

Fig. 11. The *ssss* SAP isomer (symmetry D_2). Unique edges are s_1, s_2, l_1, l_2, l_3.

pected all the compounds in this category have large bites (z = 1.14—1.22) with the exception of Sr(biuret)$_4$ which is a special case (z = 1.08) and its geometry is distorted towards the cube not the Dod.

The shape characteristics for each molecule are quoted in Table 11 together with Δ values and δ angles. Unlike the *mmmm* Dod, the symmetry of the SAP is lowered by the chelate rings (from D_{4d} to D_2). There are two different *s* edges dependent on whether they are occupied by the chelate or not and three types of *l* edges. The *ssss* SAP can be distorted towards three types of Dod (Fig. 11) depending upon which *l* edges become the *a* edges of the Dod, thus choosing $l_1 \rightarrow$ *mmmm* Dod, $l_2 \rightarrow$ *mmgg* Dod and $l_3 \rightarrow$ *gggg* Dod. All examples here bar one are distorted towards the *mmmm* Dod. It is clear that the major requirement for the *ssss* structure is that $s_1 = s_2$ and this is the case for the majority of molecules listed here. When discussing M(acac)$_3$(OH$_2$)$_2$, it was shown that significant differences between sides in the 'square' faces of the SAP led to puckering of the faces. Clearly large differences between s_1 and s_2 preclude a molecule from having the *ssss* structure.

There are two forms of M(acac)$_4$ both of which can be considered to have *ssss* geometry but the α form is very much distorted towards the *gggg*(D_2) Dod (Table 13) and the β form is less distorted towards the *mmmm* Dod. It is interesting that while for some metals both α and β forms exist, the largest Th (z = 1.16) only forms α and the smallest Zr (z = 1.22) only forms β. This is unexpected as the smaller bites are usually distorted towards the *mmmm* isomer. There are no startling packing effects in the two forms. In the βM(acac)$_4$ molecules, the six-membered chelate rings are folded about the line joining the oxygen atoms by angles in the 21.5—25.8° range. This type of folding is a familiar occurrence in β-diketone structures and is usually ascribed to intermolecular forces; certainly there seems no good reason why it should be an intramolecular effect. All molecules have C_2 symmetry with the axis running through the l_1 edges. They are distorted towards the *mmmm* Dod by

very small amounts as is apparent from the δ angles which indicate only a slight folding of the two squares. Unlike other examples in Table 11, $Zr(acac)_4$ has $s_1 > s_2$ and as a consequence l_2 is significantly less than l_1 and l_3.

The first molecule of $[Eu(bzac)_4]^-$ is more distorted than the second. It has the C_2 structure with the crystallographic axis through the l_1 edge but the folding of the squares is considerable ($\delta = 7.9°$). This is also shown by the two measurements of θ (the angle subtended at the metal by diagonal atoms in the same square) being different at 59.0 and 55.0°. In the second molecule, the squares are almost coplanar and bond lengths are slightly less (and z larger) than in the first molecule. The lowest Δ value of the Dod is given by the *mmgg* isomer. $[Gd(bzac)_4]^-$ is distorted in a similar fashion to the first $[Eu(bzac)_4]^-$. Both molecules show considerable variation in equivalent edges l_1 and l_2.

The bite of $Sr(biuret)_4$ is less than in these other complexes but as indicated by the δ angles, there are two good planes in the SAP. The high Δ value is due to some extent to the differing s edges ($= z$ 1.08 and $\neq z$ 1.23) but also to the differences in l values; l_1 and l_3 being much smaller than l_2 (1.23, 1.41). This distortion is towards a cube where $l_2 = \sqrt{2}\, l_1 = \sqrt{2}\, l_3$. ($\delta$ angles of 60.3° also show the influence of a cube). As the metal size increases L···L repulsions become less important and even the cube becomes a viable structure as shown by $U(bipy)_4$. In $Sr(biuret)_4$, the angles of folding around the O···O edges of the chelates are 49.6 and 1.8°.

It is apparent from the polyhedron shapes in Table 11 that the l/s ratio is considerably greater than 1.00 in most cases as predicted by the MFP.

Molecules which have structures intermediate between the *mmmm* Dod and the *ssss* SAP are listed in Table 12. There is of course no clear division between these examples and those given in Tables 10 and 11. The majority of these compounds have bites slightly less than those for the ideal *ssss* SAP in Table 11 (mean 1.12 vs. 1.17). It is tempting to argue that the smaller bites lead to greater distortion of the squares in the SAP and hence puckering of the faces along the path to the Dod. The majority of the compounds in Table 12 have D_2 symmetry but a couple show considerable differences in the two smaller δ angles. Apart from the value of z, these compounds have very little in common.

The reasons for the type of distortion from ideal are far from obvious. Thus $V(S_2CCH_2Ph)_4$ can be compared with the two crystal forms of $V(S_2CPh)_4$ both of which have the *mmmm* Dod geometry with a maximum deviation of an atom from a trapezoid of 0.05 Å. In $V(S_2CCH_2Ph)_4$, the deviations are up to 0.27 Å. It is clear that $[Er(hac)_4]^-$ is distorted from a SAP because of the inequalities of the s edges ($= z$ 1.11, $\neq z$ 1.25) but not why the structure is not a Dod although the z value is higher than found in most examples of that stereochemistry. One possible explanation though not readily confirmable is hydrogen bonding. We can see that hydrogen bonding does affect bond lengths; thus in $[Ce(ttbd)_4]^-$, there are seven bonds of 2.42—2.49 Å, with an eighth to the only atom that participates in hydrogen bonding of 2.56 Å and

TABLE 12

$M(L{-}L)_4$ complexes which have geometries intermediate between the *mmmm* Dod and the ssss SAP structures

Compound	Ref.	z	Δ (Å)				δ angles
			Dod *mmmm*	*mmgg*	SAP *ssss*	BCTP	
$V(S_2CCH_2Ph)_4$	[102]	1.09	0.105	0.140	0.123	0.155	4.9, 30.4, 45.3, 45.6
$[Sc(trop)_4]^-$	[120,121]	1.13	0.094	0.166	0.127	0.135	13.2, 30.1, 42.3, 44.0
$[Nb(trop)_4]^+$	[122] [a]	1.16	0.084	0.181	0.102	0.167	18.9, 20.8, 40.6, 45.1
$[Sc(thacox)_4]^-$	[123]	1.14	0.097	0.157	0.084	0.163	9.3, 20.7, 42.4, 46.7
$[Pr(dmdtp)_4]^-$	[124]	1.12	0.084	0.178	0.116	0.172	20.6, 21.3, 45.2, 46.4
$[Er(hac)_4]^-$	[65]	1.11	0.108	0.164	0.090	0.180	14.5, 14.5, 48.2, 48.2
$[Ce(ttbd)_4]^-$	[125]	1.14	0.112	0.165	0.106	0.197	10.7, 13.2, 36.6, 40.4

[a] Coordinates slightly inconsistent with molecular dimensions.

distortions from ideal polyhedra will surely take less energy than such extreme bond lengthening. In $[Sc(trop)_4]^-$, two of the four chelate rings are symmetrical while the other two are asymmetric in different ways which has been related [120] to the degree of hydrogen bond involvement. However there is no hydrogen bonding in $[Nb(trop)_4]^+$. The O···O bite [2.43 Å] is significantly less than the previously determined shortest value for trop of 2.490 Å and thus z is smaller than might have been expected though larger than other examples in Table 12. The two a edges are particularly short (O···O 2.44 Å) and it is stated [122] that this is due to overlap between the lone pairs of the oxygen atoms in adjacent A sites. This attraction would be particularly important in complexes with d^0 metal and could work against the coulombic repulsion forces. However such a theory is untenable because *mmmm* isomers show a decrease in a with increased z and the values of a at 1.16 are longer, not shorter than expected for Dod with m (= z) of 1.16. Thus the reason for the distortion from the Dod is repulsion between the oxygens over the a edges not attraction.

In $[Pr(dmdtc)_4]^-$ the Pr—S bond lengths are 2.98 Å thus ensuring that most S···S contacts are well above the sum of van der Waals radii. The bite of the dithiophosphate is 3.33 compared to 2.93 Å for the dithiocarbamates. Despite the large bite of 1.12, the S···S distances over the a edges of the Dod are only 3.56 Å which is still somewhat below the van der Waals diameter and the distortion from ideal could be due to steric effects. The distortion from the Dod is along the D_2 pathway to the SAP and different from the type found in the $[Np(dedtc)_4]^-$ structure discussed earlier.

The effect of hydrogen bonding in $[Ce(ttbd)_4]^-$ on bond lengths has already been mentioned. As a Dod, θ_A and θ_B are 44.4 (a = 1.40) and 67.7° respectively, values rather unlike those usually found in the *mmmm* Dod for z = 1.14 (36, 75°), but this is presumably due to the considerable distortion towards the SAP caused by the bulky side groups potentially close over the a edges. The angles of fold in the unique β-diketones along the O···O axis are 0 and 18°.

Four of the molecules in Table 12 maintain D_2 symmetry but in the other three, one of the squares of the SAP is much more buckled than the other

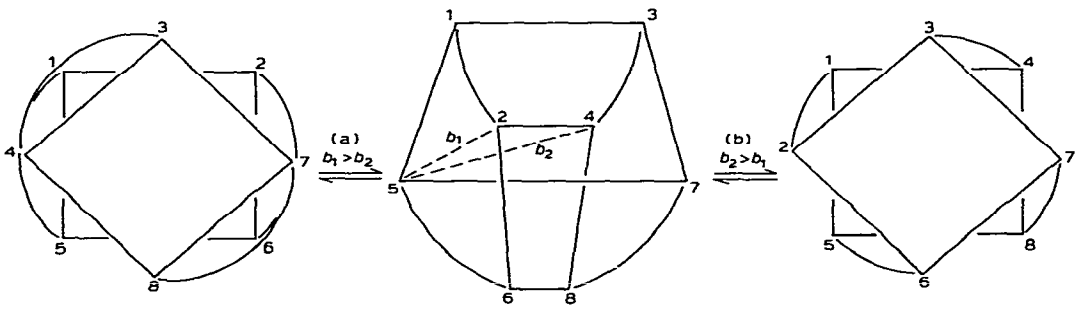

Fig. 12. The *gggg*(D_2) Dod isomer. (a) With $b_1 > b_2$ distorted towards *ssss* SAP; (b) with $b_1 < b_2$ distorted towards *llll* SAP.

TABLE 13

M(L—L)$_4$ complexes with the *gggg*(D_2) Dod structure

Compound	Ref.	Δ (Å)		δ angles				θ_A	θ_B	b_1	b_2	m	a	$g(=z)$	$g(\neq z)$
		gggg Dod	*ssss* SAP												
[Y(hfac)$_4$]$^-$	[126]	0.035	0.127	21.7	21.7	32.4	32.4	38.6	68.5	1.55	1.46	1.19	1.24	1.19	1.20
[Eu(hfac)$_4$]$^-$	[127]	0.043	0.127	19.9	19.9	33.0	33.0	38.8	67.9	1.56	1.46	1.19	1.26	1.18	1.19
[Am(hfac)$_4$]$^-$	[127]	0.059	0.110	17.0	17.0	35.6	35.6	39.1	67.0	1.58	1.43	1.20	1.26	1.16	1.21
[Pr(ttbd)$_4$]$^-$	[128]	0.058	0.158 [a]	16.9	17.9	24.3	30.6	41.4	65.6	1.47	1.58	1.19	1.32	1.16	1.19
[Nb(ttbd)$_4$]$^-$	[129]	0.070	0.137	12.2	25.4	31.4	32.2	40.1	68.4	1.53	1.49	[b]	1.28	1.16	[b]
αTh(acac)$_4$	[130]	0.110	0.075	5.1	19.6	43.7	45.3	37.7	70.2	1.59	1.38	1.19	1.23	1.16	1.26
αCe(acac)$_4$	[131]	0.093	0.079	9.7	21.1	42.9	44.0	37.6	70.5	1.59	1.39	1.19	1.22	1.18	1.23
Zr(8quin)$_4$	[132] [c]														

[a] Best SAP is the *llll* isomer. [b] Wide range of edges, see text. [c] Unpublished coordinates.

and the resulting geometry could be called the BCTP. The equal popularity of the two types of structure suggest that there is very little energy difference between them for $M(L—L)_4$ molecules.

The only other geometry for which several examples exist is the *gggg*(D_2) Dod illustrated in Fig. 12. As predicted [24], the bites of such compounds (Table 13) are in a narrow range (1.16—1.19) and also the geometry is more frequently found that the *gggg*(S_4) isomer. Unlike the *mmmm* isomer, the symmetry of the D_{2d} Dod is reduced (to D_2) in this *gggg* isomer. There are therefore two types of *b* edge and of *g* edge. Rather surprisingly all *g* edges are similar whether occupied by a chelate or not and of course much reduced to ca. 1.18 from that observed in the *mmmm* isomers. Other changes in shape characteristics are that the *a* edges are not that much longer than in the *mmmm* isomer; it is the positions of the B sites that have changed. θ_B is very much smaller than in the *mmmm* isomer and this is due to the atoms in the B sites being pulled up towards the A sites in the chelate.

It is clear that these compounds could not have the *mmmm* geometry because of crowding over the *a* edges but it is not apparent why they don't have the *ssss* geometry if it is of lower energy for such *z* values.

While the two types of *g* edge are comparable, the two types of *b* edge are not and as shown in Fig. 12 this leads to distortion towards two types of SAP When $b_1 > b_2$, as in the majority of examples, the distortion is towards the *ssss* SAP; the b_1 edge becoming a face diagonal and b_2 an *l* edge. Because of these differences, the δ angles over the b_1 edges are less than those over the b_2 edges and thus reflect the distortion towards the *ssss* SAP.

The α form of $M(acac)_4$ is on this D_2 pathway to the *ssss* SAP and indeed is rather closer to that geometry than the *gggg*(D_2) Dod. A discussion on the difference in structure between the two forms came to no definite conclusion [143]. With acac replaced by the bulky dpdm ligand, only the *mmmm* Dod structure is formed [130].

$[Pr(ttbd)_4]^-$ is a most interesting molecule as $b_1 < b_2$ and is thus distorted

TABLE 14

$M(L—L)_4$ complexes with unusual geometries

Compound	Ref.	*z*	δ angles				Δ (Å)	Isomer
$Nb(tmd)_4$	[133]	1.28	1.1	1.1	49.2	49.2	0.018	SAP *llll*
$[Ti(ox)_2]_n^{n-}$	[134][a]	1.26						SAP *llll*
$Mo(dedtc)_4$	[135]	1.11	18.6	18.6	36.0	36.0	0.083	Dod *gggg*(S_4)
							0.129	SAP *llss*
$Zr(Netsal)_4$	[136][a]							Dod *gggg*(S_4)
$V(S_2CMe)_4$	[103]	1.10	17.7	17.7	33.1	43.2	0.098	Dod *mmgg*
							0.122	SAP *llss*
$U(bipy)_4$	[137]	1.05	0.3	0.4	0.7	1.3	0.074	Cube

[a] Unpublished coordinates.

towards the *llll* SAP isomer (Fig. 12). The lower δ angles are thus over the b_2 edges. In the molecule the ligand is asymmetrical; the two types of donor atom are distributed among the 3B and 1A sites and 1B and 3A sites respectively. It is interesting that $[Ce(ttbd)_4]^-$ with a different cation and unit cell is on the D_2 *ssss* SAP ⇌ *mmmm* Dod pathway. Perhaps the smaller size of the Pr ion is responsible for the change. The details of $[Nd(ttbd)_4]^-$ are rather surprising as the four chelate bites are 2.96, 2.71, 3.02 and 2.68 Å with a spread in z of 1.10—1.21. $Zr(8\text{-quin})_4$ has oxygen in the B sites and nitrogen in the A sites as predicted by Orgel's rule (section v) with Zr—O 2.106 and Zr—N 2.405 Å. This is a molecule which is precluded from being a *mmmm* isomer with this distribution of atoms because of steric effects.

The remaining compounds of the $M(L—L)_4$ type (Table 14) have varying geometries and will be considered in turn. $Nb(tmd)_4$ has a very regular *llll* structure stabilised by the enormous bite (z = 1.28) and confirming predictions [24] that with z up to 1.30 this D_4 isomer would be the only minimum on the potential energy surface. There are two molecules in the asymmetric unit both having regular geometry with s = 1.18 and $l(=z)$ 1.28 and l ($\neq z$) 1.27. This comparability of edges occupied or not by chelates is reminiscent of the g edges in the *gggg*(D_2) polyhedron. Bond lengths in these two molecules are equivalent and θ = 56.9°. Polymeric sheets of $[Ti(ox)_2]_n^{n-}$ (z = 1.26) also have this structure with individual coordination spheres bridging through oxalates. The general lack of examples of the *llll* isomer is surprising * particularly as examples of $M(L—L)_3L_2$ complexes chelated via l edges are well known.

$Mo(dedtc)_4$ has a geometry intermediate between the *gggg*(S_4) isomer and the *llss* SAP isomer [Fig. 13(a)]. There seems no good reason why it should not have the *mmmm* Dod structure although clearly the z of 1.11 is too small for other polyhedra such as the *gggg*(D_2)Dod and the *ssss* SAP. The geometry of the compound is by no means as regular as the *gggg*(D_2) Dod though this may be to some extent because of the small bite. Shape characteristics are a = 1.26, m = 1.20, b_1 = 1.42, b_2 = 1.58, g_1 = 1.11, g_2 = 1.28, θ_A = 38.6, θ_B = 68.6°. Note the considerable differences between g edges [not found in the *gggg*(D_2) isomer] and also b edges. b_1 is considerably less than b_2 presumably because site 2 is pulled towards site 1 (Fig. 13) by the chelate. This distortion takes the geometry towards the *llss* isomer. It seems likely that all other

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* $Th(tfac)_4$ [144] is also supposed to have this geometry. However, the published coordinates show an *llll* isomer in which θ for one face is 72° and for the other is 50°. This results in a Δ value from the SAP of 0.209 Å. The geometry is not close to any other polyhedron with δ angles of 5.3, 8.6, 48.3 and 48.3°. The only reasonable explanation for such distortion is that the structure is 9 coordinate with a capped SAP geometry with the missing atom on the crystallographic two-fold axis. This would account for the θ angles which are characteristic of the CSAP geometry (section D) and also for the difference in M—O bond lengths; those in the uncapped face being 2.36 and those in the capped 2.41 Å. The data are photographic and an oxygen atom in the presence of thorium could be missed.

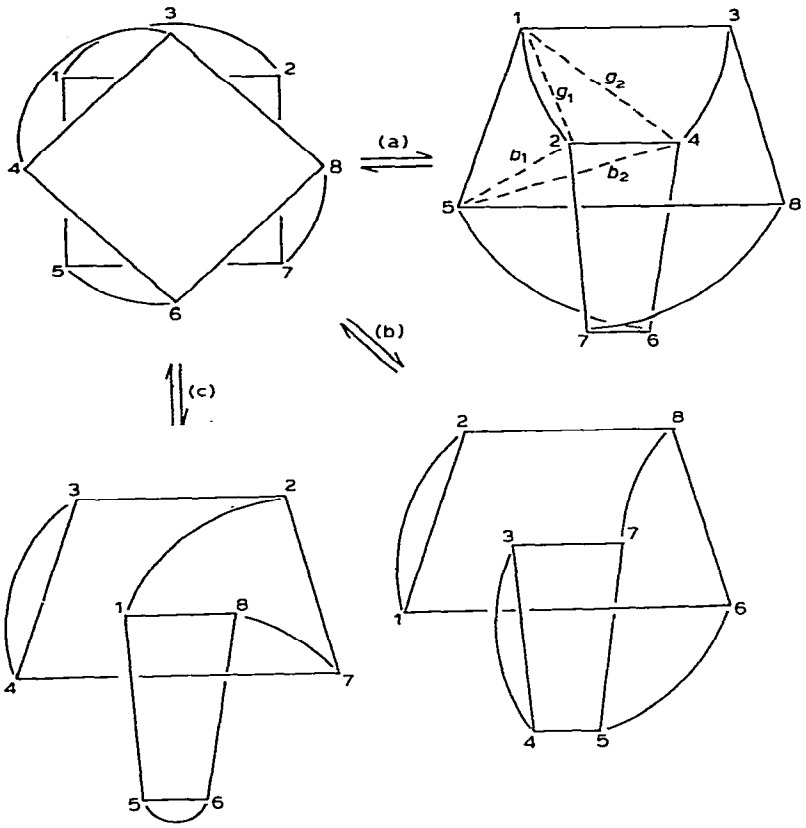

Fig. 13. The *ssll* (SAP) isomer can be distorted towards (a) *gggg*(S_4) Dod — $Mo(dedtc)_4$; (b) *mmgg* Dod — $V(S_2CMe)_4$; (c) *abmg* Dod — $Zr(acac)_3(NO_3)$.

gggg(S_4) structures would be distorted in this way and that they could not have the ideal Dod geometry. This is also true for the *llss* isomer which can be distorted towards three types of Dod dependent upon which *l* edges are chosen as the *a* edges in the Dod. $Zr(Netsal)_4$ also has the *gggg*(S_4) geometry with nitrogen in A sites (2.539 Å) and oxygen in B sites (2.055 Å) and θ_A 34.6, θ_B 73.3°. The rather strange angles may be a consequence of the weak Zr—N bond lengths.

$V(S_2CMe)_4$ is a most fascinating molecule as not only does it have a unique geometry, intermediate between the *mmgg* and *llss* isomers [Fig. 13(b)] but also because it is in the same asymmetric unit as a molecule having the normal *mmmm* geometry. Both molecules contain equivalent bites and therefore strong packing effects must cause this unique structure to be created. It is interesting that there are two molecules with *mmmm* structures to every one with the *mmgg* structure and it may be that the packing requirements of the former are dominant and cause the unusual *mmgg* isomer to be formed. As

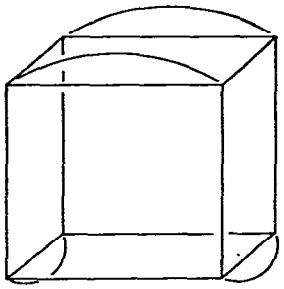

Fig. 14. Wrapping pattern of the bidentate ligands in $U(bipy)_4$.

in previous examples the *mmgg* Dod adjusts shape characteristics in order to maintain as regular a polyhedron as possible. Edges are $a = 1.24$, $m = 1.09$, 1.25, $g = 1.11$ and 1.25. There are three types of b edges, between sites 1 and 3, $b_1 = 1.40$, between 6 and 7 $b_2 = 1.30$ and between 1 and 7, 3 and 6 $b_3 = 1.62$. This is expected as b_2 is shortened relative to the others by the two chelates on the g edges. Thus the distortion towards the *llss* SAP is obligatory.

The final compound is a suitably unique one on which to complete discussion of the $M(L—L)_4$ complexes. $U(bipy)_4$ has a cubic structure with the wrapping pattern as shown in Fig. 14. For this molecule $z = 1.05$ but the large metal size makes the minimum N···N distances between chelates a massive 3.02 Å well above van der Waals diameter. In the face of such values, the cubic structure is as good as any other and maybe better because of f orbital participation.

Two other $M(L—L)_4$ compounds have been briefly reported $Pb(ac)_4$ [145] and $[Hg(NO_2)_4]^{2-}$ [146] but no information was given about their isomeric structure.

(f) Molecules of the form M(bidentate)$_4$ with non-equivalent ligands. The geometry of nearly all $M(L—L)_4$ compounds with equivalent ligands fall into three categories, *mmmm* and *gggg*(D_2) Dod and *ssss* SAP or have structures intermediate between these forms. There are only isolated examples of the *llll*, *gggg*(S_4), *mmgg* and *llss* isomers. The reasons for such preferences are well understood and include the fact that chelates with equivalent z are unlikely to span edges of differing sizes and environment as the *mmgg*, *llss* and *aabb* isomers. However complexes of the type $M(L—L)_n(L—L)_{4-n}$, $n = 1$ or 2, in which these ligands have different z bites, might be expected to have this type of structure. This is a neglected area of crystallographic work and there are only a few examples of such complexes (Table 15) and more analyses should be forthcoming. For example, compounds of the type $M(A—A)_n(B—B)_{4-n}$ (for all n; A—A = 5-methylpicoline, B—B = 5,7-dichloroquinolinol) have been prepared [154] and give every indication of having a variety of structures.

Molecules with $n = 1$ in Table 15 will be considered first. The number of possible isomers increases considerably from those given in Table 9 for

TABLE 15

$M(L—L)_4$ complexes with non-equivalent L—L

Compound	Ref.	Δ (Å)		δ angles				M—L	M—L′	z	z′
		Dod	SAP								
$Eu(acac)_3(phen)$	[147]	*m′mmm* (0.161)	*s′sss* (0.073)	0.8	0.9	47.5	50.4	2.38	2.64	1.19	1.03
$Nb(ttbd)_3(bipy)$	[148]	*m′mmm* (0.147)	*s′sss* (0.091)	0.9	6.6	42.4	46.7	2.44	2.70	1.17	1.05
$Zr(acac)_3(NO_3)$	[149]	*a′bmg* (0.116)	*l′lss* (0.185)	31.8	30.9	39.8	47.5	[a]	[a]	1.26	0.90
$[Nb(O_2)_3(phen)]^-$	[150]	*m′mmm* (0.208)	*s′sss* (0.281)	20.9	43.0	22.7	45.1	1.98	2.31	0.76	1.16
		m′mmm (0.204)	*s′sss* (0.273)	20.2	42.1	26.5	42.9	1.99	2.31	0.75	1.16
$[Nb(O_2)_2(ox)_2]^{3-}$	[151]	*m′mm′m* (0.219)	*s′ss′s* (0.280)	5.8	54.8	38.3	42.7	1.98	2.14	0.72	1.26
$Mn(NO_3)_2(dppn)_2$	[152]	*m′mm′m* (0.175)	*s′ss′s* (0.194)	0.3	29.6	37.8	50.4	2.42	2.30	0.87	1.15
$Zr(acac)_2(NO_3)_2$	[153]	*m′mm′m* (0.135)	*s′ss′s* (0.204)	26.7	40.8	28.0	31.2	2.10	2.30	1.26	0.93

[a] See text.

$M(L—L)_4$ complexes because the unique ligand can occupy any of the various edges. Thus while for *ssss*, *llll*, *gggg*, and *mmmm* there is still only one isomer, for *aabb*, *mmgg*, *llss* there are now two and for *abmg* four. Examples in Table 15 all have geometry on the *m'mmm* = *s'sss* pathway with the exception of $Zr(acac)_3(NO_3)$. This molecule is unique as it has the *a'bmg* isomeric structure. It can be argued that this structure is the only possible one for a compound of this stoichiometry in which the acac ligands have $z \geqslant 1.20$ and the nitrate $z = 0.90$. The relatively large bite of acac prohibits two acac ligands from occupying the same trapezoid which rules out the common *m'mmm* isomer. The nitrate bite at 0.90 is unsuitable for either edge in the SAP and therefore the *a'bmg* structure is logical. There is only one precedent for the *a* edge being occupied by a chelate, namely the *aa* isomers of $ML_4(L—L)_2$ compounds (Table 5). The *a* edges are not occupied in any other tetrachelated compound. This complex is also unique in having the *b* edge occupied by a chelate. Not surprisingly this edge is much larger at 1.30 than the *g*(1.25) and *m*(1.22) edges occupied by acac but less than the other *b* edges. Bond lengths are Zr—O_a 2.31, 2.42; Zr—O_m 2.16, 2.13; Zr—O_b 2.16, 2.11 and Zr—O_g 2.20, 2.09 Å. It is expected that the longer bonds are to the nitrate groups in the crowded A sites. Taking into account the different edges used and the lack of overall symmetry the Δ value of 0.116 Å from the Dod is reasonably small. The distortions are necessarily towards the *llss* isomer of the SAP [Fig. 13(c)].

$Eu(acac)_3(phen)$ and $Nd(ttbd)_3(bipy)$ have equivalent geometries, the best fit being to a *s'sss* SAP. In both molecules the *z* bite is considerably longer than the *z'* bite and indeed the latter would not be found spanning an *s* edge except in present company. There are particularly long M—N bond lengths in both molecules which facilitate formation of the SAP. The two molecules of $[Nb(O_2)_3(phen)]^-$ have wildly dissimilar bites for the ligands which is reflected in the δ angles and Δ values. However the trapezoids in both compounds are planar, even those which contain peroxide and phen ligands, and are mutually perpendicular.

The three complexes with $n = 2$ have highly distorted geometries and this is no doubt due to the large difference between *z* and *z'*. There are two *mmmm* isomers for $M(L—L)_2(L—L)_2$ complexes dependent upon whether ligands of the same type are in the same trapezoid or not. All three molecules here are of the second type which would appear particularly suitable for compounds with unequal bites. Despite the high Δ values and unusual (to say the least) δ angles, in $[Nb(O_2)_2(ox)_2]^{3-}$ both trapezoids, containing peroxide and oxalate, are planar and mutually perpendicular. $Zr(acac)_2(NO_3)_2$ contains the largest bite ($z = 1.26$) ever found in an *m* edge of a Dod. Clearly it would be impossible for both acac ligands to appear in the same trapezoid.

This series of complexes together with the $M(L—L)_4$ complexes discussed in section(e) have covered all the isomers originally listed by Hoard and Silverton (Table 9) with the exception of *abab*. It seems most unlikely that any molecule will have this geometry because such a wide difference in bites

TABLE 16

Structures of other monomeric 8 coordinate complexes

Compound	Ref.	Type	Geometry
$Mo(tptp)(O_2)_2$	[155][a]	$M(L{-}L{-}L{-}L)(L{-}L)_2$	Dod
$U(salen)Cl_2(thf)_2$	[156]	$M(L{-}L{-}L{-}L)L_4$	Dod
$Zr(nta)_2$	[157][a]	$M(L{-}L{-}L{-}L)_2$	Dod
$U(pc)_2$	[158,159][a]	$M(L{-}L{-}L{-}L)_2$	SAP
$Th(pc)_2$	[159][a]	$M(L{-}L{-}L{-}L)_2$	SAP
$Zr(edta)(OH_2)_2$	[160][a]	$M(L{-}L{-}L{-}L{-}L{-}L)L_2$	Dod

[a] Unpublished coordinates.

would be required. If the geometry were to exist $Zr(acac)_2(NO_3)_2$ would be the ideal candidate; one cannot think of a more suitable molecule.

(g) Other monomers. There are a few monomeric structures (Table 16) that do not fit into any of the above categories. In $Mo(tptp)(O_2)_2$, the tetradentate ligand is coplanar with the metal and the peroxides occupy axial positions. The geometry could be called a Dod in which the porphyrin ring occupies the B sites ($\theta_B = 90°$) and the peroxides the A sites ($\theta_A = 25°$). The molecule has S_4 symmetry with the oxygens of the peroxides eclipsed with respect to the Mo—N bonds of the macrocycle as expected for a Dod. $U(salen)Cl_2(thf)_2$ is an almost perfect Dod (Δ value 0.05 Å) with the tetradentate planar salen ligand occupying one trapezoid and the four monodentate ligands the other. There are four molecules in the asymmetric unit with only minor differences in geometry. In $Zr(nta)_2$, each tetradentate ligand occupies two A and one B site in one trapezoid and a B site in the other. The molecule has imposed C_2 symmetry with $Zr{-}O_A$ 2.251, $Zr{-}O_B$ 2.124, 2.136 and $Zr{-}N_A$ a long 2.439 Å. $U(pc)_2$ and the Th analogue are SAP with the two planar tetradentate ligands occupying the squares. The two planes are rotated by 8° from a SAP and are thus 37° from the cube in which the two planes would exactly superimpose. In $Zr(edta)(OH_2)_2$ the A sites are occupied by nitrogen atoms and water molecules, the B sites by oxygen atoms.

(h) Uranyl complexes. Uranyl complexes (Table 17) are HP with the uranyl group occupying axial positions. This is a most unlikely structure from the point of view of steric repulsions but is feasible because of the strength of the uranyl group and the large size of the uranium atom which allows six ligands to form a hexagonal girdle. However steric effects are important and there are only a few limited categories of chelates found in the girdle.

The first category consists of the three small bidentate ligands packed into the girdle. With peroxide, nitrate and acetate ligands, the girdles are relatively planar with maximum deviations of 0.06, 0.09 and 0.04 Å respectively. A slightly higher deviation (0.15 Å) was obtained for carbonate. Naturally steric

TABLE 17

Structures of 8 coordinate complexes containing the uranyl group

	Compound	Ref.	Max. distance of contributing atom from UL_6 hexagonal plane
(a) $UO_2(L—L)_3$			
	$[UO_2(CO_3)_3]^{4-}$	[161]	0.15
	$[UO_2(ox)_2]_n^{2n}$	[162]	0.58
	$[UO_2(ox)_3]^{4-}$	[163]	0.08
	$[UO_2(O_2)_3]^{4-}$	[164]	0.06
	$[UO_2(dedtc)_3]^-$	[165]	0.30
	$[UO_2(NO_3)_3]^-$	[166]	0.09
	$[UO_2(ac)_3]^-$	[167]	0.04
	$[UO_2(cupferrate)_3]^-$	[168] [a]	
(b) $UO_2(L—L)_2L_2$			
	$UO_2(NO_3)_2(OH_2)$	[169]	0.10
		[170]	0.02, 0.08 [b]
		[171]	0.02
		[172]	0.15
	$UO_2(NO_3)_2(etc)_2$	[173]	0.02
	$UO_2(NO_3)_2(tpao)_2$	[174]	0.08
	$UO_2(NO_3)_2(tppo)_2$	[175]	0.04
	$[UO_2(NO_3)_2(ONO_2)_2]^{2-}$	[176]	0.05
	$UO_2(imda)_2$	[177]	0.13
(c) $UO_2(L—L—L)_3$			
	$[UO_2(dipic)_2]^{2-}$	[178]	0.004
	$[UO_2(oxyd)_2]^{2-}$	[179] [a]	
(d) Others			
	$\{[UO_2(NO_3)_2]_2(sal)_2\}$	[180]	0.11

[a] Unpublished coordinates. [b] Two molecules in asymmetric unit.

effects in the girdle are reduced by atoms being alternatively above and below the plane. In $UO_2(dedtc)_3^-$, the mean S—U—S angle is 73.5°, much bigger than the 60° necessary for a planar girdle and the girdle is considerably puckered; distances of atoms from the least squares plane being respectively 0.30, —0.17, 0.25, —0.26, 0.23 and —0.20 Å.

The oxalate ligand is similarly large and in $[UO_2(ox)_3]^{4-}$ a planar girdle is obtained only by one oxalate chelating via a four-membered ring and the other two in the usual way via five-membered rings. However in polymeric $[UO_2(ox)_2]^{2-}$ the three oxalates do chelate through five-membered rings but not surprisingly the girdle is very puckered, oxygen atoms deviating from the least squares plane by distances of 0.58, —0.51, 0.32, —0.24, 0.32 and —0.47 Å. As pointed out by Lippard [2], this type of hexagonal ring puckering distorts the HP towards a cube (Fig. 7). For $[UO_2(ox)_2]^{2-}$ the Δ value from a cube is 0.176 Å. Of course the normalisation procedure which equates the

uranyl U—O bonds with the others helps to lower this value. The smallest Δ value from a Dod is 0.186 Å with δ angles of 10.3, 26.5, 27.1 and 29.8°.

Uranyl compounds of the type $UO_2(L—L)_2L_2$ also give 8 coordinate HP structures with the monodentate ligands in *trans* positions. The girdles are closely planar in fact more so than the $UO_2(L—L)_3$ compounds but this is due no doubt to the restriction of examples of the bidentate ligand just to the small nitrate ligand. Monodentate ligands include H_2O (four examples) ethylcarbamate, tpao, tppo and monodentate nitrate. Bond lengths are not significantly longer than in 7 coordinate complexes. $UO_2(imda)_2$ is a polymeric example of this type of structure, each ligand being bidentate to one uranium atom and monodentate to another.

Not surprisingly $UO_2(L—L—L)_3$ compounds can be formed and structural examples include L—L—L = dipic and oxyd, in which the girdle is planar. There are no other 8 coordinate complexes of the type $ML_2(L—L—L)_2$ but one would expect their geometry to be different with a considerable angle of intersection between the planar terdentate ligands.

The final uranyl compound is a centrosymmetric dimer in which two hexagonal girdles share an edge. Both girdles are coplanar to within 0.11 Å.

(i) Eight-coordinate polymers. Eight coordinate polymeric structures are listed in Table 18 together with Δ values from the Dod and SAP and δ angles. Several of these are of considerable interest and will be discussed in some detail in this section. Both $[Ce_2F_{14}]^{6-}$ and $[Yb_2(paphy)_2(OH_2)_6(OH)_2]^{4+}$ are centrosymmetric dimers, best described as Dod sharing an *m* edge. Both dimers have relatively undistorted geometries; in the latter the tridentate planar ligand occupies three sites of a trapezoid. Both coordination spheres of $Pr_2(fod)_6$, $2H_2O$ are highly distorted from ideal, no doubt because three of the oxygens are shared by both metals. In $\{[MoN(dedtc)_3]_2Mo(dedtc)_3\}^{3+}$, an 8 coordinate moiety, $MoN_2(dedtc)_3$, bridges through nitrogen to two 7 coordinate Mo atoms. In the 8 coordinate polyhedron the three bidentate ligands occupy *a*, *m*, *m* edges (type 1a in Fig. 10). The coordination sphere of $[Eu(nic)_2(OH_2)_4]^+$ is of the $ML_4L'_4$ type as it contains no chelating ligands. The oxygen atoms of nic occupy the B sites (2.39 Å) of a Dod where chain formation is probably easier than in the crowded A sites (water at 2.54 Å). Both coordination spheres in Dy(nta), $4H_2O$ contain a terdentate (O···N···O) nta ligand, three carboxylate oxygens from different nta ligands and two water molecules. Their geometries are considerably distorted from ideal. In $Er(isonic)_2(OH_2)_2$ the two faces of the SAP are considerably folded and this has been related to the bridging pattern of the polymer. Both $Er_2(malonate)_3$, $8H_2O$ and $Er[Er(oxyd)_3]$, $6H_2O$ contain 8 and 9 coordinate Er in an extensive polymer. Despite this the coordination spheres have geometries close to the ideal SAP. $Pb(nic)_2$ forms an extensive polymer but with each coordination sphere containing two bidentate ligands (z = 0.83). Best fit is to a cube but the Δ value is high no doubt because of the small bites occupying two of the edges. Individual coordination spheres in Sc_2ox_3, $6H_2O$ (z = 1.18) and the isomorphous Yb analogue

TABLE 18

Polymeric structures

	Δ (Å)		δ angles	Ref.
	Dod	SAP		
(a) Dimers, trimers				
$[Ce_2F_{14}]^{6-}$	0.073	0.137	19.3, 29.6, 35.2, 39.8	[181]
$[Yb_2(paphy)_2(OH_2)_6(OH)_2]^{4+}$	0.088	0.157	27.9, 29.3, 36.5, 45.4	[182]
$Pr_2(fod)_6$, $2H_2O$	0.191	0.209	15.3, 30.7, 45.0, 46.6	[183]
	0.181	0.209	12.7, 32.8, 25.4, 51.7	[183]
$[M(nic)_3(OH_2)]_2$				[184] [a]
$\{[MoN(dedtc)_3]_2Mo(dedtc)_3\}^{3+}$				[185] [b]
(b) Polymers				
$[Eu(nic)_2(OH_2)_4]^+$	0.059	0.138	25.1, 25.1, 28.1, 42.2	[186]
$Dy(nta)$, $4H_2O$	0.127	0.177	23.6, 29.9, 32.0, 41.4	[187]
	0.110	0.141	15.1, 29.4, 39.6, 46.5	[187]
$[Er(isonic)_2(OH_2)_2]^+$	0.129	0.156	25.2, 25.2, 49.8, 49.8	[188]
$Er_2(malonate)_3$, $8H_2O$	0.146	0.043	0.0, 10.1, 50.2, 50.4	[189]
$Er[Er(oxyd)_3]6H_2O$	0.119	0.046	9.7, 9.7, 47.0, 47.0	[190]
$Pb(nic)_2$	[c]	—	3.6, 4.7, 6.8, 27.8	[191]
$Sc_2(ox)_3$, $6H_2O$	0.129	0.089	14.5, 22.1, 38.7, 46.5	[192]
also Yb				[193] [d]
$Ho(isonic)_3(OH_2)$	0.133	0.103 [e]	0.4, 25.7, 47.0, 47.0	[194]
$La(isonic)_3(OH_2)_2$				[194] [a]
$[Er(HOCH_2CO_2)(OCH_2CO_2)(OH_2)]$	0.074	0.148	23.5, 30.1, 34.5, 42.2	[195]
$Nd_2(imda)_3$ $2HCl.2H_2O$				[196] [f]
$Nd(glycine)_3Cl_3.3H_2O$				[197] [b]
$Th(formate)_4.3H_2O$				[198] [bg]
$Cd(maleate)$, $2H_2O$				[199] [h]
$Ce_2(SO_4)_3.2OC(NH_2)_2.5H_2O$				[200] [d]

[a] Contains eight bonds of usual length with a ninth about 0.5 Å longer. [b] Unpublished coordinates. [c] 0.170 Å from a cube. [d] Coordinates inconsistent. [e] 0.117 Å from a BCTP. [f] Only rough coordinates (Nd—O 2.3—2.6 Å). [g] Eight bonds to formate (mean 2.48 Å) and two to water at 3.1 Å. [h] Contains 6 and 8 coordinate Cd. The latter coordination sphere is much distorted by the small bite and by bridging to other metals.

are of the type $M(ox)_3(OH_2)_2$ with the geometry of type (1a) in Fig. 10 and bridge through oxalates. The L—M—L angle is 147.4°. $Ho(isonic)_3(OH_2)_2$ is an excellent example of a BCTP, a geometry probably imposed by the bridging requirements of the polymer. The two water molecules occupy the capping positions in the BCTP, the remaining sites being filled by carboxylate oxygen atoms. There is no chelation. The coordination sphere of $[Er(HOCH_2CO_2)(OCH_2CO_2)(OH_2)]$ contains just one chelating ligand (z = 1.13) which occupies the a edge of a Dod.

In general the polymeric structures are by no means as predictable as monomeric 8 coordinate structures because the bridging pattern is dominant in the choice of geometry particularly so when donor atoms are shared by metals.

However many examples do maintain a geometry close to ideal and in a few this is consistent with that expected for a monomeric complex of equivalent stoichiometry.

(iv) The bicapped trigonal prism — fact or fiction?

A considerable number of 8 coordinate complexes have a geometry that is intermediate between the Dod and the SAP. These geometries can be divided into two categories. In the first, they are situated on the D_2 pathway between the two ideal forms and have two equivalent small and two equivalent large δ angles. Examples are given in Table 19 and follow the pathway from the SAP as the two squares are folded by equal amounts up to the Dod. The two smaller δ angles form a continuous series from 0 to 29.5°. In the second category, one of the two squares is folded while the other remains planar and this type of geometry is called the BCTP. Several molecules that might be considered to have this geometry (Fig. 15) are listed in Table 20 together with their shape characteristics. In previous sections the BCTP was considered to be equivalent to a tricapped trigonal prism (TCTP) with one capping atom removed but keeping D_{3h} symmetry. The HSM with this geometry has δ angles of 0, 21.8, 48.2 and 48.2° and ϕ angles of 14.1°. It is immediately clear that this restriction to D_{3h} is unjustified because all compounds in Table 20 have $v_1 > v_2$ with an average ratio of 1.2. The triangular faces of the prism are also distorted with h_1 well above h_2. This is not surprising; starting from a TCTP and removing the third capping atom allows the unique quadrilateral face to contract and v_2, h_2 are shortened with respect to v_1, h_1. A much smaller effect is noted for c_1 and c_2 with the former edge slightly shorter. These changes

TABLE 19

8 Coordinate complexes with structures on the D_2 pathway between the Dod and SAP

Structure	δ angles	Δ (Å)	
		Dod	SAP
Ideal Dod	29.5, 29.5, 29.5, 29.5	0.000	0.150
$Te(mtc)_4$	30.2, 30.8, 34.6, 35.6	0.016	0.165
$[Mn(NO_3)_4]^{2-}$	29.6, 29.6, 35.3, 38.1	0.051	0.204
$Mo(CN)_4(CNMe)_4$	26.7, 26.7, 39.9, 39.9	0.045	0.135
$Ho(acac)_3(OH_2)_2$	22.0, 26.5, 34.9, 35.9	0.049	0.134
$Pr(dmdtp)_4^-$	20.6, 21.3, 45.2, 46.4	0.084	0.116
$[Am(hfac)_4]^-$	17.0, 17.0, 35.6, 35.6	0.059	0.110
$[Er(hac)_4]^-$	14.5, 14.5, 48.2, 48.2	0.108	0.090
$[Ln(NCS)_4(OH_2)_4]^-$	13.1, 13.1, 51.0, 51.0	0.132	0.072
$[EuCl_2(OH_2)_6]^+$	12.0, 12.0, 43.5, 49.9	0.120	0.070
$[Gd(bzac)_4]^-$	9.9, 9.9, 44.6, 44.6	0.111	0.062
$U(acac)_4$	5.9, 5.9, 48.2, 48.2	0.133	0.046
Ideal SAP	0.0, 0.0, 52.4, 52.4	0.150	0.000

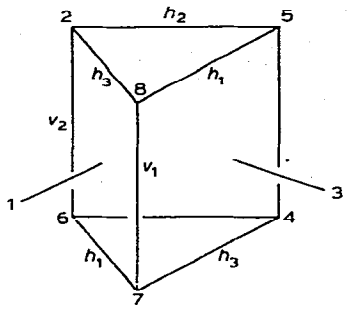

Fig. 15. The bicapped trigonal prism (C_{2v}). Values for edges in the MFP are

Edge	Symbol	Value
(13)	t	1.78
(26)(45)	v_2	1.25
(78)	v_1	1.50
(67)(58), (28)(47)	h_1, h_3	1.36
(25)(46)	h_2	1.13
(37)(38)(17)(18)	c_1	1.18
(35)(34)(12)(16)	c_2	1.21

are reflected in the Δ values for the molecules in Table 20. These represent distortion from three types of BCTP, (a) with D_{3h} symmetry, (b) with v_1 and v_2 independent but the three-fold axis otherwise maintained and (c) with just C_{2v} symmetry and the three-fold axis ignored. The fit to type (c) is very much lower for all molecules than the fit to types (a) and (b) which are similar to

TABLE 20

8 coordinate complexes with structures comparable to the BCTP

Compound	Ref.	Δ (Å) BCTP			δ angles			
		(a)	(b)	(c)				
$[UF_8]^{4-}$	[41]	0.116	0.106	0.058	0.0	36.3	44.6	45.9
$Ho(isonic)_3(OH_2)_2$	[194]	0.117	0.090	0.041	0.4	25.7	47.0	47.1
$V(S_2CCH_2Ph)_4$	[102]	0.155	0.140	0.054	4.9	30.4	45.3	45.6
$Nd(acac)_3(OH_2)_2$	[76]	0.144	0.120	0.068	5.7	26.5	40.0	45.8
$WMe_4[ON(Me)NO]_2$	[66]	0.156	0.126	0.046	6.0	27.0	47.6	48.0
$Y(acac)_3(OH_2)_2$	[74]	0.138	0.114	0.053	6.8	24.6	41.0	41.9
$Sc(thacox)_4$	[123]	0.163	0.129	0.043	9.3	20.7	42.4	46.7
$\alpha Ce(acac)_4$	[131]	0.165	0.129	0.046	9.4	19.7	42.1	43.0
$[Sc(trop)_4]^-$	[120,121]	0.135	0.122	0.061	13.2	30.1	42.3	44.0
$[Nb(trop)_4]^+$	[122]	0.167	0.136	0.063	18.9	20.8	40.6	45.1
$Mo(S_2CPh)_4$, Dod	[101]	0.209	0.191	0.107		(29.1)*4		
$Zr(acac)_4$, SAP	[115]	0.181	0.099	0.018	3.2	3.2	49.6	49.6

each other. For comparison values from an ideal Dod and SAP are given in the Table 20. As expected the Dod does not fit at all well to the C_{2v} model but the SAP Zr(acac)$_4$ does with a Δ value of only 0.018 Å.

From this set of Δ values, it is clear that the words 'trigonal prism' are not really suited to the coordination geometry unless it can be argued that the word 'bicapped' implies a large distortion of the trigonal prism, so large in fact that the three-fold axis is almost unrecognisable. It is only with the removal of the restrictions of trigonal symmetry that a good fit is obtained and this is to the basic C_{2v} model. One should always bear in mind that all SAP fit this C_{2v} model but the two geometries can always be distinguished by inter alia δ angles and differences between t and v_1.

From Table 20, the pathway between the SAP and BCTP is signposted. In the former t and v_1 are equal (as diagonals), as are c_1, v_2 and h_2 (as s edges) and c_2, h_1 (as l edges). As the BCTP is formed c_1, c_2 remain similar but t becomes much larger than v_1 which becomes an edge, v_2 increases but remains much less then v_1, and h_1 increases considerably while h_2 decreases. It is peculiar that h_1 and h_2, sides of triangles in the so-called trigonal prism, are more different than they are in a SAP when they become l and s edges.

The change from the BCTP to the Dod involves h_1 and h_3 edges becoming b and g edges respectively. It is interesting that many molecules of Table 20 have h_1 and h_3 edges different despite them being equal in the C_{2v} model. The other b edges are formed from v_1 and the diagonal across the uncapped quadrilateral face.

Some of the distortions from the BCTP towards the other two geometries are enhanced by the chelating pattern in the molecules (Fig. 16) particularly as only type 4 is consistent with C_{2v} symmetry. We have discussed that in types 3 and 4, the arrangement of the bidentate ligands in the two square faces is different and that this could lead to the folding of one square more

t	v_1	v_2	c_1	c_2	h_1	h_3	h_2	Structure type
1.81	1.39	1.26	1.19	1.16	1.36	1.36	1.18	—
1.78	1.50	1.24	1.18	1.18	1.31	1.31	1.22	—
1.80	1.47	1.27	1.18	1.22	1.36	1.32	1.09	(1)
1.76	1.52	1.24	1.19	1.19	1.35	1.27	1.17	(3)
1.80	1.52	1.24	1.20	1.20	1.34	1.31	1.14	(4)
1.77	1.51	1.25	1.18	1.20	1.35	1.26	1.17	(3)
1.76	1.55	1.24	1.19	1.23	1.33	1.30	1.13	(1)
1.75	1.55	1.18	1.18	1.22	1.39	1.29	1.20	(2)
1.77	1.43	1.25	1.16	1.21	1.37	1.34	1.15	(1)
1.77	1.56	1.24	1.18	1.21	1.38	1.23	1.16	(1)
1.80	1.46	1.26	1.18	1.23	1.46	1.27	1.10	(1)
1.71	1.68	1.18	1.20	1.21	1.29	1.24	1.22	(1)

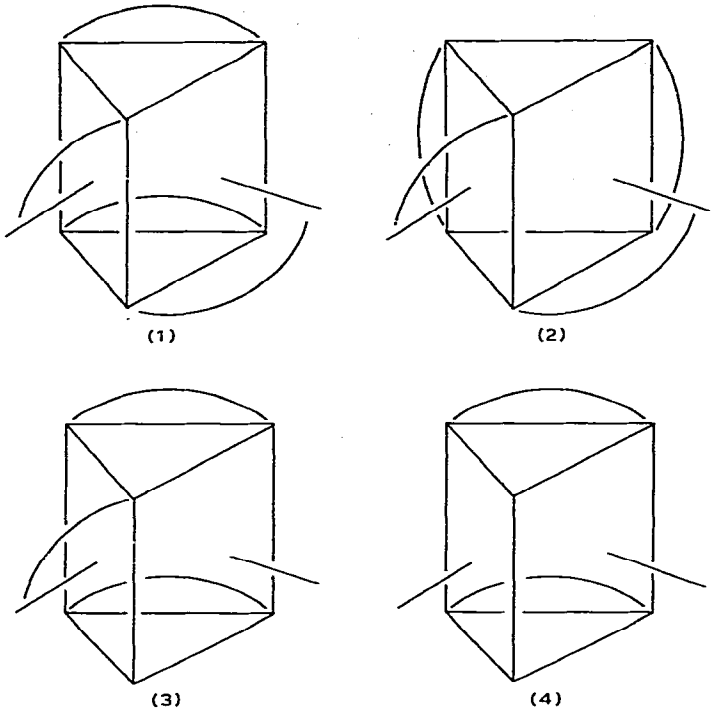

Fig. 16. Wrapping patterns in BCTP. (1) $h_2h_2c_1c_1$ [*mmmm* Dod, *ssss* SAP]; (2) $v_2v_2c_1c_1$ [*gggg*(D_2)Dod, *ssss* SAP]; (3) $h_2h_2c_1$ [*mmm* Dod, *sss* SAP]; (4) h_2h_2 [*mm* Dod, *ss* SAP].

than the other to give the BCTP. However for molecules of type 1 or 2, it is not obvious why one face in the SAP should fold more than another but it is clear that there are a number of examples where it does. Significantly the majority of examples of the BCTP contain chelating ligands but of the two monodentate examples $[UF_8]^{4-}$ has this geometry because of the ninth weakly bonded fluorine and $Ho(isonic)_3(OH_2)_2$ because of the polymeric chain formation.

There are more examples of molecules intermediate between the SAP and Dod that have D_2 than C_{2v} symmetry. However over half the examples in the first category listed in Table 19 have crystallographically imposed symmetry and thus it may be that packing effects favour the D_2 over the C_{2v} symmetry because for molecules with no imposed symmetry they are equally common.

In conclusion, we find that the BCTP is a distinct geometry and separate from the D_2 pathway. The name bicapped trigonal prism is unsuitable for this geometry but the name has become established and it is not worth changing. However the polyhedron should be considered to have C_{2v} symmetry with not even an approximate threefold axis. Shape characteristics of a MFP

can be abstracted from Table 20 as t 1.78, v_1 1.50, v_2 1.25, c_1 1.18, c_2 1.21, h_1 1.36, h_2 1.13; rather different from $c_1 = c_2 = h_1 = h_2 = 1.16$, $v_1 = v_2 = 1.49$ in the D_{3h} HSM [7].

(v) Orgel's rule

In 1960 Orgel [57] proposed that in dodecahedral molecules of type MX_4Y_4, the X and Y donor atoms would be distributed among the A and B sites of the polyhedron in such a manner as to facilitate d_π—p_π interactions. Thus the partially or completely filled metal d_{xy} (or $d_{x^2-y^2}$ dependent upon the coordinate system) is of appropriate symmetry for d_π—p_π overlap with π acceptor ligands in B sites. However for complexes of d^0 ions, π donor ligands should occupy the B sites so as to facilitate p_π—d_π interactions involving the vacant d_{xy} orbitals. To examine Orgel's rule, all 8 coordinate structures with two sets of donor atoms have been collected together and are listed in Table 21.

Only two of these structures are incompatible with Orgel's rule $[Mo(diars)_2Cl_4]^+$ and $Ti(demtc)_4$. The former containing a d^1 metal has an identical structure to the d^0 Ti, Nb, Ta analogues, but this is not really surprising because of the excellent steric freedom obtained in the Dod with 2 *a* edges occupied by diars. Clearly in this rather crowded molecule, steric considerations would override any electronic effect. This is not the case however for $Ti(demtc)_4$ where there are two oxygen and two sulphur atoms in A and B sites. It is possible that there could be weak S···S interactions which lead to this geometry but even so it does throw considerable doubt on the validity of Orgel's rule.

Of the molecules compatible with Orgel's rule, the d^0 $[M(diars)_2Cl_4]$ series and $MoH_4(PMe_2Ph)_4$ are crowded molecules in which steric effects predominate and cannot be used as evidence in favour. However in $Mo(CN)_4(CNR)_4$, steric effects are not important and the distribution of —CN in A and —CNR

TABLE 21

Distribution of donor atoms in MX_4Y_4 dodecahedra

Compound	Ref.	Electron configuration	Structure
$Zr(Netsal)_4$	[136]	d^0	Dod *gggg*(S_4), O in B, N in A
$Zr(8\text{-quin})_4$	[132]	d^0	Dod *gggg*(D_2), O in B, N in A
$Ti(demtc)_4$	[104]	d^0	Dod *mmmm*, mixed
$Ti(diars)_2Cl_4$	[58]	d^0	Dod *aa*, As in A, Cl in B
$[Mo(diars)_2Cl_4]^+$	[59]	d^1	Dod *aa*, As in A, Cl in B
$[M(diars)_2Cl_4]^+$ [M = Nb, Ta]	[61,60]	d^0	Dod *aa*, As in A, Cl in B
$Mo(CN)_4(CNMe)_4$	[43,44]	d^2	Dod, —CN in A, —CNR in B
$MoH_4(PMe_2Ph)_4$	[42]	d^2	Dod, H in A, P in B
$[Ln(NCS)_4(OH_2)_4]^-$	[45,46]	—	SAP; (as Dod, O in A, N in B)
$M(hfap)_4$, M = Th, U	[93]	—	Dod *mmmm*, mixed

in B sites is consistent and indeed the Mo—CNR bonds are shorter than Mo—CN bonds presumably due to increased π bonding to the B sites.

$W(8quinBr)_4$ is a particularly interesting molecule in this context. It is a d^2 complex and therefore might be expected to have oxygen in A sites and nitrogen in B sites which it does with the *mmmm* Dod structure. However the shape of the ligand is such that it would be impossible for this molecule or the comparable d^0 Zr or Ti complexes to have the reverse arrangement in the *mmmm* isomer with oxygen in B and nitrogen in A sites because of contacts over the *a* edges. The only way to comply with Orgel's rule for a d^0 complex is to switch to the energetically less favourable *gggg* isomers and this is what occurs in $Zr(Netsal)_4$ and $Zr(8\text{-quin})_4$.

In Table 21, two *f* electron compounds are included for comparison. There are not really enough examples to check on Orgel's rule completely but the evidence is just in favour of it being valid.

D. NINE-COORDINATION

The packing of nine ligands around a metal requires a significantly greater metal size than for eight and examples are restricted with the exception of $[ReH_9]^{2-}$ to lanthanides and actinides. The majority of 9 coordination complexes are polymeric rather than monomeric because the lanthanide ions Ln^{3+} only require a small number of ligands to achieve electronic satisfaction but a greater number to complete the large coordination sphere. Also against monomeric structures is the compactness of the coordination sphere as only the simplest type of bidentate ligand can be fitted in without excessive crowding.

(i) Characteristics of the ideal polyhedra

Structures of 9 coordination complexes are always described in terms of the tricapped trigonal prism (TCTP) or the capped square antiprism (CSAP). The differences between the two geometries though small are easily recognisable. Guggenberger and Muetterties [16] used eqn. (2) for ML_9 molecules and found a minimum for the TCTP with all values of n but were unable to find any evidence for any CSAP minimum. However the calculated energy barrier between the two is less than 0.1% of the total energy of either form.

(a) Capped square antiprism. In the CSAP (symmetry C_{4v}), an atom caps a square face of the 8 coordinate SAP. This capped face is spread out to accommodate the newcomer so that the angle made by the M—L bonds with the unique axis is increased from 54—59° found in the SAP to ca. 70°. The uncapped face is slightly contracted ($\theta \approx 53°$). The CSAP is shown in Fig. 17 together with the shape characteristics for the HSM calculated [16] using $n = 6$ in eqn. 2. There are three different sites and four types of edge of which all but s_1 are suitable to take chelate bites.

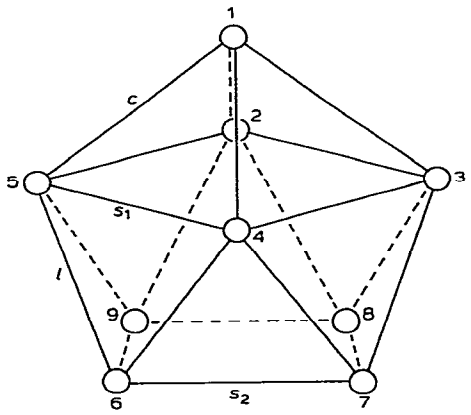

Fig. 17. The capped square antiprism (C_{4v})

	Values in	
	HSM	$[ThF_8]^{4-}$
4*c* edges	1.13	1.13
8*l* edges	1.17	1.18
$4s_1$ edges	1.32	1.32
$4s_2$ edges	1.13	1.15

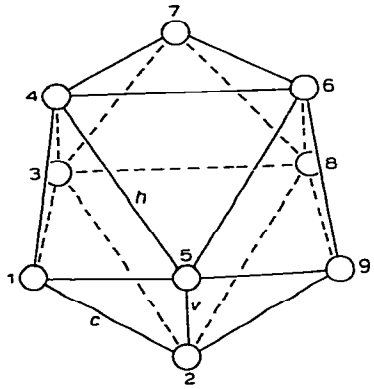

Fig. 18. The tricapped trigonal prism (D_{3h}).

	Values in		
	HSM	$[ReH_9]^{2-}$	
3*v* edges	1.42	1.43	1.37
6*h* edges	1.22	1.21	1.26
12*c* edges	1.14	1.14	1.13

(b) Tricapped trigonal prism. In the TCTP (symmetry D_{3h}), the three quadrilateral faces of the trigonal prism are all capped. The geometric features of the TCTP are shown in Fig. 18. There are only two types of atom site, three capping atoms L_c and six prism atoms L_p and three unique edges of which only the *h* and *c* edges are suitable for small chelate bites.

It is interesting to follow the changes in the shape of the 6 coordinate trigonal prism as successive quadrilateral faces are capped to give the 7 coordinate monocapped, 8 coordinate bicapped and 9 coordinate tricapped trigonal prisms. In the 6 coordinate trigonal prism, the *h* and *v* edges are equivalent at 1.30 [201]. When one face is capped, *c* is 1.28, *v* and *h* values in the capped face are 1.30 and 1.48 and in the uncapped faces 1.20 and 1.23 respectively [7]. When two faces are capped in the BCTP, *c* is reduced to 1.20 and v_1, v_2, h_1 and h_2 are 1.50, 1.25, 1.36 and 1.13 respectively (Fig. 15). In the TCTP *c* is reduced still further to become the shortest edge at 1.14 and *h* at 1.22 becomes much less than *v* 1.42. Thus the smallest edge changes from *v* in the 7 coordinate to *h* in the 8 coordinate and to *c* in the 9 coordinate polyhedron.

(ii) Reaction pathways between the ideal polyhedra

The C_{2v} reaction path between the TCTP and CSAP is shown in Fig. 19; it involves the stretching of the 68 edge in the TCTP. While Fig. 19 shows just one pathway it is obvious that any of the three capping atoms of the TCTP can become the capping atom in the CSAP and that in the CSAP either pair of atoms opposite to each other in the uncapped face can join the capping

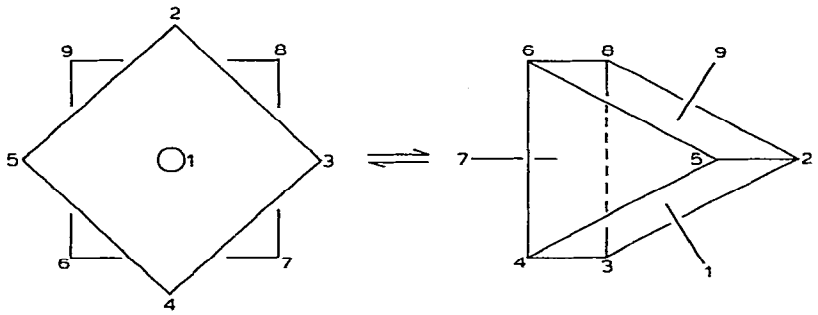

Fig. 19. The reaction path between the TCTP and CSAP. Shape characteristics

δ angle	Values in	
	• $[ReH_9]^{2-}$	CSAP
9(68)7	25.8, 29.1	0.0
1(25)9, 1(34)7	25.8, 29.1	37.4
1(23)8, 1(45)6	47.5, 47.2	37.4
9(28)3, 9(56)4	47.5, 47.2	51.6
7(46)5, 7(38)2	47.5, 47.2	51.6

atom as the three capping atoms in the TCTP. There are several types of δ angles that can be used to monitor this pathway. We have chosen the first five angles * of Fig. 19 as these are particularly sensitive to changes between the two ideal geometries. Values from $[ReH_9]^{2-}$ and $[ThF_8]^{4-}$ that are quoted are representative of many structures but the only requirements from symmetry are that particular angles are equivalent or in the case of the 9(68)7 angle in the CSAP equal to 0°.

Guggenberger and Muetterties [16] looked at both monomeric and polymeric ML_9 and M_9 complexes but were unable to find any examples of this reaction path. Indeed nearly all the ML_9 and all the M_9 complexes had the TCTP geometry. Other rearrangement processes from the TCTP were considered but no evidence for them was found. In this review a wider range of 9 coordinate compounds has been considered and several that contain polydentate ligands have geometries intermediate between the two ideal forms. However the small bidentate bites which such compounds often have make the geometry distorted off the pathway.

It is even more necessary, than with 8 coordinate complexes, to consider compounds with equivalent types of polydentate ligands together and this is done in section (iii). Only $M(L—L)_3L_3$, $M(L—L—L)_3$ $M(L—L)_4$ and $M(L—L)_2L_5$ are at all common. There is a much smaller range of ligands than in 8 coordination, only nitrate being regularly found. It was noted that polymeric examples in which atoms did not directly bridge two metals have similar geometries to monomers and these are therefore included under the appropriate ligand type whenever possible.

The δ angle approach was much less useful than for the 8 coordinate compounds, not only because of the large number of equivalent sets of angles that could be considered but also because of the large number of compounds that contain small chelate bites and therefore are highly distorted from ideal. The Δ values were much more use in deciding upon a geometry for such compounds.

(iii) Structures of nine-coordinate complexes

(a) ML_9 molecules. Structures of ML_9 complexes with TCTP geometry are listed in Table 22 together with their shape characteristics. This geometry is also found in a number of polymeric fluorides and metal clusters [16].

The two $[ReH_9]^{2-}$ anions in the asymmetric unit have imposed D_{3h} symmetry but exhibit interesting variations both in bond lengths and in the lengths of the edges, the difference between v and h being 0.22 and 0.12 respectively. In one anion $M—L_c > M—L_p$ and in the other the reverse is true.

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* A different set of δ angles has been proposed [16] but in a radical departure from the type chosen for lower coordination number, these are for the most part between triangular faces that do not share an edge (i.e. the angle between the two triangular faces of the prism in the TCTP) and such angles were found to be less useful than the present set.

TABLE 22

Structures of ML_9 complexes with TCTP geometry

Compound	Ref.	Δ (Å)		*v*	*h*	*c*	M—L_c	M—L_p	δ angles
		TCTP	CSAP						
$[ReH_9]^{2-}$	[202]	0.000	0.093	1.43	1.21	1.14	1.72	1.67	25.8, 25.8, 25.8, 47.5, 47.5
$[ReH_9]^{2-}$	[202]	0.000	0.096	1.38	1.26	1.13	1.62	1.70	29.2, 29.2, 29.2, 47.2, 47.2
$[M(OH_2)_9]^{3+}(C_2H_5SO_4)_3$									
M = Pr	[203]	0.040	0.115	1.41	1.23	1.09, 1.18	2.59	2.47	27.0, 27.0, 27.0, 47.7, 47.7
M = Yb	[203]	0.034	0.100	1.41	1.23	1.09, 1.18	2.52	2.32	26.8, 26.8, 26.8, 47.7, 47.7
M = Ho	[204]	0.037	0.106	1.42	1.22	1.09, 1.19	2.51	2.39	26.6, 26.6, 26.6, 45.6, 45.6
$[M(OH_2)_9]^{3+}(BrO_3)_3$									
M = Pr	[203]	0.000	0.098	1.35	1.27	1.12	2.52	2.49	24.3, 24.3, 24.3, 47.0, 47.0
M = Yb	[203]	0.000	0.100	1.35	1.28	1.12	2.43	2.32	24.7, 24.7, 24.7, 46.9, 46.9
$[Nd(OH_2)_9]^{3+}$	[207] [a]								
$Ln[Fe(CN)_6]$, $5H_2O$	[205]	0.005	0.094	1.41	1.23	1.13	2.59	2.61	27.4, 27.4, 27.4, 48.0, 48.0
$La_2(SO_4)_3$, $9H_2O$	[55]	0.027	0.101	1.46	1.18	1.10, 1.19	2.51	2.56	23.6, 23.6, 23.6, 48.1, 48.1
$Dy(NCS)_3(OH_2)_6$	[209]	0.079	0.130	1.28	1.32	1.08	various		25.4, 32.6, 33.3, 44.3, 47.1

[a] Unpublished coordinates.

The $[M(OH_2)_9]^{3+}$ ions fall into three distinct groups dependent upon the anion. A series of isomorphous structures with different lanthanide metals have been determined with both $[BrO_3]^-$ and $[C_2H_5SO_3]^-$ as the anion. The bromates have imposed D_{3h} symmetry but the ethylsulphates only C_{3h} symmetry with two types of *c* edges. It is thought that the lower symmetry for the ethylsulphates may arise from hydrogen bonding.

The shape characteristics of the two types are independent of bond length but are different from each other. The ethyl sulphates have $v = 1.41$, $h = 1.23$, $c = 1.09, 1.18$ and the bromates $v = 1.35$, $h = 1.27$, $c = 1.12$. The normalisation of the polyhedra masks some interesting variations in bond lengths found in the Pr and Yb compounds [203]. The difference in $M—O_p$ bond lengths is about the 0.155 Å expected from the lanthanide contraction but that in $M—O_c$ bonds is only 0.08 Å, the $Yb—O_c$ bonds being longer than expected. It is suggested that this elongation is necessary in order to increase O···O contacts over the *c* edges which are of course dependent upon metal size. The same pattern is observed in $M(OH)_3$ compounds [206] with $M—O_c$, $M—O_p$ ranging linearly from 2.551, 2.588 Å with M = La to 2.442, 2.409 Å with M = Y respectively.

$[Nd(OH_2)_9]^{3+}$ occurs in a unit cell with chloride ions, isotropine and water molecules and its geometry was described as intermediate between the TCTP and the CSAP. The coordination sphere of Ln in $Ln[Fe(CN)_6]5H_2O$ has C_{3h} symmetry, with three waters in capping positions and six nitrogen atoms in prismatic positions.

In polymeric $La_2(SO_4)_3 9\ H_2O$, there are 9 and 12 coordinate polyhedra. In the former, the metal is bonded to six water molecules in prism sites and three oxygen atoms from bridging sulphates in capping sites. The symmetry is reduced to C_{3h} with two unique *c* edges 1.10 and 1.19. $Dy(NCS)_3(OH_2)_6$ is distorted from the TCTP towards the CSAP as shown by one of the three δ angles over *v* edges being less than the other two. The thiocyanate ligands are distributed over both types of site. The shape characteristics of this polyhedron are unusual as $v < h$.

There is therefore a much wider range of shapes for the TCTP in ML_9 complexes than for the Dod and SAP in ML_8 complexes. Some correlation between shape and metal size has emerged for the $[M(OH_2)_9]^{3+}$ series but even so relative values of *h* and *v* remain unpredictable. The TCTP polyhedra are usually quite regular though this could be a packing effect as the only two molecules without imposed symmetry are distorted towards the CSAP. The only other type of distortion found is the rotation of the L_c atoms with respect to the prism while maintaining C_{3h} symmetry. This is quite distinct from distortion towards the CSAP.

There are no examples of CSAP among ML_9 monomers with identical ligands. There are however a number of complex fluorides with this geometry [16] but these have extensive internal constraints in the form of edge and/or face sharing. Only one example therefore $[ThF_8]^{4-}$ has been included in Table 23 together with $Pr(NCS)_3(OH_2)_6$ and $[LaCl(OH_2)_7]_2$. This latter centrosymme-

TABLE 23

Structures of ML_9 complexes with CSAP geometry

Compound	Ref.	Δ (Å)		c	l	s_1	s_2	δ angles
		TCTP	CSAP					
$[ThF_8]^{4-}$	[208]	0.108	0.074	1.13	1.18	1.32	1.15	5.1, 25.2, 45.7, 36.3, 45.6
$Pr(NCS)_3(OH_2)_6$	[209] [a]	0.160	0.111	1.11	1.24	1.30	1.06	0.6, 36.1, 38.6, 42.2, 50.1
$[LaCl(OH_2)_7]_2$	[210]	0.107	0.034	1.14	1.17	1.32	1.13	0.5, 34.2, 38.0, 34.7, 42.0

[a] No angle was quoted for the monoclinic unit cell. 90° was assumed.

tric dichloro-bridged dimer is the best CSAP. The two chlorine atoms occupy an *l* edge. The shape of $[ThF_8]^{4-}$ is very similar to this but is more highly distorted due no doubt to its polymeric form and cation···F interactions. $Pr(NCS)_3(OH_2)_6$ is not isomorphous with the Dy analogue and its geometry was said to be closer to a CSAP than to a TCTP. The shapes of the CSAP are more regular than those of the TCTP though this could change when more examples are forthcoming. It is apparent that δ angles are a good test of the two ideal forms and of the pathway between them, although values of alternative sets of angles should always be considered. Δ values take into account the complete polyhedron and therefore indicate when δ angles are unrepresentative.

(b) Molecules of the form M(unidentate)$_3$(bidentate)$_3$. All $M(L{-}L)_3L_3$ monomers (Table 24) contain lanthanide metals and nitrate ligands with a variety of monodentate ligands such as dmso, tmu and urea. All bar one have an equivalent structure [(1) in Fig. 20]. Polymeric structures (Table 25) with more varied constituent ligands have a wider range of structures.

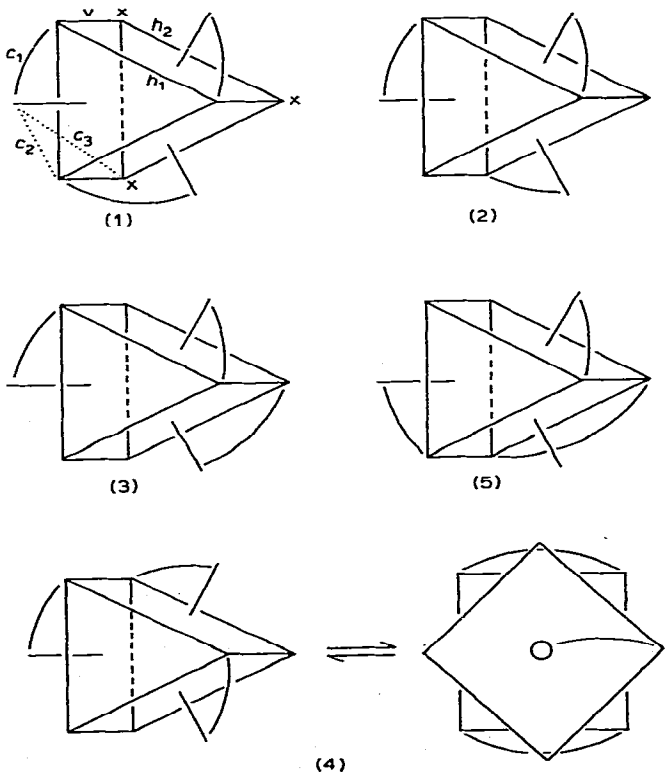


Fig. 20. Structures of $M(L{-}L)_3L_3$ complexes.

TABLE 24

Structures of $M(L—L)_3L_3$ monomeric complexes

Compound	Ref.	Structure type	Δ (Å)		υ	h_1	h_2
			TCTP	CSAP			
$Lu(dmso)_3(NO_3)_3$	[211]	(1)	0.148	0.181	1.35	1.21	1.33
$Er(dmso)_3(NO_3)_3$	[212]	(1)	0.147	0.183	1.40	1.22	1.29
$Yb(dmso)_3(NO_3)_3$	[213]	(1)	0.152	0.211	1.36	1.25	1.34
$Nd(atp)_3(NO_3)_3$	[214]	(1)	0.168	0.214	1.35	1.22	1.34
$Eu(tmu)_3(NO_3)_3$	[215]	(3)	0.154	0.202	1.35	—	—

Structure (1) is best considered as a distorted TCTP with C_3 symmetry in which three monodentate ligands X occupy one triangular face and the three bidentate ligands (L—L) span c edges between capping atoms and the other triangular face. As shown by calculation [16] and the ML_9 molecules, this c edge is the shortest in the TCTP. Shape characteristics for this polyhedron found in the three isomorphous $M(dmso)_3(NO_3)_3$ molecules and $Nd(atp)_3(NO_3)_3$ are given in Table 24. There are high Δ values from the D_{3h} polyhedron because the small nitrate bite over just three of the 12 c edges distorts the geometry from ideal but not towards the CSAP. For the nitrate $M—O_c > M—O_p$, the difference being greater with the smaller metals Lu and Yb. Bond lengths to the monodentate ligand are much shorter. There are six independent edges in the C_3 polyhedron and values are similar in the four molecules. As expected the triangular face occupied by monodentate ligands is larger ($h_2 > h_1$) and further from the capping atoms ($c_3 > c_2$) than the other occupied by oxygen atoms of the nitrate groups. An alternative way of looking at the polyhedron is to consider the nitrate as a monodentate ligand and to calculate the geometry from the three nitrogen positions and the three 'real' monodentate ligands. If this is done then a distorted octahedron is obtained.

The odd one out of the monomeric structures is $Eu(tmu)_3(NO_3)_3$ in which the three monodentate ligands do not occupy a triangle though all three bites occupy c edges. There are three isomers consistent with this description namely (2), (3) and (4) in Fig. 19. The present compound has structure (3) in which the monodentate ligands are closest together. As in the other $M(NO_3)_3L_3$ compounds there is a large Δ value from the TCTP but the distortion caused by the small bites takes the polyhedron no closer to the CSAP.

There are a wide variety of polymeric structures (Table 25). Despite $Er(ac)_3$, 4 H_2O being a dimer in which two oxygen atoms bridge metals, it has the common monomeric structure (1). $[Ce(ac)_5]^{2-}$ contains three bidentate ac ligands and has structure (3) but unlike $Eu(tmu)_3(NO_3)_3$ it is distorted towards the CSAP. It is interesting that all compounds both monomeric and polymeric in which the values of z for all three bites are less than 0.90 have

c_1	c_2	c_3	M—X	M—L_c	M—L_p	δ angles				
0.89	1.15	1.22	2.28	2.53	2.39	30.3	30.7	31.2	38.6	55.0
0.91	1.16	1.21	2.27	2.52	2.42	22.8	27.0	37.0	40.8	54.9
0.85	1.19	1.22	2.24	2.44	2.41	26.1	30.6	36.0	37.1	54.5
0.84	1.15	1.24	2.35	2.56	2.53	28.1	29.1	35.3	39.3	51.1
0.86	—	—	2.33	2.53	2.48	24.6	33.4	38.8	39.9	56.9

structures (1) or (3): and that compounds with larger bites have different structures.

The next four compounds in Table 25 have three bites of ca. 1.05, not that much smaller than the calculated value for the *c* edge. It seems unlikely that such molecules would have structure (1) because the three ligands are too large to occupy the triangular face and in fact they have either structure (2) or (4). In all four cases the values are much lower than for the nitrate complexes. All geometries are distorted between the two ideal polyhedra as shown by the δ angles, but only $Gd(glycollate)_3$ is closest to the CSAP. The pathway between the two ideal geometries is shown for structure (4) in Fig. 20. In the CSAP which has C_s symmetry, the *c*, s_2, s_2 edges are occupied by the bidentate ligands.

$Eu_2(malonate)_3$, 8 H_2O is a most interesting structure because it contains three chelates with z = 0.82, 0.82, 1.18 from four- and five-membered rings respectively. The two small bites occupy the *c* edges to the same trigonal face as expected but the large 1.18 bite, clearly too large for the *c* edge, occupies an *h* edge to give structure (5) with C_s symmetry. There are several other isomers for $M(L—L)_3L_3$ with this edge occupied but it is expected that this structure is rare and that other $M(L—L)_3L_3$ molecules will have structures (1) and (3) for bites $z < 0.90$ and (2) and (4) for z ca. 1.05.

Another rarity is $Eu(fod)_3$. $Co(acac)_3$ a molecule with imposed C_3 symmetry [216]. The Eu atom is 9 coordinate with the TCTP geometry; it is bonded to three bidentate fod ligands (z = 1.14) which occupy *c* edges to one triangular face as in structure (1). The other triangular face, occupied by three oxygens from different acac ligands is shared with the Co octahedron.

(c) Molecules of the form M(unidentate)(bidentate)$_4$. Just as the $M(L—L)_3L_3$ stoichiometry suits the M^{3+} lanthanide ion together with L and $(L—L)^-$, so $M(L—L)_4L$ suits the M^{4+} actinide ions with L and $(L—L)^-$. Examples given in Table 26 contain bites of 1.04—1.13 because with smaller ligands such as nitrate a higher coordination number would be found. Geometries are relatively close to one or both of the ideal forms; there are just seven geometric

TABLE 25

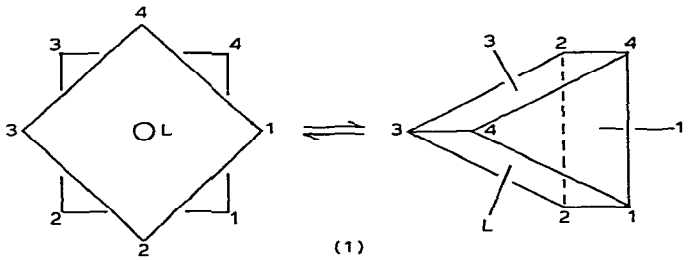
$M(L{-}L)_3L_3$ polymeric structures

Compound	Ref.	Structure type	z			Δ (Å)		δ angles				
						TCTP	CSAP					
$Er(ac)_3 4H_2O$	[217]	(1)	0.84	0.89	0.89	0.150	0.164	19.4	33.1	38.7	37.0	54.8
$[Ce(ac)_5]^{2-}$	[223]	(3)	0.81	0.85	0.85	0.203	0.176	5.7	31.4	54.1	34.1	47.4
$Eu(glycollate)_3$	[218]	(2)	1.04	1.08	1.08	0.070	0.098	19.5	33.0	33.4	44.7	46.1
$Gd(glycollate)_3$	[219,220]	(4)	1.06	1.06	1.07	0.091	0.062	8.6	36.9	38.9	36.8	45.6
$M_2(ox)_3, 10.5H_2O$												
M = Nd	[221]	(2)	1.05	1.07	1.07	0.080	0.094	20.1	27.4	36.6	37.4	50.9
M = Ln [a]	[222]	(2)	1.05	1.06	1.08	0.084	0.105	23.7	23.9	37.7	37.7	51.4
$Eu_2(malonate)_3 8H_2O$	[189]	(5)	0.82	0.82	1.18	0.136	0.159	23.4	23.4	46.5	46.5	50.3

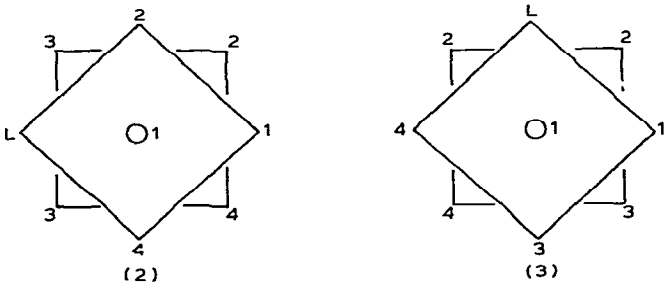
[a] M = Ce, Pr, Nd also in ref. [222].

isomers for $M(L{-}L)_4L$ complexes in the CSAP if the s_1 edge (calculated at 1.32) is considered unsuitable for a bidentate ligand. Three of these seven isomers (Fig. 21) have been found in structures. These CSAP are often distorted towards the TCTP and reaction paths for three of the isomers are shown in Fig. 21.

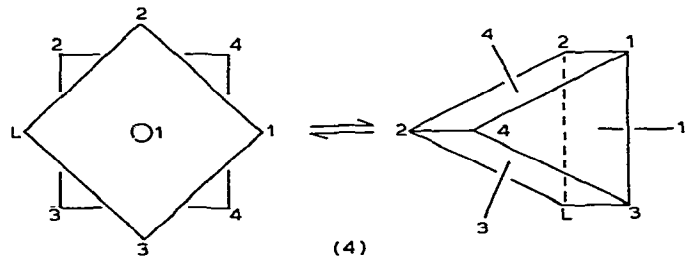
Three monomers have structure (4) with C_s symmetry. Only $Th(tta)_4(topo)$ is on the TCTP side of the pathway and this could be because of its large bite (z = 1.12). In this molecule the three δ angles over the v edges are 17.2,



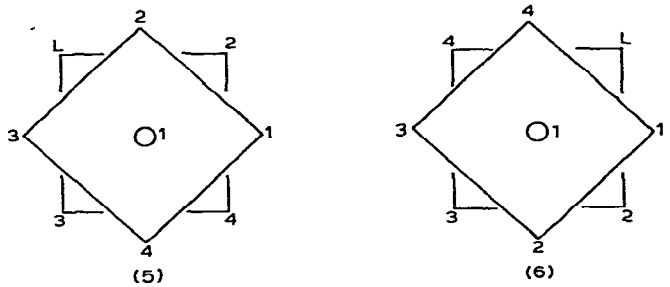
(1)



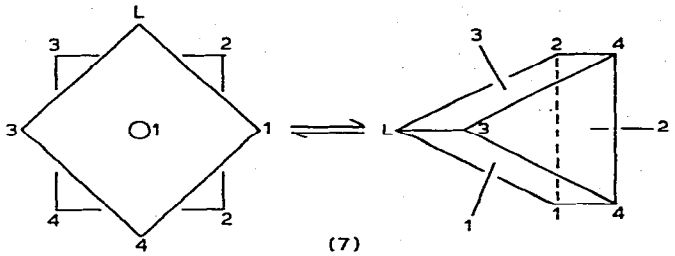
(2) (3)



(4)



(5) (6)



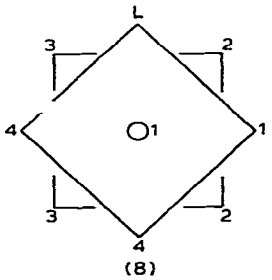


Fig. 21. Structures of M(L—L)$_4$L complexes. Monodentate ligand is L, bidentate ligands are (11), (22), (33), (44), (1) is *llll*, (2), (3), (4), (7) are *clls*$_2$, and (5), (6) are *clll* isomers of the CSAP. (8) is a *cs*$_1$*s*$_2$*s*$_2$ isomer.

TABLE 26

Structures of M(L—L)$_4$L complexes

Compound	Ref.	Δ (Å)		z	δ angles				
		TCTP	CSAP						
Th(trop)$_4$(dmf)	[18]	0.118	0.103	1.04	6.6	29.2	38.9	32.7	45.9
Sr(diacetamide)$_4$(OH$_2$)	[224]	0.121	0.058	1.08	0.0	33.9	33.9	40.9	40.9
Th(ttbd)$_4$(topo)	[225]	0.063	0.078	1.12	17.2	21.8	34.4	45.4	44.0
Th(γtrop)$_4$(OH$_2$)	[226]	0.115	0.118	1.04	13.1	25.1	35.1	33.7	51.7
Th(trop)$_4$(OH$_2$)	[227]	0.178	0.129	1.04	13.0	11.0	57.3	36.6	45.4
Th(8quin)$_4$(dmso)	[228] [b]								
[Ph(phen)$_4$(ClO$_4$)]$^+$	[229] [b]								
M(Hox)(ox), 3H$_2$O									
M = Er	[230]	0.125	0.050	1.11	2.5	35.7	35.7	39.5	39.5
M = Y	[231, 232]								
[Y(ox)$_2$(OH$_2$)]$^-$	[233]	0.052	0.068	1.13	15.4	27.3	27.3	44.7	44.7

[a] For TCTP *v*, *h*, *c* and for CSAP *c*, *l*, *s*$_1$, *s*$_2$ in that order. [b] Unpublished coordinates.

21.8 and 34.4°. Now three possible CSAP can be derived from a TCTP dependent upon which of the three capping atoms is chosen as the capping atom in the C_{4v} polyhedron. δ angles over the v edge in the TCTP become angles over the diagonal of the CSAP. Therefore the most appropriate choice is that corresponding to the smallest δ angle. This is confirmed by Δ values of 0.078, 0.097 and 0.139 Å for the CSAP with δ angles 17.2, 21.8 and 34.4° respectively. Another factor which may distort $Th(tta)_4(topo)$ rather more than $Th(trop)_4(dmf)$ and $Sr(acetamide)_4(OH_2)$ is the strength and bulkiness of the monodentate ligand.

The two $Th(trop)_4(OH_2)$ molecules have different geometries. The first has structure (7) and is intermediate between the two ideal geometries as shown by Δ values and δ angles. The second has a most surprising structure [(8) in Fig. 21] in which an s_1 edge is occupied by one of the bidentate trop ligands. The molecule is highly distorted by this and indeed the s_1 edge opposite to that occupied by the chelate increases to 1.53. The capping atom is much closer to the atom from the same chelate (1.05) and to L (1.01) than to the two atoms of the chelate (1.21). As shown by the variety of δ angles this molecule is not distorted towards the TCTP. From a diagram in the paper, it is possible that $Th(8quin)_4(OH_2)$ also has s_1 edges filled by chelates and has the C_2 $s_1s_1s_2s_2$ structure. If the s_1 edge is considered suitable for the bidentate ligand, then the number of isomers for $M(L—L)_4L$ compounds increases to 14. However it is expected that these edges will be only rarely occupied and the additional seven isomers have not been shown in Fig. 21. They consist of one $s_1s_1s_2s_2$, lls_1s_2, $cs_1s_2s_2$ and four cs_1s_2l structures.

It is perhaps surprising that structure (1) ($llll$) is not found in monomers. This is analogous to the fact that very few $M(L—L)_3L$ molecules have the

M—X	$M—L_c$	Other M—L	Structure type	Shape characteristics [a]
2.52	2.49	2.45	(4)	1.14, 1.17, 1.33, 1.14
2.60	2.69	2.61	(4)	1.15, 1.17, 1.32, 1.13
2.30	2.47	2.42	(4)	1.45, 1.20, 1.14
2.57	2.42	2.39—2.56	(7)	1.45, 1.20, 1.15
2.61	2.50	2.36—2.49	(8)	see text
2.47	2.47	2.34—2.43	(1)	1.14, 1.17, 1.32, 1.13
2.34	2.34	2.38—2.41	(1)	1.47, 1.18, 1.15

C_3 structure in which the unidentate ligand occupies the unique position of a capped octahedron [8]. However two polymers have this structure. Both contain bridging oxalate ligands but no sharing of oxygen atoms by metals. The first has an almost ideal CSAP geometry but the second $[Y(ox)_2(OH_2)]^-$ is distorted along a C_2 pathway towards the TCTP. These examples bring to mind that $[Ti(ox)_2]^-$ is one of only two complexes with the 8 coordinate *llll* structure and also contains bridging oxalates. In both polymers the imposed symmetry and formation of chains may dictate the choice of isomer.

While there are not enough examples of $M(L—L)_4L$ compounds to draw definite conclusions about preferred structures, it can be noted that all monomers have a *c* edge occupied by a chelate and contain the unidentate ligand in the capped face. Structure (4) is the most popular arrangement. A number of molecules are considerably distorted from the CSAP towards the TCTP in a manner that suggests the existence of a reaction pathway. Certainly the distortions are not due to small *z* as values therein are not much less than those calculated for *c*, *l* and s_2 edges in the CSAP.

(d) Molecules of the form M(tridentate)$_3$. All the $M(L—L—L)_3$ molecules have essentially the same structure in which the planar tridentate ligands are equivalent. The central donor atom occupies the capping position and the outer donor atoms occupy opposite sites in the capped quadrilateral face (Fig. 22). Details of the structures which include several different tridentate ligands such as dipic, glycollate, terpy and oxyd are given in Table 27. *z* ranges from 1.02—1.08 and six *c* edges are therefore shorter than the other twelve (ca. 1.20). This introduces large deviations from D_{3h} symmetry. A number of the molecules have imposed symmetry which precludes any distortion towards the CSAP. It is noticeable that the majority of molecules not restrained in this way have geometries that are distorted towards the CSAP, the most striking example being the monoclinic form of $[Yb(dipic)_3]^{3-}$. Bond lengths are usually regular with the capping atom slightly further from the metal atom than the others. An exception is $[Nd(dipic)_3]^{3-}$ which contains a wide range of bond lengths. In some molecules bond lengthening can be related to hydrogen bonding.

There is one polymeric structure of this type, $Er_2(oxyd)_3$, 6 H_2O which contains both 8 and 9 coordinate Er, the latter being an $Er(oxyd)_3$ moiety

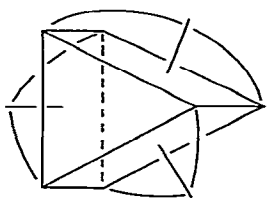


Fig. 22. The structure of $M(L—L—L)_3$ complexes.

TABLE 27

Structures of $M(L{-}L{-}L)_3$ complexes

Compound	Ref.	Δ (Å)		$M{-}L_c$	$M{-}L_p$	δ angles					z
		TCTP	CSAP								
$[Yb(dipic)_3]^{3-}$ orthorhombic	[234]	0.060	0.110	2.38	2.33	23.8	29.4	29.4	46.6	46.6	1.08
$[Yb(dipic)_3]^{3-}$ hexagonal	[235]	0.067	0.129	2.43	2.38	28.0	28.0	28.0	47.7	47.7	1.07
$[Yb(dipic)_3]^{3-}$ monoclinic	[236]	0.087	0.096	2.51	2.37	13.5	34.1	35.1	43.3	47.1	1.08
$[Nd(dipic)_3]^{3-}$ triclinic	[237]	0.117	0.176	2.60	2.49	22.8	23.8	29.4	46.3	51.0	1.05
$[Nd(diglycollate)_3]^{3-}$, also Yb	[238]	0.064	0.140	2.52	2.43	33.7	33.7	33.7	46.5	46.5	1.05
$[Ce(oxyd)_3]^{3-}$	[239]	0.100	0.174	2.58	2.48	24.7	32.7	34.7	42.2	46.7	1.02
$[Ce(oxyd)_3]^{3-}$	[240]	0.103	0.127	2.56	2.47	27.5	27.5	27.5	48.0	48.0	1.02
$[U(dipic)_3]^{2-}$	[241] [a]			2.52	2.40						
$[Eu(terpy)_3]^{3+}$	[242] [a]										
$Er_2(oxyd)_3 6H_2O$	[190]	0.088	0.133	2.49	2.34	19.1	32.7	32.7	45.9	45.9	1.04

[a] Unpublished coordinates.

TABLE 28

Structures of $M(L{-}L)_2L_5$ polymeric complexes

Compound	Ref.	Structure type	Δ (Å)		δ angles
			TCTP	CSAP	
$Nd_2(maleate)_2(fumarate), 12H_2O$ [a]	[243]	(1)	0.145	0.139	25.8, 27.0, 29.5, 47.5, 36.3
$Ce(ac)_3 0.7H_2O$	[244]	(2)	0.185	0.197	11.8, 32.2, 45.7, 13.5, 60.3
$Nd_2(malonate)_3, 8H_2O$	[245]	(3a)	0.149	0.094	8.9, 31.7, 41.9, 36.0, 46.3
$Nd_2(malonate)_3, 6H_2O$	[246]	(3b)	0.135	0.148	19.6, 28.8, 34.4, 37.6, 54.6

[a] Nine bonds 2.43–2.56 Å and a tenth at 3.06 Å. Taking the geometry as a 9 coordinate CSAP, the tenth weak bond is positioned over the uncapped face. The 10 normalised bonds give a Δ value of 0.140 Å from the 10 coordinate BCSAP.

relatively unchanged by bridging. Similar structures are reported for [Eu(terpy)$_3$]$^{3+}$ and [U(dipic)$_3$]$^{2-}$. In the former, the ligands are non-planar with dihedral angles ranging from 12—26° between neighbouring rings and the distortion was thought to be due to intramolecular ligand···lone pair interactions.

(e) Molecules of the form M(unidentate)$_5$(bidentate)$_2$. There are no monomeric examples of M(L—L)$_2$L$_5$ complexes. Polymers are listed in Table 28. The first two compounds contain chelates with bites of 0.84—0.87 which as expected occupy *c* edges of TCTP. The two structures are however different (Fig. 23). There are two crystal forms of Nd$_2$(malonate)$_3$, *x* H_2O that have slightly different structures. Both contain two chelates with $z = 0.84$ and 1.15. As previously found, such short and long bites fit *c* and *h* edges respectively in the TCTP. When considered as TCTP, both crystal forms have identical structures but they are distorted in different ways. The hexahydrate is distorted towards the s_1, s_2 CSAP (type a) rather more than towards the *c*, *l* CSAP (type b) with Δ values of 0.148, 0.155 Å respectively. However the octahydrate is well on the CSAP side of the pathway with the *c*, *l* structure.

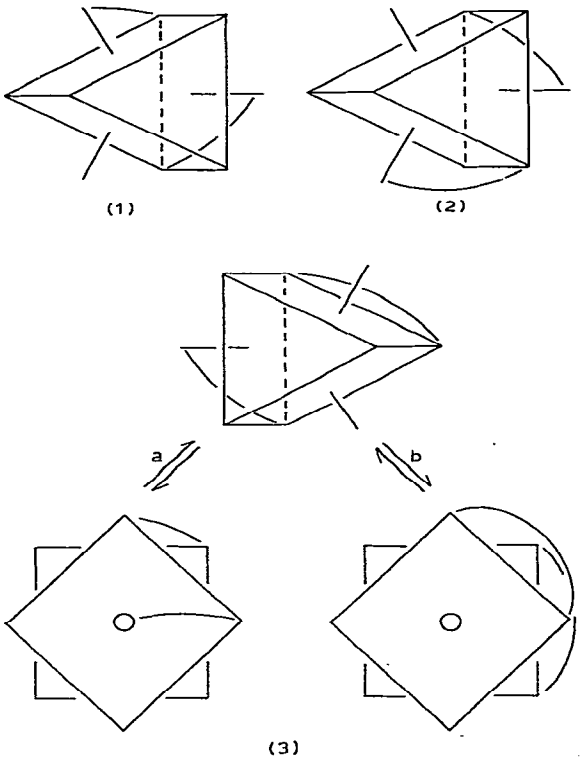


Fig. 23. Structures of M(L—L)$_2$L$_5$ complexes.

(f) Other molecules. Other 9 coordinate structures are listed in Table 29. There are just three monomers which do not fall into any of the above categories. $[Er(OH_2)_6(NO_3)(NCS)]^+$ contains just one bidentate ligand ($z = 0.85$) which occupies a *c* edge of the TCTP. In $[Pr(terpyridyl)Cl(OH_2)_5]^{2+}$ the planar tridentate ligand occupies the capping position and two opposite sites in the capped face of a CSAP. The chlorine atom is also in the capped face and thus the structure has C_s symmetry (Fig. 24a). It is unfortunate that although there have been three structure determinations of $[M(edta)(OH_2)_3]^-$ no consistent set of coordinates is available. The geometry has been described [18] as a CSAP.

The remaining molecules in Table 29 are polymeric and have geometries much distorted from ideal by small bites and/or bridging requirements. Thus $[Pr_2(Himda)_2(imda)(OH_2)_4]^{2+}$ has one bidentate ligand ($z = 0.85$) occupying a *c* edge of the TCTP and shares another *c* edge with an adjacent metal. M(nta), 3 H_2O contains a bidentate ligand ($z = 0.85$) and a tetradentate ligand (Fig. 24b). $\{Pr_2(facam)_6\}(dmf)_3$ is a dimer in which each metal atom is bonded to three bidentate facam ligands and shares three oxygen atoms of dmf ligands with the other. The geometry is described as a TCTP and is thus rather similar to type (1) of Fig. 20. In $M(sal)_3H_2O$ many edges are shared with other metals and the geometry is far from ideal. $Nd(thac)(OH_2)_4^+$ is the best CSAP of all 9 coordinate complexes despite its geometry being described

TABLE 29

Other 9 coordinate complexes [a]

Compound	Ref.	Δ (Å)		δ angles
		TCTP	CSAP	
$[Er(OH_2)_6(NO_3)(NCS)]^+$	[247]	0.135	0.162	27.3, 35.2, 44.5, 34.9, 50.3
$[Pr(terpyridyl)Cl(OH_2)_5]^{2+}$	[248]	0.119	0.063	0.0, 38.6, 38.6, 38.7, 38.7
$[M(edta)(OH_2)_3]^-$ M = Ln	[249] [b]			
M = Sm	[250] [b]			
M = Nd	[251] [c]			
$[Pr_2(Himda)_2(imda)(OH_2)_4]^{2+}$	[252]	0.127	0.123	17.3, 23.4, 44.0, 43.7, 43.9
M(nta), $3H_2O$ M = Pr	[253] [c]			
M = Nd	[254]	0.125	0.127	9.0, 20.9, 46.6, 38.7, 51.8
$[Pr_2(facam)_6](dmf)_3$	[255] [b]			
$M(sal)_3$, H_2O, M = Sm, (Am)	[256]	0.174	0.173	25.7, 37.1, 37.8, 16.0, 62.1
$[Nd(thac)(OH_2)_4]^+$	[257]	0.127	0.021	2.1, 36.9, 36.9, 38.0, 38.5
$[Nd(imda), 3H_2O]^+$	[258]	0.111	0.110	18.5, 29.6, 43.4, 35.0, 53.9
$Nd(O_2CCH_3F)_3$	[259] [c]			

[a] A number of molecules can be considered as either 8 or 9 coordinate. These are listed in Table 18; their geometry is not close to either 9 coordinate polyhedra. [b] Unpublished coordinates. [c] Inconsistent coordinates.

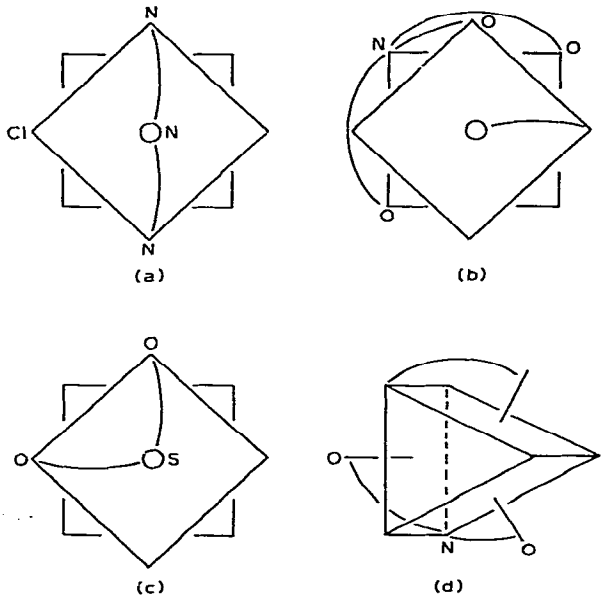


Fig. 24. Structures of some other 9 coordinate complexes: (a) $[Pr(terpyridyl)Cl(OH_2)_5]^{2+}$; (b) M(nta), $3H_2O$; (c) $Nd(thac)(OH_2)_4$; (d) $[Nd(imda), 3H_2O]^+$.

as a TCTP [257]. The tridentate ligand (O—S—O) occupies the capping position and two adjacent sites in the CSAP (Fig. 24c).

$[Nd(imda), 3\ H_2O]^+$ contains a bidentate ligand ($z = 0.84$) and a tridentate ligand (O—N—O) ($z = 1.05, 1.06$). The ligand is not planar and the two N···O bites occupy adjacent *c* edges to the same triangular face of the TCTP (Fig. 24d). This contrasts with the planar tridentate ligands in $M(L—L—L)_3$ compounds (Fig. 22). The small bidentate ligand as usual occupies the *c* edge of a TCTP. This structure illustrates the difficulty of choosing the best polyhedra just from L—M—L angles. The geometry was described [258] as a CSAP which is acceptable but the wrong one was chosen because the uncapped face therein has a δ angle of 29.6°. The alternative choice represented by the δ angle of 18.5° gives a lower Δ value.

The geometries of 9 coordinate complexes are dependent upon the same factors as those of 8 coordinate complexes but it would appear that packing effects are more important as a majority of molecules have imposed crystallographic symmetry which of course favours a particular geometry. Also equivalent molecules more often have different geometries. 9 coordinate complexes contain polydentate ligands with smaller *z* values than 8 coordinate complexes, which leads to greater distortion from ideal, but molecules of the same type [e.g. $M(L—L)_3L_3$] are often distorted in equivalent ways. All such geometries however can be described in terms of the CSAP or TCTP and there is no evidence of any other polyhedra that might form a minimum on the

potential energy surface. Although the geometries of many 9 coordinate monomers are predictable, a higher percentage, compared to their 8 coordinate counterparts are not. Polymers have a much wider range of structures and even those of the $M(L—L)_3L_3$ and $M(L—L)_2L_5$ types are unpredictable. But possibly there are not yet enough examples for patterns of structure to emerge. Though clearly the geometric requirements of chain formation are as important as intramolecular ligand···ligand repulsion in such polymers.

There is clear evidence from several structures for a reaction path between the two ideal forms. This path shows the method of intramolecular rearrangements in ML_9 and how all hydrogens in $[ReH_9]^{2-}$ are equivalent to NMR. A TCTP can be converted into three different CSAP and back again to the original or to three other TCTP and thus all ligands can be permuted around all sites.

E. TEN-COORDINATION

With 10 coordinate molecules it becomes more difficult and also less worthwhile to classify structure in terms of ideal geometry. This is because in order to obtain a 10 coordinate structure a (M—L)/(L···L) ratio of ca. 0.92 is required [18] and this can only be achieved with packing diameters between ligands significantly smaller than van der Waals values. One way of achieving such high coordination is to have chelates with small bites such as nitrate or carbonate which will leave room around the rest of the coordination sphere for the non-bonded contacts to reach the van der Waals diameter. In fact nearly all 10 coordinate complexes contain nitrate or carbonate ligands ($z \approx 0.85$) which grossly distorts molecular geometry. There are no examples of ML_{10} compounds and only one compound contains bidentate ligands with $z > 1.00$.

Several authors faced with the difficulty of describing a geometry containing small chelate bites have reduced the coordination number by considering the bidentate ligand (L—L) to be monodentate, positioned at the midpoint of L···L. Thus $[Ce(NO_3)_5]^{2-}$ was described as a trigonal bipyramid. We do not favour this idea as the nitrate *is* a bidentate ligand and because such a description is imprecise giving no indication of the positions of the oxygen atoms. An alternative approach discussed below is to find ideal polyhedra which can accommodate small bites without distortion.

(i) Characteristics of the ideal polyhedra

Structures of 10 coordinate complexes have been described in terms of a wide variety of polyhedra. Energy calculations using eqn. (2) show that the bicapped square antiprism (BCSAP) is the most stable arrangement [276]. Two other polyhedra based upon the Dod are particularly useful; namely the bicapped dodecahedron (BCDod) and the 4A, 6B-expanded dodecahedron (46Dod). A fourth geometry based on the BCTP is introduced for one molecule and will be described later. For $n = 7$, the difference in repulsive energy

between the BCSAP and the BCDod, 46Dod is approximately 11% of the total repulsive energy [276].

(a) Bicapped square antiprism. In the BCSAP (symmetry D_{4d}) both of the square faces of the SAP are capped. The polyhedron is shown in Fig. 25 together with calculated shape characteristics [276]. There are just two types of site L_c and L_s and three edges *c*, *s* and *l*. In comparison with the 8 coordinate SAP, *s* is longer and *l* considerably shorter. Thus as the square faces are enlarged by the capping atoms they are forced closer together. It is interesting that θ is only 7.5° larger than in the 8 coordinate SAP. However for the 9 coordinate SAP, θ for the capped face is larger than, and for the uncapped face smaller than, values in both 8 and 10 coordinate polyhedra. Thus when one face is capped (as in the CSAP), the square face can spread out much more than when both faces are capped.

Despite the BCSAP being the most stable arrangement for 10 coordinate polyhedra by a considerable margin, only one clear example is known of the geometry, namely $[Th(ox)_4]^{4-}$. The shape of this molecule is comparable to that of the MFP even to the extent of M—L_c being longer than M—L_s by about

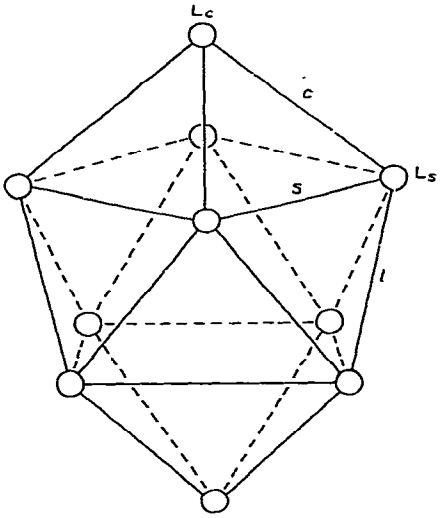


Fig. 25. The bicapped square antiprism (D_{4d}).

MFP shape characteristics

Edge	10 coordinate BCSAP	9 coordinate CSAP	8 coordinate SAP	Values in $[Th(ox)_4]^{4-}$
s	1.25	1.32, 1.13	1.19	1.27
c	1.07	1.13	—	1.06
l	1.09	1.17	1.26	1.12
θ	64.8	69.5, 53.0	57.3	63.9

5%. z is 1.05 in this molecule, a value comparable to that of the c and l edges and indeed the five bidentate ligands occupy two c and three l edges. Most other 10 coordinate molecules contain bites less than 0.90 and are distorted so far from the BCSAP that other ideal polyhedra have been derived to describe their geometry.

(b) Bicapped dodecahedron. The BCDod (symmetry D_2) is derived from the Dod by the introduction of two additional ligands on the C_2 axis passing through the midpoints of two parallel b edges. This is shown in diagrammatic form in Fig. 26. The relationship between the BCDod and the BCSAP is exactly the same as that between the Dod and the SAP. The reaction pathway can be described via the distortion from planarity of atoms 1,5,3,7; 2,8,4,6 which are the capped faces in the BCSAP or alternatively of atoms 1,2,8,7; 5,6,4,3 which are the trapezoids in the BCDod. The shape characteristics of the BCDod are shown in Fig. 27 and Table 30. Parameters in the MFP [276] are θ_A

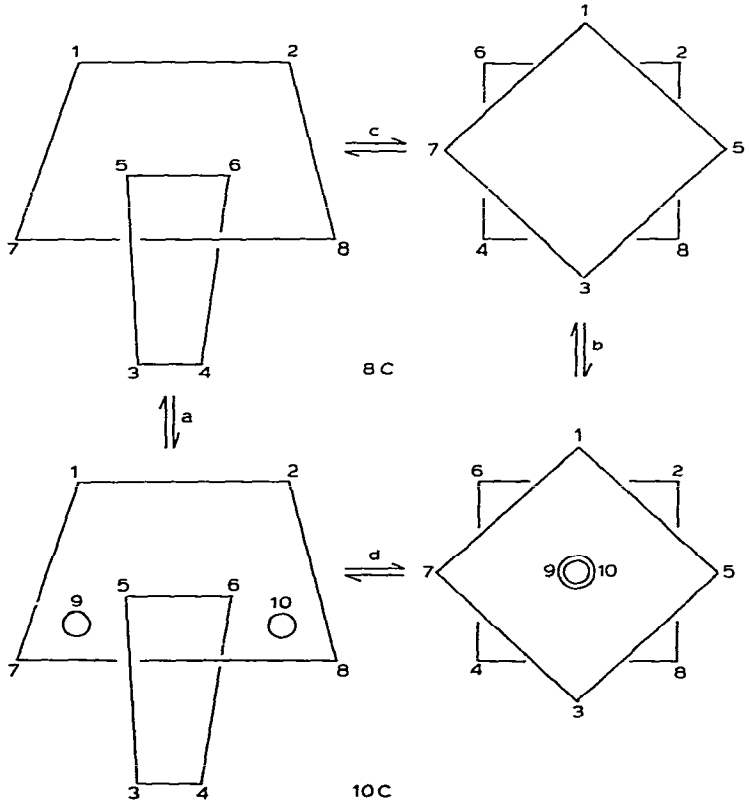


Fig. 26. The relationships between (a) the 8 coordinate Dod and the 10 coordinate BCDod and (b) the 8 coordinate SAP and the 10 coordinate BCSAP; The pathway (c) between the 8 coordinate Dod and SAP is equivalent to that (d) between the 10 coordinate BCDod and BCSAP. For both 10 coordinate polyhedra the capping atoms are drawn as circles.

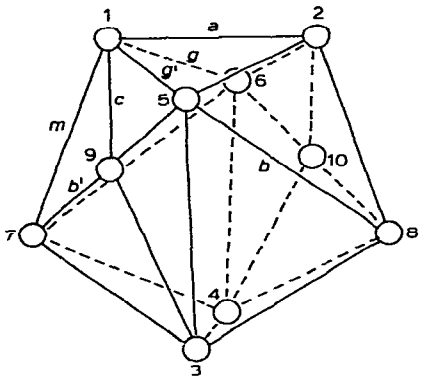


Fig. 27. The bicapped dodecahedron (D_2).

32.8 and θ_B 77.0° compared to 35.2 and 73.5° in the Dod. In the 10 coordinate BCDod with a symmetry of D_2 the trapezoids need no longer be perpendicular and in the MFP they intersect at 60°. The bonds to the ligands in capping positions are then inclined at 60° to both of the trapezoidal planes.

There are seven types of edges in the BCDod (Fig. 27) and mean values found in three molecules are listed in Table 30. In $Ln(NO_3)_3(bipy)_2$ the three nitrates occupy b', b' and a edges and the two bipy ligands two g edges (Fig. 28a). $La_2(CO_3)_3$, 8 H_2O contains two independent metal coordination spheres of which one has stoichiometry $La(CO_3)_2O_6$ and a structure in which the two bidentate carbonate ligands occupy b' edges of the BCDod (Fig. 28b). It is important to note that both molecules fit the BCDod geometry because the short bites are placed symmetrically over equivalent edges. These short

TABLE 30

Shape characteristics of the bicapped dodecahedron

Edge (Fig. 27)	$La(NO_3)_3$-$(bipy)_2$	$Ln_2(CO_3)$-$8H_2O$	$[Th(ox)_4]^{4-}$	MFP Dod
c (19, 39, 210, 410)	1.10	1.14	1.07	—
a (12, 34)	1.13 [a]	1.27	1.09	1.17
m (17, 28, 53, 64)	1.25	1.31	1.25	1.17
b (67, 85)	1.19	1.06	1.09	1.49
b' (79, 95, 610, 108)	1.01 [a]	0.93 [a]	1.07	—
g (16, 25, 47, 38)	1.09 [a]	1.13	1.09	1.24
g' (15, 37, 26, 48)	1.31	1.22	1.25	—
Mean deviation from trapezoid	0.08	0.07	0.48	0.00
Mean deviation from square plane	0.24	0.51	0.02	—
Angle between trapezoids [b]	64.6	75.0	69.5	90

[a] At least one edge of this type is occupied by a chelate. [b] Angle predicted for MFP [276] is 60°.

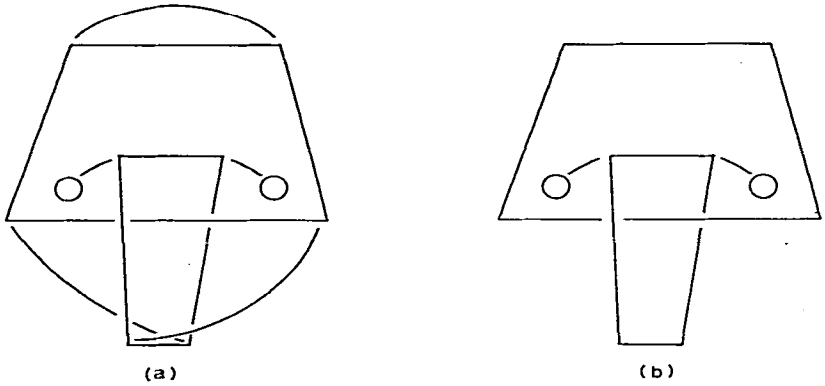


Fig. 28. Wrapping patterns of two complexes that have the BCDod structure: (a) $Ln(NO_3)_3(bipy)_2$ — b', b', a, g, g isomer; (b) $La(CO_3)_2O_6$ — $b'b'$ isomer.

bites may lead to unusual shapes for the polyhedra and therefore for comparisc values from $[Th(ox)_4]^{4-}$ are included in Table 30. While this molecule has the BCSAP geometry, mean values for edges when considered as a BCDod may well be more characteristic than in the other two molecules. It can be conclude from Table 30 that only m and g' edges are unsuitable for small chelate bites. Indeed when $[Th(ox)_4]^{2-}$ is fitted to a BCDod, the five bidentate ligands occupy a, b, b', c and g edges. The angles between trapezoids in the molecules of Table 30 are rather larger than the 60° predicted for the MFP but much less than 90°. In comparison with the 8 coordinate Dod, b and g edges are much reduced but m edges are longer. However the calculation of MFP parameters did not take account of possible values of z; and values of edges will be very much dependent upon the positions of any small bites in the polyhedron. Both the BCSAP and the BCDod contain one angle of 180° subtended at the metal by two axial atoms; and can be considered as having 1 : 4 : 4 : 1 and 1 : 2 : 2 : 2 : 2 : 1 geometries respectively. It is therefore simple to compare the geometry of a molecule with these two symmetries. The BCSAP can be distorted in two different ways towards the BCDod depending upon the choice of two-fold axes. Using the numbering system of Fig. 26, these could pass through the midpoints of edges 12 and 43, 67 and 58 as shown or alternatively through 25 and 47, 16 and 38.

(c) 4A,6B-Expanded dodecahedron. Many 10 coordinate molecules do not contain an angle of 180° and a third ideal geometry is therefore required. The 46Dod (symmetry C_{2v}) is based on the Dod with two additional atoms, obtained by transforming two B sites of one trapezoid (5, 6 in Fig. 29) into two equivalent edges (55′ and 66′) parallel to the a edge (12) of the other trapezoid. The shape characteristics of the 46Dod are shown in Fig. 30 and Table 31. Following Al-Karaghouli and Wood [276] the labelling of the polyhedron edges is consistent as far as possible with that in the Dod. There are

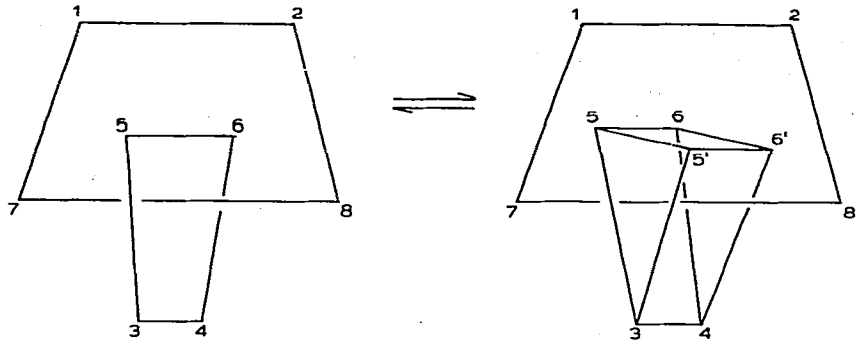


Fig. 29. Relationship between the 8 coordinate Dod and the 10 coordinate 46Dod.

four types of site (A, C, B, A') in the 2 : 4 : 2 : 2 polyhedron; θ values for these sites and for B' in the MFP [276] are quoted in Table 31. B' sites are the midpoints of the 55' and 66' edges and thus can be considered as the B sites in the original trapezoid of the 8 coordinate Dod. There are eight different types of polyhedron edges and their size fluctuates wildly from compound to compound. Shape characteristics for three compounds are given in Table 31. In $[Ho(NO_3)_5]^{2-}$, bidentate ligands occupy edges *a*, *a'*, *b*, *b* and *b'* and in $Ho(HCO_3)_3(OH_2)_4$ edges *b'*, *g'* and *g'*. The second metal coordination sphere in $La_2(CO_3)_3 \cdot 8\ H_2O$ (the first being a BCDod) has stoichiometry $La(CO_3)_3O_4$ with the carbonates occupying *a'*, *b'* and *b'* edges. These three wrapping patterns are shown in Fig. 31. Five edges *a*, *a'*, *b*, *b'* and *g'* are occupied by small chelates, and three *m*, *m'* and *g* are not, in these three compounds and this is common in other 10 coordinate complexes. As shown in the next section nearly all 10 coordinate complexes can be fitted to the 46Dod but this is primarily due to its low symmetry as it can change shape to suit the wrapping pattern of the chelates. Indeed the ease of fitting 10 coordinate complexes to the C_{2v} symmetry reminds one of the fact that all molecules fit perfectly to C_1 symmetry.

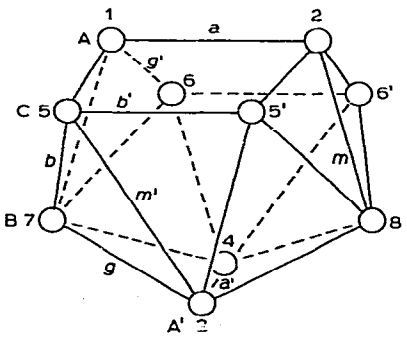


Fig. 30. The 4A,6B-extended dodecahedron (C_{2v}).

TABLE 31

Shape characteristics of the 4A,6B-expanded dodecahedron

Edge (Fig. 29)	$[Ho(NO_3)_5]^{2-}$	$La_2(CO_3)_3, 8H_2O$	$Ho(HCO_3)_3(OH_2)_4$
a (12)	0.86 [a]	1.15	1.14
a' (34)	0.89 [a]	0.84 [a]	1.22
g (37, 47, 38, 48)	1.29	1.22	1.22
g' (16, 15, 25′, 26′)	1.20	1.19	1.07 [a]
b (57, 67, 5′8, 6′8)	1.01 [a]	1.12	1.15
b' (55′, 66′)	1.01 [a]	0.82 [a]	0.95 [a]
m (28, 17)	1.22	1.18	1.22
m' (35, 35′, 46, 46′)	1.17	1.17	1.22
Angles [b]			
θ_A	25.4	35.0	34.9
θ_B	78.9	73.2	70.3
$\theta_{A'}$	26.3	24.9	37.8
$\theta_{B'}$	85.4	85.6	71.6
θ_C	83.5	85.0	69.4

[a] At least one edge of this type occupied by small chelate bite. [b] θ_A, θ_B, $\theta_{A'}$, $\theta_{B'}$, angles defined as in the Dod. θ_C is defined [276] as giving the angular separation of the ligands in C sites. This definition is ambiguous as it could mean the separation of atoms 5 & 6 or 5 & 6′. We have chosen the latter definition. MFP values for the 46Dod are 32.8, 65.8, 34.9, 77.8, 63.8° respectively [276].

Values of the θ angles for the three molecules in Table 31 are not very similar to those of the MFP but this is not surprising as the latter were calculated for ML_{10} molecules. In particular θ_C angles are dependent upon the positions of the small chelate bites. Thus the angle is 83.5° in $[Ho(NO_3)_5]^{2-}$ because two chelates occupy b edges and the C sites are pulled down towards the B sites but only 69.4° in $Ho(HCO_3)_3(OH_2)_4$ where two chelates occupy

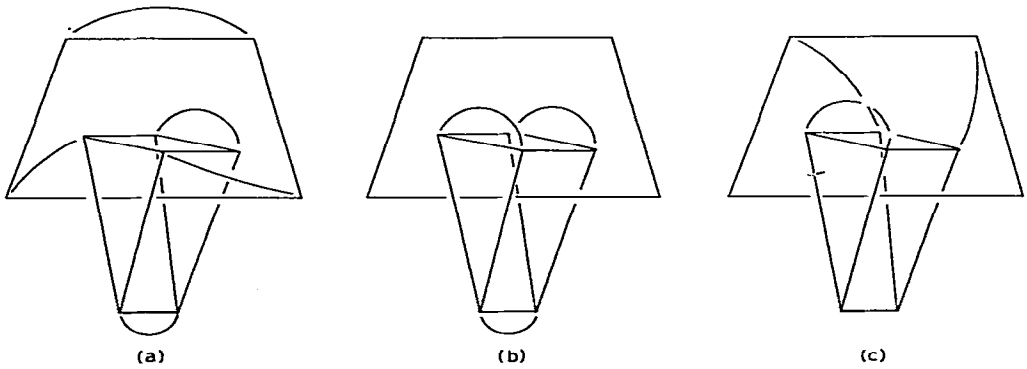


Fig. 31. Wrapping patterns of three complexes that have the 46Dod structure: (a) $[Ho(NO_3)_5]^{2-}$ — a, a', b, b, b' isomer; (b) $La(CO_3)O_4$ — a', b', b' isomer; (c) $Ho(HCO_3)_3(OH_2)_4$ — b', g', g' isomer.

g' edges and the C sites are pulled up towards the A sites. In $La(CO_3)_3O_4$, the angle is even higher at 85.0°. This is because two nitrates occupy b' edges and their oxygens are pulled away from B sites, thus allowing θ_C to approach 90°. With larger bites in b' edges, θ_C would be considerably smaller.

A number of three dimensional polymers can also be fitted to this 46Dod geometry [260] * including $Nd(B_3O_6)$, burbankite, and YbS_2. Distortion towards the other two 10 coordinate ideal geometries can occur in two ways dependent upon which pair of atoms becomes the axial atoms in the BCSAP or BCDod. Possible candidates are two B atoms 7, 8 or alternatively two C atoms either 5, 6′ or 6, 5′.

(ii) Structures of ten-coordinate complexes

Only two types of molecule are at all common, namely $M(L—L)_5$ and $M(L—L)_3L_4$ and these are described in subsequent sections. δ angles were found to be of no practical use in 10 coordination as there is such a wide range of possible sets to consider that to concentrate on just one is misleading. Because of the very wide range of shapes for the BCdod and particularly the 46Dod, the Δ value method proved to be most useful as variations in ideal polyhedra are easily accommodated.

(a) Molecules of the form M(bidentate)$_5$. Compounds with five identical bidentate ligands are listed in Table 32. As discussed earlier $[Th(ox)_4]^{2-}$ is a BCSAP. The z value of 1.05 is suitable for both c and l edges in this polyhedron but is rather short for s edges. There are two possible isomers in the BCSAP with just c and l edges occupied and these are shown in Fig. 32.

TABLE 32

Structures of $M(L—L)_5$ complexes

Compound	Ref.	z	Structure type	Δ (Å)		
				BCSAP	BCDod	46Dod
$[Th(ox)_4]^{4-}$	[13]	1.05	(2)	0.074	0.057	0.114
$[Ho(NO_3)_5]^{2-}$	[261]	0.88	(1)	0.199	0.149	0.064
$[Ce(CO_3)_5]^{6-}$	[262] [a]	0.89	(1)	0.164	0.088	0.096
$[Ce(CO_3)_5]^{6-}$	[265] [a]	0.90	(1)	0.198	0.171	0.076
$[Ce(NO_3)_5]^{2-}$	[266] [b]					
$[Ba(acetamide)_5]^{2+}$	[267]	0.99	(2)	0.164	0.159	0.104

[a] Isomorphous compounds with Th [263,264]. [b] Unpublished coordinates.

* These authors describe the C_{2v} polyhedron as a bicapped dodecahedron which is confusing. However most authors keep this name for the D_2 polyhedron [276]. There is no accepted name for the C_{2v} polyhedron and we suggest the 4A,6B-expanded dodecahedron.

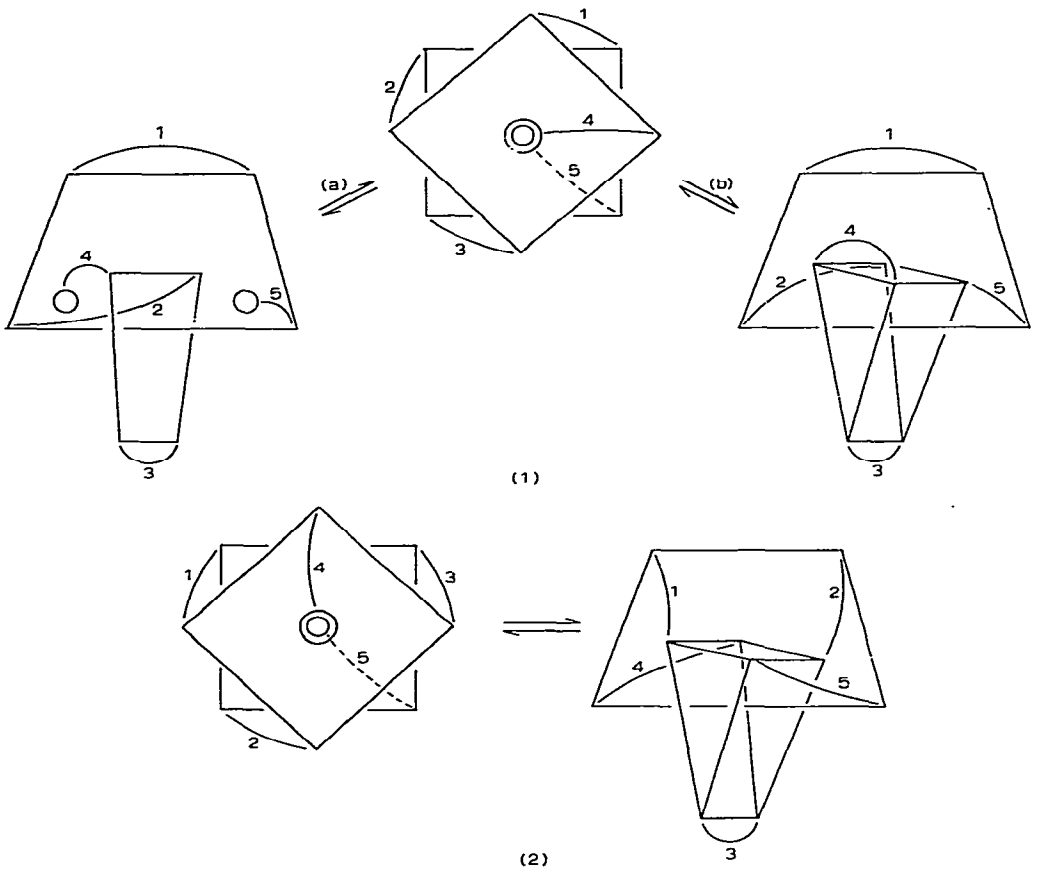


Fig. 32. Structures of M(L—L)$_5$ complexes. (1) This BCSAP can be distorted towards, inter alia, (a) the BCDod (*a*, *a'*, *b*, *b'*, *b'* isomer) or (b) the 46Dod (*a*, *a'*, *b*, *b'*, *b'* isomer). (2) This BCSAP can be distorted towards, inter alia, (a) the 46Dod (*a'*, *b*, *b*, *g'*, *g'* isomer). Other isomers are of course possible for both the BCDod and 46Dod but have not yet been observed in structures.

$[Th(ox)_4]^{2-}$ has structure (2). In this polymer the bridging to other coordination spheres is via *c* edges. As C_{2v} is a subgroup of D_{4d}, the fit of the 46Dod is lower than that to the BCSAP but the distortion is very slight.

The other four molecules that are considered here contain smaller bites and it is pertinent to consider whether their geometries approximate to the BCSAP as much as possible and thus the distortions are due to the small bites. Clearly when two *c* edges are occupied by two small chelates then two atoms will be pulled out of the square planes and the three *l* edges occupied by chelates will be shorter than the other five.

$[Ba(acetamide)_5]^{2+}$ also has structure (2) when considered as a BCSAP but is distorted towards the 46Dod with *a'*, *b*, *b*, *g'*, *g'* edges occupied by the five

bidentate ligands (Fig. 32). Just as the $M(L—L)_4$ *ssss* SAP can be distorted into three different Dod by the choice of which *l* edge becomes an *a* edge, so the BCSAP can be transformed into several 46Dod. It remains to be seen whether any others apart from those shown in Fig. 32 will be obtained in structures.

The other three molecules in Table 32 have smaller bites ($z = 0.89$) and their structures are shown in Fig. 32. The two $[Ce(CO_3)_5]^{6-}$ molecules are distorted from the BCSAP in different ways; the first towards the BCDod (*a*, *a'*, *b*, *b'*, *b'* isomer) and the second towards the 46Dod (*a*, *a'*, *b*, *b'*, *b'* isomer). In the first, the mean distance of a contributing atom from the trapezoids is 0.17 Å and from the squares is 0.22 Å and on this criterion the structure is intermediate between the two ideal forms. The angle between the trapezoids is 65.9°. As we have seen $[Ho(NO_3)_5]^{2-}$ is distorted towards the 46Dod in a similar manner to the second $[Ce(CO_3)_5]^{6-}$ molecule. It will be noted from Fig. 32 that there is little difference between the BCDod and 46Dod; just a small rearrangement of the six 'equatorial' B and C atoms in the two polyhedra being required to change from one to the other.

From these structures it can be concluded that $M(L—L)_5$ complexes are best considered as BCSAP with distortions no more than necessary to accommodate the small bites. The distortions are not however the same in all complexes and the resulting geometries can be described in terms of different isomers of the BCDod and 46Dod.

(b) Molecules of the form M(bidentate)$_3$(unidentate)$_4$. Molecules in this category are listed in Table 33. All structures have geometries that are best described by the 46Dod. We have already discussed the $La(CO_3)_3O_4$ coordination sphere where the three bidentate ligands occupy *a'*, *b'* and *b'* edges (Fig. 31b) thus conforming with C_{2v} symmetry. The two molecules of $M(NO_3)_3$-$(dmso)_4$ are isomorphous and also fit to the 46Dod but with *a*, *b'* and *b'* edges filled. Again this wrapping pattern conforms with C_{2v} symmetry (Fig. 33). The Δ value is larger than in $La(CO_3)_3O_4$ (0.074, 0.043 Å respectively) because the positions of the nitrate ligands do not conform with C_{2v} symme-

TABLE 33

Structures of $M(L—L)_3L_4$ complexes

Compound	Ref.	Δ (Å)		
		BCSAP	BCDod	46Dod(isomer)
$La_2(CO_3)_3, 8H_2O$	[268]	0.207	0.201	0.043(*a'b'b'*)
$La(NO_3)_3(dmso)_4$	[269]	0.170	0.158	0.074(*ab'b'*)
$Nd(NO_3)_3(dmso)_4$	[270]	0.154	0.145	0.083(*ab'b'*)
$Ho(HCO_3)_3(OH_2)_4$	[271]	0.178	0.175	0.097(*b'g'g'*)
$Pr(NO_3)_3(OH_2)_4$	[272,273]	0.199	0.176	0.100(*b'g'g'*)

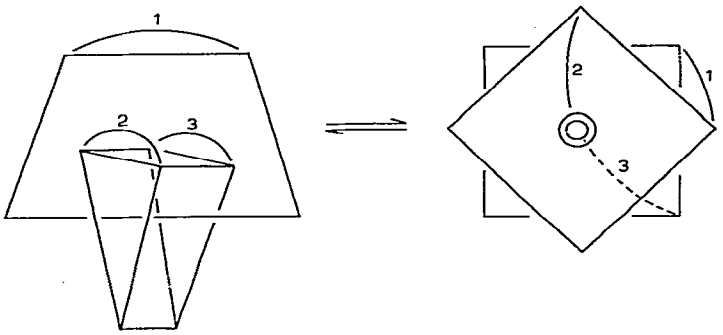


Fig. 33. The structure of $M(NO_3)_3(dmso)_4$.

try. The nitrate 1 occupying the *a* edge is rotated by about 13.5° about the C_2 axis out of its trapezoid. As if to compensate the nitrates in *b'* edges (2 and 3) are rotated in a similar fashion so that all O···O edges of the chelates are parallel. These distortions are explicable if the geometry is considered to be a frustrated BCSAP, that is the distortions arise from the occupation of *c*, *c*, *l* edges by the small nitrate bites *.

$Ho(HCO_3)_3(OH_2)_4$ and $Pr(NO_3)_3(OH_2)_4$ are also isomorphous and are best described as 46Dod with *b'*, *g'* and *g'* edges occupied (Fig. 31c), thus maintaining C_s symmetry. It will be noted that in these three different $M(L—L)_3L_4$ structures only *a*, *a'*, *b'* and *g'* edges are occupied by chelates and that the monodentate ligands occupy 2A and 2B or 2A' and 2B sites. It is only with five bidentate ligands that *b'* edges are occupied by bidentate ligands.

In these $M(L—L)_3L_4$ complexes, there are no angles close to 180° and therefore no close fit to the BCSAP or the BCDod.

(c) Other molecules. Other 10 coordinate molecules whose structures have been determined are listed in Table 34. In $M(NO_3)_4(tppo)_2$ the monodentate ligands subtend an angle of 154° at the metal but cannot be fitted to the BCSAP geometry with these atoms axial. Indeed this is the only 10 coordinate monomer that does not appear to fit any of the ideal polyhedra in a satisfactory manner; even from the 46Dod, the Δ value is 0.151 no doubt due to the asymmetrical wrapping pattern of *m'*, *g*, *b'* and *g'* edges. However it can be argued that the distortion from a BCSAP is larger for this molecule than for the $M(L—L)_5$ complexes because not only are there the small bites to contend with but also the bulky monodentate ligands which must be far apart from each other (as in $M(L—L)_3L_2$ complexes, Table 8) but also relatively far from adjacent atoms. Thus there are only three edges less than 1.20 for both L atoms put together while most of the oxygen atoms of the nitrate

* This description is consistent with that given previously [269] but the numbering system in that paper is wrong.

TABLE 34

Structures of other 10 coordinate complexes

Compound	Ref.	Type	Δ (Å)		
			BCSAP	BCDod	46Dod
$M(NO_3)_4(tppo)_2$ M = Th	[274]	$M(L{-}L)_4L_2$	0.235	0.201	0.151
M = Ce	[275]	$M(L{-}L)_4L_2$			
$M(NO_3)_3(bipy)_2$ M = La	[276,277]	$M(L{-}L)_3(L{-}L)_2$	0.120	0.101	0.154 [a]
M = Tb	[277]	$M(L{-}L)_3(L{-}L)_2$			
$Gd(NO_3)_3(paie)$	[278]	$M(L{-}L)_3(L{-}L{-}L{-}L)$	0.199	0.156	0.116
$[Ln(edta)(OH_2)_4]^-$	[279] [b]	$ML_4(L{-}L{-}L{-}L{-}L{-}L)$			
$Ln_2(CO_3)_3, 8H_2O$	[280]	$ML_6(L{-}L)_2$	0.127	0.055	0.118
$U(ac)_4$	[280]	$ML_6(L{-}L)_2$	0.132	0.119	0.083
$[Ce_2(O_2)_2(CO_3)]^{4-}$	[281]	$M(L{-}L)_3(L{-}L)_2$	0.236	0.183	0.112
$[Ce_2(ac)_8(OH_2)_2]^{2-}$	[282]	$M(L{-}L)_4L_2$	0.246	0.215	0.155

[a] Ordered molecules give Δ of 0.148, 0.128, 0.154 Å respectively. [b] Unpublished coordinates.

groups each have about 4 edges less than 1.20. It is probably best therefore to consider the molecule to be a highly distorted BCSAP (Fig. 34a) with some distortion towards the BCDod. The structure of another $M(L{-}L)_4L_2$ compound, dimeric $[Ce_2(ac)_8(OH_2)_2]^{2-}$ is also highly distorted and no decent fit could be obtained to any of the three ideal polyhedra. The L—M—L angle in this case is 73.3°. For this compound the sharing of an oxygen by two metals may give rise to the unusually distorted structure.

The structure of $La(NO_3)_3(bipy)_2$ is a BCDod with the shape characteristics listed in Table 30. The nitrate groups occupy the *a*, *b'*, *b'* edges and the bipy ligands the longer *g,g* edges (Fig. 28a). However the oxygen atoms of the nitrate group occupying the *a* edge are disordered about the imposed C_2 axis with each oxygen having two possible positions. This disorder must affect the positions of the other atoms in the coordination sphere but the extent of this would not be discernable by the structure analysis. If two oxygen positions of an ordered molecule are used, the Δ values increase considerably for all polyhedra. As in other examples, this structure could be considered as a BCSAP with distortions imposed by the small bites. Dimeric $[Ce_2(O_2)_2(CO_3)_6]^{4-}$ also has this stoichiometry, each metal atom being bonded to three bidentate carbonates ($z = 0.90$) and two bridging peroxides ($z = 0.62$). Best fit is to a 46Dod with the wrapping pattern of Fig. 31a {for $[Ho(NO_3)_5]^{2-}$} with the peroxide occupying *a* and *b'* edges and the carbonate *a'*, *b* and *b* edges.

$Gd(NO_3)_3(paie)$ contains a tetradentate ligand, the dihedral angle between the two planar halves being 28°. The best fit is to the 46Dod with the arrangement shown in Fig. 34b. Despite the highly asymmetrical wrapping pattern, the Δ value is only 0.116 Å.

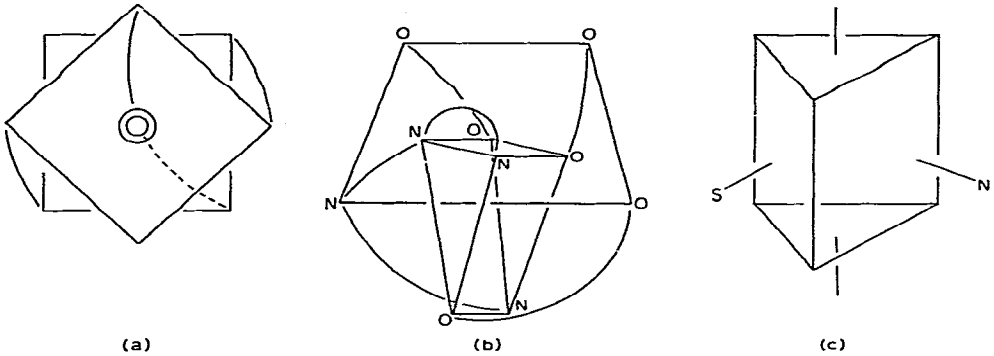


Fig. 34. The structures of other 10 coordinate complexes: (a) $M(NO_3)_4(tppo)_2$; (b) $Gd(NO_3)_3(paie)$; (c) Pb(macrocycle)(NCS).

The two molecules in the asymmetric unit of $Ln_2(CO_3)_3$, 8 H_2O have stoichiometry $Ln(CO_3)_2O_6$ and $Ln(CO_3)_3O_4$ and as we have seen are excellent examples of the BCDod (Fig. 28b) and 46Dod (Fig. 31b) respectively for the good reason that the chelates do not lower the symmetry.

$U(ac)_4$ is also a polymeric structure with individual coordination sphere of type $M(L—L)_2L_6$. The four acetates bridge adjacent metal atoms with U—O—C—O—U linkages and in addition there are two weak U···O interactions. This polymeric chain formation is probably the dominant factor in the choice of geometry; but the best fit is obtained with the b', b' isomer of the 46Dod.

Pb(macrocycle)(NCS) [283] contains an octadentate macrocyclic ligand and a thiocyanate ligand which bridges adjacent metal atoms through nitrogen and sulphur. There is no way in which this geometry can be described in terms of any of the aforementioned ideal polyhedra. However there is a very good fit (Δ 0.059 Å) to a C_{2v} polyhedron (2 : 2 : 2 : 4 down the C_2 axis) shown in Fig. 34c. The polyhedron is derived from the 8 coordinate BCTP by capping the two triangular faces of the prism. The nitrogen and sulphur atoms of the bridging —NCS group occupy the two sites capping the quadrilateral faces. The shape of the polyhedron is given by the size of the edges; $v_1 = v_2 = 0.98$, $h_1 = 1.63$, $h_2 = 1.16$, $c_3 = 1.17$, $c_4 = 1.01$. (h, v defined as for the BCTP; c_3, c_4 edges between the capped triangular and quadrilateral faces respectively and the relevant capping atom). This polyhedron is described [283] as having a 1 : 6 : 3 geometry. The problem with such a loose description (and the same applies to 1 : 3 : 4 : 2, 1 : 3 : 3 : 3, 1 : 5 : 3 : 1 etc) is that all 10 coordinate polyhedra fit it in one way or another. A polyhedron should always be described in terms of its symmetry elements.

This analysis of 10 coordinate geometry has been more difficult than that of 8 or 9 coordinate geometries. Structures are far less predictable and even for the $M(L—L)_5$ and $M(L—L)_3L_4$ types, several arrangements are equally possible. However some conclusions can be drawn.

For the majority of molecules the 46Dod is the best description of geometry. It has the advantage of low symmetry and flexibility and also that any number of small bites from 1 to 5 inclusive can be fitted to it without loss of symmetry. The BCSAP despite being at an energy minimum for ML_{10} molecules [276] is not often found, nor are the BCDod and 2 : 2 : 2 : 4 C_{2v} polyhedra. Taking into account that several molecules (e.g. $La_2(CO_3)_3$, 8 H_2O) that do fit well to ideal polyhedra have imposed crystallographic symmetry and that there are a number of molecules (particularly $M(L—L)_4L_2$ examples) that have irregular geometry, it can be concluded that the potential energy surface for 10 coordinate complexes is devoid of well-defined minima and that intramolecular contacts and/or chain formation are the dominant factors in the choice of geometry.

However this section has shown how the geometry of 10 coordinate complexes can be assessed. Identification in terms of the BCSAP or BCDod is straightforward as an angle close to 180° will give the axial atoms. It is not so easy to fit a molecule to the common 46Dod as there is no fixed set of angles. All small edges must be tried as possible a edges and this can be done via a computer program or by building an accurate model. Calculation of Δ values has proved invaluable in finding the best fit. Alternative methods that could be used include comparing (a) the lengths of equivalent edges (or L—M—L angles which is the same thing) (Table 31), (b) δ angles over equivalent edges and (c) the angles between planes of atoms such as the trapezoid (1, 2, 8, 7), the C sites (5,5′,6,6′) and the a' edge (3,4).

It has been shown in passing that several 10 coordinate molecules can be described as having geometries intermediate between two ideal forms. For 8 and 9 coordinate complexes, these would have suggested reaction pathways between ideal polyhedra but for 10 coordinate complexes with their small bites, this is not necessarily so. More relevant perhaps would be to consider, for $M(L—L)_3L_4$ complexes, whether a pathway exists between the three isomers found in 46Dod, namely b',b',a; b',b',a' and $b',g'\ g'$ (Table 33) but with such high coordination there are innumerable ways in which such conversion could be achieved.

F. STRUCTURES OF ELEVEN, TWELVE AND FOURTEEN COORDINATE COMPLEXES

There are only two 11 coordinate complexes, dimeric $[Th(NO_3)_3(OH_2)_3(OH)]_2$ [284] and monomeric $Th(NO_3)_4(OH_2)_3$ [285,286]. Both can be fitted to a 1 : 4 : 2 : 4 C_{2v} polyhedron. The two polyhedra have very different shapes but in view of the lack of comparable structures, it is not thought worthwhile to give a detailed shape analysis.

On the other hand there are enough 12 coordinate examples (Table 35) to warrant such treatment. All examples bar one are of the $M(L—L)_6$ type and their geometries can be related to the eicosahedron with I_h symmetry. This is an inevitable consequence of the increasing number of atoms in the

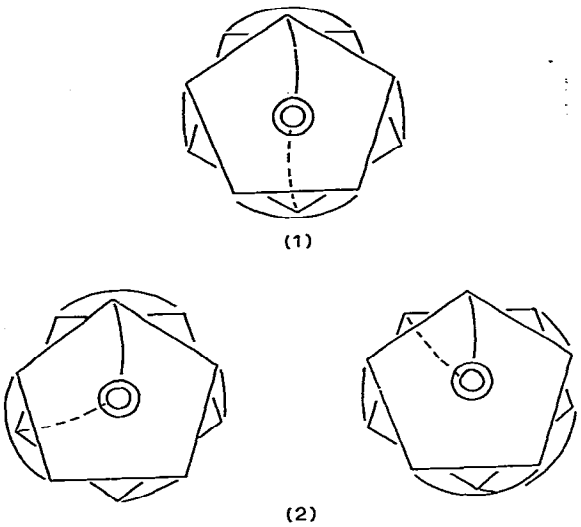


Fig. 35. Wrapping patterns of $M(L—L)_6$ complexes in eicosahedra.

coordination sphere. For 10 coordinate it is nearly possible to decribe geometry in terms of one polyhedron, the 46Dod, and for 12 coordination it is possible. In an ideal eicosahedron, like the Dod completely made up of triangles, there are six equivalent $\bar{1}0$ axes and for purposes of checking and comparing geometry, and of illustrating in two dimensions, it can best be considered as a bicapped pentagonal antiprism. None of the $M(L—L)_6$ molecules has ideal I_h symmetry because they contain small bites. Two types of wrapping pattern are found and illustrated in Fig. 35. In the first, the ligands are arranged in a patohedron (T_h symmetry) with four 3 axes and a centre of symmetry. In terms of a bicapped pentagonal antiprism, the edges occupied by the chelate

TABLE 35

Structures of 12 coordinate complexes

Compound	Ref.	z	Δ (Å)	Imposed symmetry	Structure type
$[Ce(NO_3)_6]^{2-}$	[287]	0.85	0.115	$\bar{1}$	(1)
$[Ce(NO_3)_6]^{2-}$	[288]	0.85	0.140	3	(1)
$[Th(NO_3)_6]^{2-}$	[289]			$\bar{1}$	(1)
$La_2(SO_4)_3, 9\ H_2O$	[55]	0.87	0.107	$\bar{6}2m$	(1)
$[Pr_2(NO_3)_9]^{2-}$	[290]	0.83	0.171	3	(2)
$[Pr(naph)_6]^{3+}$	[291]	0.82	0.137	—	(2)
$Ln(NO_3)_3$(crown ether)	[295] [a]				

[a] Unpublished coordinates.

bites are *s, s, c, c, l.* In the chelates, the atom in the capping position is pulled towards the atom in the pentagonal face. Thus the two capping atoms subtend an angle of 180° at the metal.

This is the most common arrangement and found for four molecules in Table 35. The Δ values vary considerably because of differing imposed symmetry and packing effects. $La_2(SO_4)_3$, 9 H_2O is particularly interesting as it contains both 9 and 12 coordinate polyhedra. It is suggested that the failure of the heavier smaller lanthanides to form analogous hydrates is due to their inability to support a coordination number of 12. Unique bond lengths in the 12 coordinate polyhedra are 2.59 and 2.80 Å compared to 2.51, 2.56 Å in the 9 coordinate TCTP.

The second type of wrapping pattern (Fig. 35b) contains a C_2 axis but no centre of symmetry. The two diagrams of structure (2) represent different ways of looking at the same structure. $[Pr_2(NO_3)_9]^{2-}$ has imposed C_3 symmetry and oxygen atoms are shared by either two Pr or by Pr and K^+ metals which may account for the high Δ value. The other example of this second wrapping pattern is $[Pr(naph)_6]^{3+}$ which is a better fit despite the surprising lack of imposed symmetry. Each naph ligand intersects the plane of the metal and two donor nitrogen atoms at an angle of 48°. The structure of $Zr(BH_4)_4$ has been determined by electron diffraction [292] and contains a tetrahedral arrangement of the four sets of three bridging hydrogen atoms.

The relationships between the eicosahedron and the polyhedra of lower coordination numbers have been recently described [260].

The coordinates of one 14 coordinate molecule have been reported. $U(BH_4)_4$ is described [293] as a bicapped hexagonal antiprism but it is severely distorted no doubt because of the complicated bridging pattern with two or three hydrogen atoms shared with the boron atoms. Δ values of 0.186 and 0.234 Å respectively were obtained for the bicapped hexagonal antiprism and bicapped hexagonal prism. Other 14 coordinate complexes described briefly are $U(BH_4)_4.2(C_4H_8O)$ and $U(BH_4)_4OMe_2$ in which the uranium atom is bonded to 12 hydrogens and 2 oxygens and 13 hydrogens and one oxygen respectively [294].

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