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EIGHT-COORDINATION IN THE TRANSITION SERIES

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CONTENTS

ABBREVIATIONS

acac,	$CH_3COCH{=}C(CH_3)O-$
diars,	o-$C_6H_4(AsMe_2)_2$
dip,	o-$C_6H_4(PMe_2)_2$
diphos,	$Ph_2PC_2H_4PPh_2$
triars,	$MeAs(C_2H_4AsMe_2)_2$
NTA,	$N(CH_2COO)_3$

A. INTRODUCTION

Many transition metals show two distinct stereochemistries associated with the same coordination number. Bimorphism of this type is shown in tetrahedral and square-planar four-coordination, square-pyramidal and trigonal-bipyramidal five-coordination, octahedral and trigonal-prismatic six-coordination and pentagonal-bipyramidal and face-centered octahedral seven-coordination. In most cases there are distinctive features in the types of ligand which give the two stereochemi-

cal forms, for example trigonal-prismatic complexes have so far been obtained only with certain sulphur ligands. In the case of eight-coordination two stereochemical forms are again found, the dodecahedron and the square antiprism, but there is no such discrimination in the type of ligand. With the same metal ion in the same oxidation state, very closely similar ligands give complexes of different geometry. This situation, which may be termed *ambimorphism*, is unique to eight-coordination, the only case which approaches it at all closely is that of five-coordination. Eight-coordination is also unique in that the configuration with maximum symmetry (the cube) is not one of the two forms adopted.

The object of this review is to examine the origins of this ambimorphism and the factors influencing the choice of stereochemistry. The discussion is prefaced by a consideration of the factors governing the formation of complexes of high coordination number (i.e. coordination numbers greater than six). The treatment will be that appropriate to *d*-block transition metals but much of what is said would apply equally to other systems.

B. FACTORS INFLUENCING THE COORDINATION NUMBER

(i) *Electronic configuration of the metal ion*

The simplest approach to the correlation of electronic configurations with coordination numbers is the valence-bond approach, by which the coordination number might be expected not to exceed the number of orbitals unused by non-bonding electrons. If the coordination number equals the number of such orbitals, this becomes the "nine-orbital" or "eighteen-electron" rule familiar in the chemistry of metal carbonyls[1]. This rule also follows from molecular-orbital or ligand-field treatments provided that the energy separation between the non-bonding and anti-bonding orbitals (the ligand-field splitting) is large. Any non-bonding electrons in excess of the number required just to fill the non-bonding orbitals would have to be accommodated in the anti-bonding orbitals with an unfavourably high energy. Thus, for complexes with ligands high in the spectrochemical series or for complexes of the heavier transition metals or first-row metals in high oxidation states, i.e. whenever maximum spin-pairing occurs, the nine-orbital rule allows prediction of the maximum coordination number from the electron configuration and *vice versa* (Table I). In these conditions, the maximum coordination is usually attained.

When large ligand-field effects do not operate, as in many of the complexes of the first-row transition metals, the nine-orbital rule does not hold. The anti-bonding orbitals are now of lower energy and there will be no restriction on the number of formal non-bonding electrons. Spin-free complexes are common as the relatively small promotion energy can easily be overcome by the gain in exchange

TABLE I

Number of d-electrons	*Maximum hybridisation*	*Examples*
0	d^5sp^3	$[ReH_9]^{2-}$
1,2	d^4sp^3	$[Mo(CN)_8]^{3-}$, $[Mo(CN)_8]^{4-}$
3,4	d^3sp^3	$[W(CO)_3(diars)Br_2]^+$, $[Mo(CO)_4X_3]^-$
5,6	d^2sp^3	$[W(CO)_2(diphos)_2]^+$, $Cr(CO)_6$
7,8	dsp^3	$Ni(PEt_3)_3Br_2$, $Ni(triars)Br_2$
9,10	sp^3	$[CuCl_4]^{3-}$, $Ni(CO)_4$

energy and reduction in inter-electronic repulsion. In these circumstances the coordination number cannot be deduced simply from a knowledge of the number of *d*-electrons on the metal ion. For instance, the complexes of chromium(II) (d^4) are usually six-coordinate but with strongly π-bonding ligands, seven-coordination is achieved as predicted by the nine-orbital rule, e.g.[2] $M(triarsine)(CO)_2X_2$. In the second and third rows, where spin-pairing predominates, the nine-orbital rule is a useful guide. Thus, complexes of zero-valent (d^6) and univalent (d^5) molybdenum and tungsten are invariably six-coordinate, while those of the divalent elements are usually seven-coordinate[3]. Whether spin-pairing will force an increase or decrease in the coordination number clearly depends on the number of non-bonding electrons. For the first-row transition metals the common coordination number is six, regardless of electron configuration. For spin-paired complexes, where the nine-orbital rule applies, the coordination number is governed by the number of non-bonding electrons, as shown above, and low coordination numbers will be found in the later Groups of the Periodic Table. In the nickel–palladium–platinum triad, for instance, the "natural" coordination numbers for divalent ions (d^8) are six (Ni) and four (Pd, Pt).

For the heavier metals or for ligands high in the spectrochemical series, then, the occurrence of high coordination numbers would be expected to be restricted to the earlier Groups, since several orbitals may be made available without unduly raising the oxidation state of the metal. As will be shown below, a high oxidation state will probably lead to a relatively low coordination number.

For the higher oxidation states and for the first-row transition metals, the available orbitals are not necessarily all used in σ-bond formation. For instance, d^0 complexes are usually four- or six-coordinate, rather than nine-coordinate as would be expected from rigorous application of the nine-orbital rule. It should be noted, however, that in these complexes the nominally non-bonding orbitals may be involved in π-bonding.

(*ii*) *Energy of the metal orbitals*

High coordination numbers will involve the use of several (more than two) *d*-orbitals. For effective bybridisation the orbitals to be hybridised should have

similar energies. In molecular-orbital terms, the orbitals on the metal should have energies comparable to that of the ligand σ-orbitals. In either case, increasing energy separations between the $(n-1)d$-, ns- and np-orbitals will prejudice the simultaneous use of all the (available) orbitals, and inhibit the attainment of high coordination numbers. As the energy separation increases, the hybridisation will tend towards the d^3s- or sp^3-type (or even sp-type)[1]. Fig. 1 shows that the separation between the $(n-1)d$- and np-orbitals of the neutral atoms increases sharply along the transition series. For positively charged ions the trends are similar. This effect is, of course, due to the steadily increasing effective nuclear charge acting on the d-electrons. The ns- and np-electrons are better shielded and their energy falls more slowly.

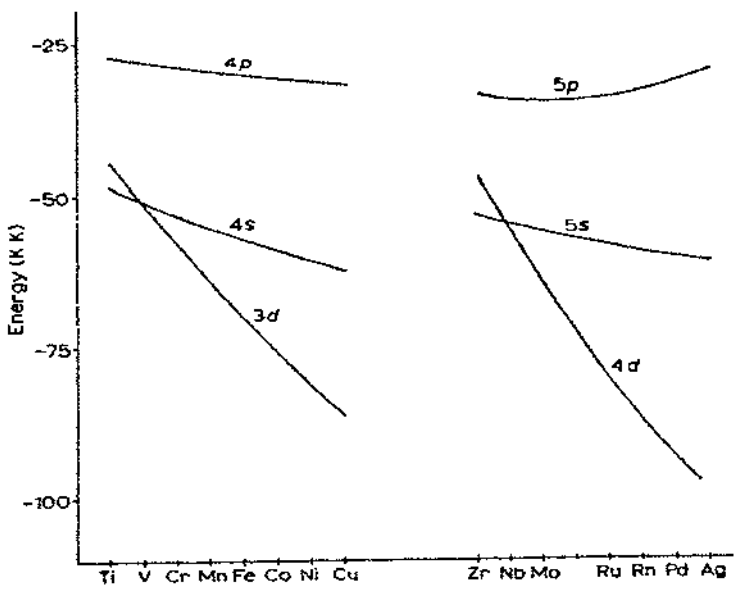


Fig. 1. Orbital ionisation energies. Values for first-row transition elements are from BALLHAUSEN AND GRAY, *Molecular Orbital Theory*, Benjamin, New York and Amsterdam, 1964; those for the second-row elements were computed from Moore's data (N.B.S. Circular 467, 1949–1952). Both sets have been smoothed.

It is thus only in the earlier Groups, where several orbitals are readily available, that the energies of the orbitals are suitable for the formation of complexes of high coordination number.

It is interesting that the energies and energy separations for the first- and second-row transition metal atoms are similar. It will be necessary, therefore, to seek elsewhere for the reasons for the apparent reluctance of the first-row metals to assume high coordination numbers.

(iii) Oxidation state of the metal

The electroneutrality principle[4] suggests that the metal ion in a complex will accept sufficient charge from the ligands to make it approximately electrically neutral. For metals in low oxidation states, complexes are usually obtained predominantly with π-acceptor ligands which are able to remove some of the charge placed on the metal by π-bonding. The discussion above has shown that for such ligands the coordination number is limited by the number of non-bonding electrons.

For higher oxidation states, the coordination number may be limited by the polarising power of the metal ion. A small, highly-charged metal ion would polarise the ligands to a high degree and excessive charge transfer to the metal might occur unless the ligands were very electronegative. The polarising power is determined by the charge : radius ratio, and it may be this effect which apparently inhibits the first-row metals from taking high coordination numbers. Again it seems likely that complexes of high coordination number are more likely to occur in the early Groups where the ionic radii are larger and sufficient orbitals may be made available without too high an oxidation state.

Electrostatic considerations suggest that a certain minimum charge on the metal ion is necessary, the magnitude of which depends on the coordination number. The charges on the metal ion and the ligands will lead to repulsion between the ligands and attraction between the metal and ligands. For any given arrangement of ligands to he stable, the attraction must at least balance the repulsion. As the number of ligands increases, the repulsion between them increases and a higher charge on the metal atom is needed for electrostatic stability. This is illustrated in Fig. 2, wbere the net electrostatic energy of a complex $[M^{z+}(X^{-})_n]^{(n-z)-}$ is plotted as a function of the charge, z, on the metal ion for various coordination numbers, n, assuming constant metal–ligand distances (shielding by the metal atom is ignored). The charge, z_0, which is necessary just to achieve an electrostatic balance increases steadily as the coordination number increases. If the not-unreasonable assumption is made that the effective charge on the metal increases with increasing oxidation state, then higher coordination numbers require higher minimum oxidation states[1].

It should he noted that to ensure ahsolute electrostatic stability for any complex, relative to those of lower coordination number, a charge rather larger than z_0 is necessary, although this increase is offset to a considerable extent by the decrease in the radius of the metal ion as the charge increases. (Note also that z_0 is independent of radius, but that the slope of the line through z_0 is inversely proportional to the metal–ligand distance.) Fig. 2 also shows the superiority of the even coordination numbers over five- and seven-coordination.

On this basis, high coordination numbers would be expected to be favoured by oxidation states high enough to overcome the effects of ligand–ligand repulsion but not so high as to make the metal ion too polarising.

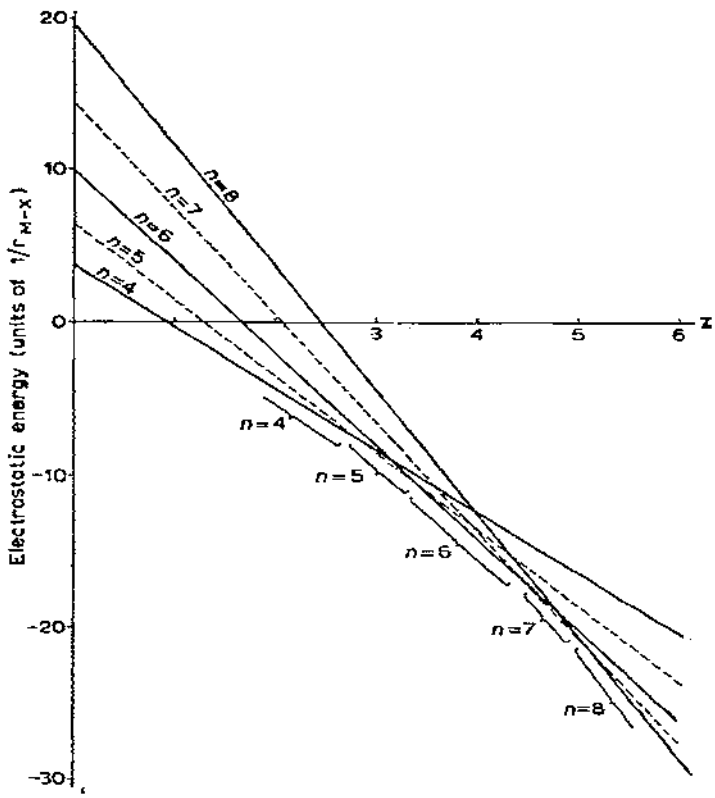


Fig. 2. Net electrostatic energies for complexes of various coordination number. The energies are those of complexes $M^{z+}(X^-)_n^{(n-z-)}$. The M–X distances are assumed identical and shielding by the metal atom is ignored.

(iv) Crystal-field stabilisation

For complexes containing non-bonding *d*-electrons, crystal-field effects might have an influence on the coordination number. The one-electron energies of the *d*-orbitals in fields of various geometry have been tabulated by Basolo and Pearson[5]. These values and the estimated values for eight-coordination[6] are shown in Fig. 3. For complexes with few *d*-electrons the advantages of increasing coordination number are obvious. The gain in stability on going from the tetrahedron to the cube amounts to 2.67Dq and distortion of the cube to either of the observed eight-coordinate geometries results in further stabilisation. With a Dq of 1 to 3 kcal/mole, crystal-field stabilisations could contribute a few kcal/mole as an incentive for an increased coordination number.

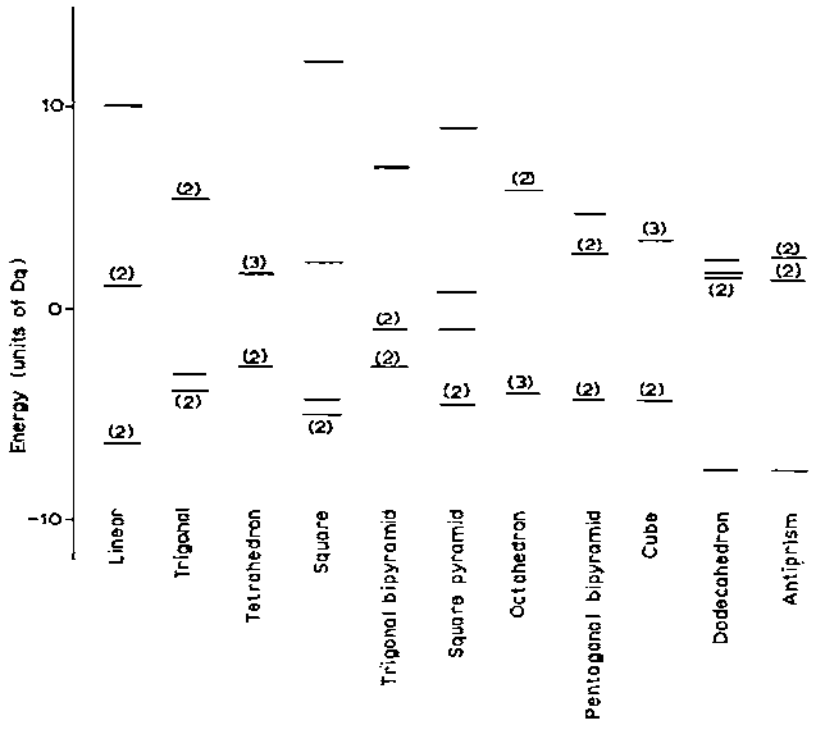


Fig. 3. Crystal-field *d*-orbital energies. Figures in parentheses are orbital degeneracies.

(v) *Type of ligand*

Steric effects apart, the nature of the ligand will have a major effect on the coordination number, since the metal ion relies on the transfer of charge from the ligands to achieve its own electroneutrality. Clearly, neutrality may be achieved with a small number of polarisable ligands or a large number of less-polarisable ligands. The use of readily-polarisable ligands might therefore be expected to militate against the attainment of high coordination numbers. The relative stabilities of $[FeCl_6]^{3-}$ and $[FeF_6]^{3-}$ have been attributed to this effect[7]. (The instability of $[FeCl_6]^{3-}$ with respect to $[FeCl_4]^-$ is not a steric effect, since FeX_6 arrangements are perfectly satisfactory in the lattices[8] of $FeCl_3$ and $FeBr_3$. (Presumably charge transfer to the metal is reduced in these lattices because each halogen is in contact with two metal atoms.) On this basis, higher coordination numbers would be favoured by "hard" ligands, low in the nephelauxetic series, such as F^- and O-donors. A number of complexes is known in which high coordination numbers are achieved with "soft" donors like As, Cl^-, CN^-. For d^1 and d^2 complexes some reduction of the charge on the metal may be achieved through π-bonding, although this is unlikely to be extensive for metals in high oxidation

states. This mechanism cannot in any case operate for d^0 complexes. The implicit assumption was made above that increase in the coordination number necessarily gave increased charge on the metal ion. This would probably be true if the metal–ligand bond distance were constant. However, the effects of ligand–ligand repulsion lead to increased distances for higher coordination numbers. For instance, the Ti–Cl distances in $TiCl_4$, $[TiCl_6]^{2-}$ and $TiCl_4 \cdot 2$ diars] are 2.18, 2.34 and 2.46 Å respectively[9, 10]. Similarly, for $SnCl_4$ (2.32 Å) and $[SnCl_6]^{2-}$ (2.42 Å)[9]; in this case the Mössbauer spectra[11] clearly indicate that the charge density (*s*-electron density) is less in the anion, in accord with the increased bond length. Such increases in bond length, with concomitant decrease in charge transfer to the metal ion, could allow high coordination numbers even for polarisable ligands.

It should be mentioned, however, that bond lengths do not always increase with increasing coordination number. For instance, in the Ta^V–F system the bond lengths are[12–14]:

$[TaF_6]^-$ 2.13–2.15 Å, $[TaF_7]^{2-}$ 1.94–2.01 Å, $[TaF_8]^{3-}$ 1.93–2.01 Å.

C. EIGHT-COORDINATION

The preceding analysis suggested overwhelmingly that high coordination numbers would be restricted to metals of the earlier Groups in moderately-high oxidation states. Examination of Table II shows that these conclusions are confirmed for the eight-coordinate complexes reported to date, with the exception of some nitrato complexes (which will be discussed later). Thus, eight-coordinate complexes are found predominantly in metals of Groups IV, V and VI, in oxidation states of +4 and +5, with electron configurations of d^0, d^1 and d^2 (spin-paired). The ligands most likely to give high coordination numbers seemed to be hard ligands, low in the nephelauxetic series, although softer ligands were not entirely excluded. In practice, the majority of eight-coordinate complexes are found with fluoro- and oxygen-donor atoms, but a substantial number of complexes with polarisable ligands is known.

As mentioned previously, ambimorpbism is the most remarkable aspect of eight-coordination. This is most strikingly shown (Table III) by the zirconium(IV) complexes, where, for instance, tbe two forms of the basic sulphate have different geometry although the coordination spheres differ only in that two hydroxide groups are replaced by water molecules[42, 43].

With the lower coordination numbers it is usually possible to find distinct differences between the ligands which give the two types of complex. For instance, tetrahedral complexes are usually found with polarisable ligands, low in the spectrochemical series and square-planar complexes with ligands high in this series; trigonal-prismatic coordination has so far been achieved only with certain unsaturated sulpbur-ligands. No such distinction is evident for eight-coordination. To give

TABLE II

EIGHT-COORDINATE COMPLEXES OF THE *d*-BLOCK METALS

III[15]					
$[Sc(tropolone)_4]^-$		$[Y(tropolone)_4]^-$		$[La(tropolone)_4]^-$	
IV					
$Ti(diars)_2Cl_4$	10	$Zr(diars)_2Cl_4$	10	$Hf(diars)_2Cl_4$	10
$Ti(diars)_2Br_4$	10	$Zr(diars)_2Br_4$	10	$Hf(diars)_2Br_4$	10
$Ti(dip)_2Cl_4$	20				
		ZrF_4	21	HfF_4	21
		$[ZrF_6]_n^{2n-}$	22	$[HfF_6]_n^{2n-}$	22
		$ZrF_4 \cdot 3\,H_2O$	23	$HfF_4 \cdot 3\,H_2O$	24
		$[Zr(C_2O_4)_4]^{4-}$	30, 31	$[Hf(C_2O_4)_4]^{2-}$	30
		$Zr(acac)_4$	32		
		$[Zr(NTA)_2]^{2-}$	33		
$Ti(S_2CNR_2)_4$	34	$Zr(S_2CNR_2)_4$	34	$Hf(S_2CNR_2)_4$	34
$Ti(NO_3)_4$	35, 36	$Zr(NO_3)_4$	37		
		$Zr(BH_4)_4$	38	$Hf(BH_4)_4$	38
		$Zr(IO_3)_4$	39		
		$ZrSiO_4$	40		
		$Zr(SO_4)_2 \cdot 4\,H_2O$	41		
		$Zr(OH)_2SO_4$	42, 43		
		$Zr_2(OH)_2(SO_4)_3 \cdot 4\,H_2O$	43		
		$Zr(OH)_2(NO_3)_2 \cdot 4\,H_2O$	43		
		$ZrOCl_2 \cdot 8\,H_2O$	44		
		$ZrOBr_2 \cdot 8\,H_2O$	44		
V					
$V(diars)_2Cl_4$	17	$Nb(diars)_2Cl_3$	17		
		$Nb(diars)_2Br_4$	17		
		$Nb(diars)_2I_4$	17		
				$[TaF_8]^{3-}$	14
$[V(O_2)_4]^{3-}$	45	$[Nb(O_2)_4]^{3-}$	45	$[Ta(O_2)_4]^{3-}$	45
		$Nb(S_2CNMe_2)_4$	34		
VI					
				$W(diars)Cl_6$	16
		$[MoF_8]^{2-}$	25	$[WF_8]^{2-}$	26, 27
				$[WF_8]^{3-}$	26, 27
$[Cr(O_2)_4]^{3-}$	46				
		$[Mo(C_2O_4)_4]^{4-}$	29		
		$[Mo(CN)_8]^{3-}$	47	$[W(CN)_8]^{3-}$	48
		$[Mo(CN)_8]^{4-}$	47, 50, 51	$[W(CN)_8]^{4-}$	48, 51
		$[Mo(CN)_4(OH)_4]^{3-}$	53	$[W(CN)_4(OH)_4]^{3-}$	54
		$[Mo(CN)_4(OH)_4]^{4-}$	47, 55	$[W(CN)_4(OH)_4]^{4-}$	54
		$[Mo(CN)_4(OH)_3(OH_2)]^{3-}$	47, 55	$[W(CN)_4(OH)_3(OH_2)]^{3-}$	54
		$[Mo(CN)_4(OH)_2(OH_2)_2]^{2-}$	55	$[W(CN)_4(OH)_3(OH_2)_2]^{2-}$	54
		$Mo(CN)_4(CNR)_4$	56, 58	$W(CN)_4(CNR)_4$	57, 58
		$MoCl_4(Ph_3AsO)_4$	59	$[WBr_3(RNH_2)_5]^{2+}$	60
VII					
		$[Re(diars)_2Cl_4]^+$	19	$[Tc(diars)_2Cl_4]^+$	19
		$[Re(diars)_2Br_4]^+$	19		
		$[ReF_8]^{2-}$	28		
		$[Re(CN)_8]^{3-}$	49		
		$[Re(CN)_8]^{2-}$	49, 52		
VIII					
$[Fe(NO_3)_4]^-$	62				
$[Co(NO_3)_4]^{2-}$	62				

TABLE III

EIGHT-COORDINATE COMPLEXES OF KNOWN STRUCTURE

	Average θ-values		*Edges spanned*	*Eight-coordinate species*	*Ref.*
Antiprismatic					
$Zr(acac)_4$	57.3		*ssss*		32
ZrF_4	57			$Zr(\mu\text{-}F)_8$	21
$ZrOCl_2 \cdot 8\,H_2O$			*ss*	$Zr(OH_2)_4(\mu\text{-}OH)_4$	44
$Zr(SO_4)_2 \cdot 4\,H_2O$	56.7			$Zr(OH)_4(\mu\text{-}OSO_2)_4$	41
$Zr(OH)_2SO_4$				$Zr(\mu\text{-}OH)_4(\mu\text{-}OSO_3)_4$	42
$Zr(IO_3)_4$	58.0			$Zr(\mu\text{-}OIO_2)_4$	39
Na_3TaF_8	59.0				14
K_3ReF_8	57.7				28
Dodecahedral					
$Ti(diars)_2Cl_4$	36.3	74.6	*aa*		10
$Ti(NO_3)_4$*	37.2	80.7	*mmmm*		35
$Na_4Zr(C_2O_4)_4$	35.2	73.5	*mmmm*		31
K_2ZrF_6	35.3	74.6	*mm*		22
$Zr_2(OH)_2(SO_4)_3 \cdot 4\,H_2O$			*m*	$Zr(OH_2)_2(\mu\text{-}OH_2)(\mu\text{-}OSO_4)$	43
$Zr(OH)_2(NO_3)_2 \cdot 4\,H_2O$			*m*	$Zr(OH_2)_2(\mu\text{-}OH)_4(\mu\text{-}ONO_2)_4$	43
$K_4Zr(NTA)_2$			*amg*		33
$ZrSiO_4$					40
$K_3Cr(O_2)_4$	43.4	86.8	*mmmm*		46
$K_4Mo(CN)_8 \cdot 2\,H_2O$	34.2	74.0			50
$K_4W(CN)_8 \cdot 2\,H_2O$					48
$(Ph_4As)_2Co(NO_3)_4$	46.5	81	*mmmm*		72

* I am indebted to D.S.C. Wallwork for making this results available.

further examples[14,28], $[TaF_8]^{3-}$, $[ReF_8]^{2-}$ and[21] the polymeric ZrF_4 and HfF_4 are antiprismatic, while in K_2ZrF_6 and K_2HfF_6 the anions form chains of linked dodecahedra[22]. The complex $K_4Mo(CN)_8 \cdot 2\,H_2O$, the first eight-coordinate complex to be investigated by X-ray methods[50], was found to have the well-known dodecahedral structure. Recent E.S.R. evidence[63,64] suggests that the corresponding complex of the pentavalent metal, $[Mo(CN)_8]^{3-}$, is antiprismatic in solution (the configuration of $[Mo(CN)_8]^{4-}$ in solution is not known[51]).

The ambimorphism of the eight-coordinate system presumably implies that the energy difference between the two configurations is small (although this does not necessarily mean that the barrier to interconversion is low). The factors which may be expected to influence the choice of configuration are[65]:

(i) direct bonding interactions,

(ii) mutual repulsion of the ligands,

(iii) the presence of non-bonding electrons,

(iv) the constraints imposed by chelating ligands.

Before these factors are examined individually it is necessary to describe the detailed shapes of the two coordination polyhedra.

Both configurations are most-readily visualised as distortions of a cube (Fig. 4). The antiprism is obtained by rotating a pair of opposite faces until they

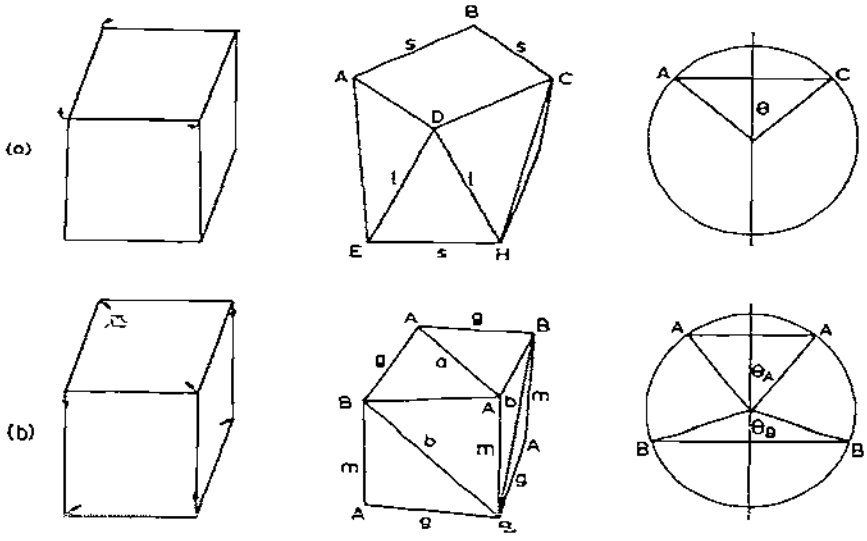


Fig. 4. Geometry of: (a), the square antiprism; (b), the dodecahedron.

are mutually at 45°. Four-fold symmetry is maintained about the axis of rotation and the final symmetry is D_{4d}. All ligands are in equivalent positions and none lie on any of the symmetry elements. To derive a dodecahedron, the cube is divided into its positive and negative tetrahedra, one of which is elongated and the other flattened along the same axis. The ligands thus form two non-equivalent sets (A and B). The symmetry, regardless of the degrees of elongation and flattening, which need not be the same, is D_{2d} and the planes of symmetry each contain four ligands (two each of A and B). Both polyhedra may be characterised by the angles (θ, θ_A, θ_B) which the metal–ligand bonds make with the major symmetry axes. The observed ranges for these angles are θ = 56–59°, θ_A = 34–37°, θ_B = 72–74° (Table III). When the antiprism is viewed along one of the minor two-fold axes, the corresponding angles are very close to the dodecahedral angles[66], but the two polyhedra differ fundamentally in the twisting about the major axis. When the polyhedra are distorted the differences between them become less marked; in practice dodecahedra are sometimes twisted towards the antiprismatic structure. For instance, in $Na_4Zr(ox)_4$ the dodecahedral planes are slightly skewed[31] and in $ZrF_4 \cdot 3\,H_2O$ and $HfF_4 \cdot 3\,H_2O$ (which are not isostructural) pronounced skewing occurs[23,24]. Nevertheless, it is usually relatively easy to discern the ideal shape to which the actual configuration corresponds.

(i) Direct bonding interactions

Eight hybrid orbitals directed towards the corners of an antiprism or dodecahedron can be constructed from the *d–s–p* set of orbitals on the metal. A set

of eight hybrids with cubic symmetry cannot be realised without the use of at least one *f*-orbital, as the d_{z^2}-orbital is now of the wrong symmetry. This restriction applies only for exact cubic symmetry. A dodecahedron of non-equivalent ligands in which $\theta_A = \theta_B = 54° 44'$ could in principle be obtained from d^4sp^3 hybridisation, although arguments based on group overlap integrals show that the d_{z^2}-orbital would contribute nothing to the bonding.

Both antiprismatic and dodecahedral hybridisation have been examined by the Pauling method, assuming that all $(n-1)d$-, ns- and np-orbitals have identical radial functions[67-69]. In D_{4d} symmetry the d_{z^2} and s-orbitals both transform as A_1 and both will be involved in σ-bonding, the highest bond strength being obtained with a $d^{4.15}s^{0.85}p^{3.00}$ set[67, 68]. The strength of these hybrids is 2.99 and they correspond to $\theta = 61°$. Better agreement with the experimental θ-values is obtained by omitting the d_{z^2}-orbital, the contribution of which is very small; a d^4sp^3 set gives a strength of 2.98 and $\theta = 57.6°$. Similar conclusions are reached from calculations of group overlap integrals[70], which give the optimum θ-values as 57–59°. In both cases the bond strength is insensitive to variation in θ, the changes being about 0.06% per degree over a range of 5–10° from the optimum.

For the dodecahedron, the best hybrid orbital strength is obtained by maximising the combined strength of the A and B sets. The hybrids thus found are[68,69]

set A, $d^{2.16}s^{0.42}p^{1.42}$, strength 2.99_5, $\theta_A = 34.6_5°$
set B, $d^{1.84}s^{0.58}p^{1.58}$, strength 2.97, $\theta_B = 72.8°$.

Set A gives bonds which are marginally stronger (and longer) than set B, and the average strength, 2.98, is virtually identical to that of the antiprismatic set. Group overlap integrals give a result a few percent larger than for the antiprism[70]. The maximum is again rather flat, although slightly steeper than for the antiprism, the variation being about 0.1% per degree.

It appears that there is probably no great difference in the bond strengths of the two configurations. The optimum shapes coincide with those observed, but the variations of bond strength with angle would not be sufficient to define the shapes to better than 5–10° (the total bond strength probably amounts[65] to 50–60 kcal/mole in a system like ZrO_8).

π-bonding is possible in both systems, several orbitals having the right symmetry. As a first approximation, it could be assumed that only orbitals not engaged in σ-bonding would be available for π-bonding. This restricts discussion to the d_{z^2}-orbital in the antiprism and the $d_{x^2-y^2}$-orbital in the dodecahedron. It has been suggested that the use of the d_{z^2}-orbital in π-bonding would be ineffectual and unconventional. It is certainly not the latter, as this type of π-bonding is very familiar in tetrahedral complexes like $[SiO_4]^{2-}$, $[PO_4]^{3-}$, $[CrO_4]^{2-}$ and $[MnO_4]^-$. The relative effectiveness of π-bonding in the two configurations may be assessed from the group overlap integrals[70], which are $2\sqrt{6}\sin\theta \cdot \cos\theta \cdot$

$S(d_z, \pi)$ for the antiprism and $2(\sin\theta_A + \sin\theta_B)S(d_\pi, \pi)$ for the dodecahedron. For observed angles in the two systems, e.g. $\theta = 58°$, $\theta_A = 36°$, $\theta_B = 73°$, the π-bond strengths are in the ratio 1 : 1.40 (antiprism : dodecahedron). π-Bonding involving the d_{z^2}-orbital is thus considerably weaker than that with $d_{x^2-y^2}$ but is by no means negligible. In considering the effects of π-bonding on stereochemistry it might be anticipated that the dodecahedron would be favoured by strongly π-donating (d^0) or strongly π-accepting ligands (d^2). It is difficult to find evidence for this effect but it may contribute to the change from antiprismatic $[W(CN)_6]^{3-}$ (d^1) to dodecahedral $[W(CN)_8]^{4-}$ (d^2), although Coulombic interactions will also be important in this case. In a dodecahedral complex the B set of ligands are better able to participate in π-bonding than the A set; at $\theta_A = 36°$, $\theta_B = 73°$ the overlaps are in the ratio 1 : 1.63 (A : B). It has been suggested[71] that this is the factor responsible for the observed substitution of only four CN-groups in the photo-hydrolysis of $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$.

The effect of significant π-bonding would be to increase θ_B (and possibly θ_A). In the antiprism, the maximum π-bond strength would be obtained for $\theta = 45°$, and a decrease in θ would be expected. No evidence for such effects has been obtained.

(ii) Mutual repulsion of the ligands

The relative ligand–ligand repulsion energies may be assessed[6,65,66] by computing the sum of twenty-eight terms of the type r_{ij}^{-n}, where r_{ij} is the distance between the ith and jth ligand and n is determined by the type of interaction considered, being unity for Coulombic interaction and 6 to 12 for Born repulsions between closed electron shells. The repulsion is a function of the metal–ligand distance and the characteristic angles of the polyhedra. If the repulsions are minimised for constant bond lengths, the optimum angles are very close to those observed in crystalline complexes (Table IV), although θ_B is perhaps a little low. It is douhtful whether this agreement is really significant, as the repulsion minima are very shallow. The

TABLE IV

RELATIVE LIGAND–LIGAND REPULSION ENERGIES AND OPTIMUM SHAPES[a]

The relative repulsion energies are the sums Σr_{ij}^{-n}

	$n =$	1	2	6	7	10	12
Antiprism		19.675	14.337	5.186	4.168	2.242	1.503
	θ	55.9	56.2	57.1	57.3	57.7	57.9
Dodecahedron		19.682	14.352	5.245	4.239	2.329	1.592
	θ_A	38.3	38.0	37.4	37.2	37.1	37.0
	θ_B	72.0	71.8	71.4	71.3	71.0	70.8
Cube ($\theta_A = \theta_B = 54.7°$)		19.741	14.500	5.758	4.803	2.941	2.170

closed-shell repulsions will have a greater effect in determining the shape of the polyhedra, as the minima become better defined for the higher n-values (approximate rate of change for the repulsion energies are 0.01% per degree ($n = 1$), 0.5% per degree ($n = 6$) and 2% per degree ($n = 12$)).

The differences in the repulsion energies for the two polyhedra are very small, being only 0.03% for Coulombic repulsion and 1.13 to 5.86% for $n = 6$ to 12, the differences always being in favour of the antiprism. (The cube is even less favourable, 0.33% and 13–44% respectively.) It is unlikely that these differences could influence the choice of configuration, since the energies involved are very small. The electrostatic repulsion energy in a complex of the type $[ML_8]^{4-}$ could amount to about 1000 kcal/mole but the difference between the two configurations would be only 0.3 kcal/mole[6]; for neutral complexes the difference would be even smaller. For Born repulsions ($n = 7$) Hoard and Silverton have estimated a value of 56 kcal/mole for the ZrO_8 system[65]. In this case the difference would amount to about 1 kcal/mole.

Two factors can lead to stabilisation of the dodecahedral configuration. The full symmetry of this arrangement is maintained even if the M–A and M–B bond lengths are not the same. It has been shown that increasing the M–A/M–B ratio lessens the repulsion by reducing interactions between A–A pairs, the largest of the component interactions[65]. In the ZrO_8 system, the M–A/M–B ratio varies from 1.01 to 1.06. Kepert has shown[66] that increase in this ratio has little effect on the optimum shape for Coulombic repulsion, but for the Born repulsions θ_A is reduced and θ_B increased by about 0.5°. There is no obvious reason why similar distortion should not occur for the antiprism (except, perhaps, the intuitive "law of maximum symmetry") but the effect has not been considered theoretically. In practice, variations in the bond lengths in a single antiprism do occur but the variations are not as great as in the dodecahedral complexes nor are they systematic. It seems that these variations are best attributed to crystal-packing effects.

The second factor is the shielding which the metal atom will give to non-adjacent ligands. Shielding of this type will be effective only for small values of n, since for larger values the interactions are short-range only. While it is not possible to estimate accurately the effects of shielding, qualitatively it is obvious that this becomes more effective in the series antiprism < dodecahedron < cube. Estimates suggests that in highly-polar complexes the dodecahedral (and cubic) configuration might be considerably stabilised[6]. This is a possible contributory factor to the difference between $[M(CN)_8]^{3-}$ (antiprismatic) and $[M(CN)_8]^{4-}$ (more polar, dodecahedral). It may also be significant that for zirconium, for which a large range of eight-coordinate complexes has been investigated, all the anionic complexes are dodecahedral.

(iii) Effect of non-bonding electrons

Non-bonding electrons could affect the shape of eight-coordinate complexes in three ways: by repulsion of the ligands, by giving rise to crystal-field stabilisation effects and by involvement in π-bonding. The effect of π-bonding has already been treated.

In the antiprism the non-bonding electrons must be accommodated in the d_{z^2}-orbital which lies along the $\bar{8}$-axis. All eight ligands would therefore be affected equally and no irregularity in bond lengths would be produced. At the normal angle of $\theta = 58$–$59°$, interaction of the σ-bond pairs of the ligands is slightly greater with the equatorial belt of the d_{z^2}-orbital than with the axial lobes (the overlap is zero at 54°44′). Similarly, for a ligand with π-electrons, interaction would be greatest with the equatorial belt (π-overlap is maximum at 45°, as θ increases the improved overlap with the belt is more than offset by decreased overlap with the axial lobes). In both cases, therefore, the effect of non-bonding electrons might be expected to produce a slight decrease in θ.

For a dodecahedral complex the non-bonding electrons must occupy the $d_{x^2-y^2}$-orbital. In this case repulsion effects, both on σ- and π-electrons of a ligand, would be most pronounced for the ligands of the B-set. The effect would presumably be a slight lengthening of the M–B bonds and a slight decrease in θ_B. Both these changes would lead to a small increase in θ_A.

Detailed X-ray data for complexes with non-bonding electrons are available[28,46,50] only for $[Mo(CN)_8]^{4-}$ (d^2), $[ReF_8]^{2-}$ (d^1) and $[Cr(O_2)_4]^{3-}$ (d^1). For the last the constraints imposed by the ligand will have a greater effect on the shape than any possible non-bonding interactions. For the other two complexes the observed angles are not all abnormal, but repulsion might account for the equality[65] of the M–A and M–B bond lengths in $[Mo(CN)_8]^{4-}$.

Crystal-field stabilisation effects would occur for both configurations and are comparable in magnitude, with possibly a slight advantage to the dodecahedron. Within the range of observed shapes the ranges are[6]: dodecahedron ($\theta_A = 34$–$37°$, $\theta_B = 72$–$74°$), $1.1\,\alpha_4$ to $1.4\,\alpha_4$; antiprism ($\theta = 56$–$59°$) $0.8_5\,\alpha_4$ to $1.2\,\alpha_4$. These values would be increased by π-bonding. Differences of several kcal/mole are possible between these extremes. The effect of these stabilisations would be to increase θ in the antiprism and to decrease both angles in the dodecahedron.

(iv) Nature of the ligand

The nature of the ligand may influence the stereochemistry in several ways. In the above discussions, it was assumed that all eight ligands were identical. If this identity is removed, say by using two different ligands, $ML'_4L''_4$, the balance between the two configurations, hitherto very even, may be upset. Intuitively the dodecahedron appears to have an advantage since, provided L′ and L″ are

distributed in the A and B positio ns respectively, there will be no loss of symmetry. While there is no justification for this intuitive "law of maximum symmetry", there are distinct advantages in the dodecahedral arrangement. It has already been noted that the B-position is more favourably positioned for π-bonding. Equally, there is an advantage in lengthening tbe M–A bonds, whicb might encourage the less electronegative ligand to occupy these positions. Finally, if the ligands differ in size, the larger would be better accommodated on the B-sites. It is presumably significant, then, that all eight-coordinate complexes for which the two sets of ligands differ appreciably and whose structures are known, are dodecahedral (Table III). Kepert has suggested the term "stoicheiometric control" of stereochemistry for these complexes[66].

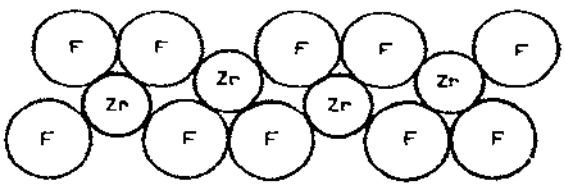
The mixed mono–bi–denated complexes, $M(diars)_2X_4$, also capitalisme on the peculiarities of the dodecahedron[10], in that the As atoms occupy the A-sites, with the ligand spanning the *a*-edges. The *m*-edges are of the right length to accommodate the chelate, but this would mean that the four halide ions would be distributed between two A- and two B-sites, giving tbem an unlikely degree of non-equivalence. The remaining possibility, that of placing the Cl atoms in the A-positions, requires the ligand to span the *b*-edges which would be too long (4.0 Å compared to 3.2 Å for *a* and *m*).

For tetrakis-bidentate complexes several configurations are possible. These may be labelled by specifying the edges which are spanned by the ligands. For a given bond length (e.g. 2.2 Å in the ZrO_8 system) the edges *a* and *m* of the dodecahedron and *s* for the antiprism all have the same lengtb (2.6 Å). Edges *g* and *l* are slightly longer (2.7 and 2.8 Å, respectively) and *b* is much longer (3.2_5 Å). It does not seem possible to make a choice between the polyhedra on this basis, nor even between the possible isomers (e.g. the ring span of acetylacetone is 2.67 Å). It is probable that a *gggg* configuration could be ruled out as requiring too great a ring span, and mixed configurations in which some ligands occupy *g*-edges and the remainder other edges would require impossibly large differences between the spans of nominally-identical ligands. When the effects of non-bonding interactions are also taken into account the most likely configurations appear to be *llll*, *ssss* and *mmmm*[65].

From the limited data available, these do appear to be the favoured arrangements. For antiprismatic complexes the *s*-edges appear to be preferred, as in[32] $Zr(acac)_4$ and[44] $ZrOHal_2 \cdot 8\ H_2O$; the latter has a tetrameric unit in which ZrO_8 antiprisms share *s* edges (a form of chelation). Several other compounds give extended three-dimensional structures but edge-sharing does not occur often; more usually each antiprism is joined to several others.

Antiprismatic structures with chelating ligands are very rare. While this may simply reflect the small number of structure determinations which have been made, it is more likely that it is due to the ability of the dodecahedron to minimise Coulombic repulsion. The *mmmm* configuration has the least repulsion of any

of the chelate arrangements and is the configuration commonly adopted[65]. Sharing of *m*-edges in dimeric or polymeric structures will also minimise repulsion, leading to the structure of[43] $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ and the chain structure of K_2ZrF_6 and K_2HfF_6[22], although it is not at all clear why this structure should be preferred to the normally acceptable K_2PtCl_6 structure.



D. NITRATO COMPLEXES

The major exceptions to the occurence of eight-coordinate complexes in the early transition-metal Groups are[61] $[Fe(NO_3)_4]^-$ and[62] $[Co(NO_3)_4]^{2-}$. A tetrakis-trifluoroacetato-complex of cobalt(II)[72] is now known not to be eight-coordinate[73]. The structure has been determined for $[Ph_4As]_2Co(NO_3)_4$. The anion has almost exact dodecahedral symmetry with bidentate nitrate groups spanning the *m*-edges; $\theta_A = 47.5°$, $\theta_B = 81°$, M–A = 2.07 Å, M–B = 2.45 Å[62]. The ionic radius of cobalt(II) (0.8 Å) is adequate on the hard-sphere model for the coordination of eight oxygen atoms but it is surprising that a bivalent ion can withstand the effect of donation from so many ligands. It is interesting that in $Ti(NO_3)_4$ all Ti–O bonds have closely-similar lengths (2.068 ± 0.014 Å)[35]. The observed distortion in the cobalt complex may help to alleviate the build-up of charge on the metal. In $[Co(CF_3COO)_4]^{2-}$ the lengthening of the M–B bonds is carried even further so that the complex is effectively four-coordinate with at most only a very weak interaction between the metal and the second set of oxygen atoms[73].

The spectroscopic and magnetic properties of $[Co(NO_3)_4]^{2-}$ are very similar to those for tetrahedal cobalt(II) complexes, and Cotton has suggested that this may be explained by taking a "centre of gravity" for the two oxygen atoms of each nitrate group. These centres form a tetrahedron with angles of[62] 107°. An essentially-similar explanation has been proposed by Addison[74], who postulates that bidentate nitrate groups are bound by a three-centre bond involving only one orbital on the metal.

It has also been suggested that the tetra-peroxy complexes, $[M(O_2)_4]^{3-}$, should be regarded as tetrahedral π-complexes rather than as dodecahedral σ-complexes[75]. The observed shortening of the O–O distance, however, is consistent with σ-donation from the lone pairs in p_π* antibonding orbitals of the peroxy groups.

E. SUMMARY

The occurrence of eight-coordination in *d*-block transition metals agrees with that expected, namely for metals of the early Groups in relatively-high oxidation states. Consideration of the relative bond strengths, interligand repulsion energies and the effects of non-bonding electrons shows that the energies of the antiprismatic and dodecahedral configurations are very similar, differing by not more than about one kcal/mole for each effect. The only significant factor not considered is that of crystal packing. The ambimorphism shown by these systems is therefore not surprising and it is not possible to predict which configuration would be adopted by any given complex. The only exceptions seem to be that the dodecahedron is favoured by Coulombic repulsions in highly-polar complexes or when two markedly-different ligands donate to the same metal atom. The highly-symmetrical cube compares very unfavourably in terms of ligand–ligand repulsion (except in highly-polar complexes) and gives poorer overlap with ligand σ-orbitals. No discrete cubic complexes have yet been reported; even under favourable conditions some distortion occurs[58].

Bond strengths are maximum and interligand repulsions minimum at the observed shapes of both polyhedra, but the maxima and minima are very flat. Born-type repulsions between closed electron shells are probably the interactions which are most important in determining the shape, being the least insensitive to bond angles. An essentially similar conclusion has been reached by Kettle[76].

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