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THE RELATIONSHIP BETWEEN THE BONDING AND STEREOCHEMISTRY OF TRANSITION METAL COMPLEX IONS

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It is common for text-books of chemistry to contain a section in which the phenomenon of molecular structure is discussed and "explained". Two such "explanations" are encountered. The more common is based on valence bond theory and uses a hybrid orbital approach[1]. So, according to this theory, the tetrahedral structure of methane is a consequence of sp^3 hybridization of the central carbon atom, the energy required to promote an s electron into the empty p orbital in the isolated carbon atom being more than compensated for by the increased exothermicity of the subsequent step in which the carbon atom combines with a number of hydrogen atoms. In addition, it is usually noted that sp^3 hybrid orbitals, being directed, give a better overlap with the hydrogen orbitals. Unfortunately, in T_d symmetry, s and p orbitals cannot mix, so that sp^3 hybridization is impossible. If s–p mixing were essential to molecule formation, methane would be of C_1 symmetry.

The second approach to molecular stereochemistry is to say that molecular geometry is governed by steric forces. A detailed review of this explanation has been given by Nyholm and Gillespie[2] who showed that it gave a consistent account of small departures of bond angles from ideality. However, not all molecules obey their "rules". So, it is not apparent why the $C(CN)_3^-$ ion should be planar, or the $[R_3Al–F–AlR_3]^-$ ion and the Li_2O molecule linear. π-Bonding does not provide an entirely convincing explanation.

It seemed worthwhile to remove the symmetry based objections to the valence bond theory and to see whether molecular orbital theory alone, with the neglect of steric interactions, was able to give a qualitative account of molecular geometry, and this is the subject of the present paper. As far as possible we make the same approximations as the VB approach (*e.g.* neglect of π-bonding) but consider only d orbitals on the metal *i.e.* neglect s and p. It is well outside the scope of theory at present to predict bond angles of large molecules at all accurately so the procedure that will be adopted is to calculate the relative stabilities of a variety of possible structures for a molecule within an independent electron approximation and to compare the results with the structure observed.

Consider the equation

$$\begin{vmatrix} H_{11}-E & \mathrm{k}S_{12} \\ \mathrm{k}S_{12} & H_{22}-E \end{vmatrix} = 0 \tag{1}$$

Its solutions are

$$E = \tfrac{1}{2}\left[H_{11}+H_{22} \pm (H_{11}-H_{22})\left(1+\frac{4\mathrm{k}^2S_{12}{}^2}{(H_{11}-H_{22})}\right)^{\frac{1}{2}}\right]$$

If this interaction is to contribute to the molecular stability then only the orbital corresponding to the lower of these roots is occupied. If the square root is expanded then it is easy to show that the stabilization relative to the occupation of the more stable of the interacting orbitals is

$$\Delta E_{\text{stab}} = \frac{\mathrm{k}^2S_{12}{}^2}{(H_{11}-H_{22})} - \frac{\mathrm{k}^4S_{12}{}^4}{(H_{11}-H_{22})^3} + \frac{2\mathrm{k}^6S_{12}{}^6}{(H_{11}-H_{22})^5} - \ldots \tag{2}$$

or

$$\Delta E_{\text{stab}} = \beta S_{12}{}^2 - \beta' S_{12}{}^4 + \beta'' S_{12}{}^6 \ldots \tag{3}$$

If in (1) the off-diagonal matrix elements are approximated by $\mathrm{k}S_{12}-ES_{12}$ then it may be shown that an expression identical to (3) is obtained for ΔE_{stab}, although the β's do not have the values given in (2).

We shall consider transition metal complex ions $ML_4 \rightarrow ML_8$. It is convenient to consider first the case of d^0 complexes with neglect of π-bonding. We shall subsequently extend the treatment to d^n configurations and discuss the effect of π-bonding. Only the interaction between the n ligand orbitals and the d orbitals of the central atom will be considered. In all cases it will be possible to reduce the problem to a set of 2×2 determinental equations, as in (1), as in none of the geometries to be considered do two d orbitals transform independently as the same irreducible representation under the operations of the appropriate point group. Quite often, however, two ligand orbital combinations so transform, but by taking a maximum overlap combination the problem can always be reduced to a 2×2 one. We neglect metal s orbitals. As ligand overlap with this orbital can show no directional preference this neglect is not too drastic. The effect on our calculations is that we slightly over-estimate the steric significance of any orbital which transforms under the totally symmetric representation (if it is included). The neglect of metal p orbitals is probably not too drastic either. They are energetically well separated from the ligand σ orbitals and so unlikely to determine stereochemistries.

The method is simple. We sum the ΔE_{stab}'s for all of the occupied orbitals. This means evaluating the group overlap integrals, S_{12}, which appear in equation (3), the β's being identical for each occupied orbital. Now, the term

$$2\sum_i S_{12}{}^2(\Gamma_i)$$

is independent of the geometry of the complex[3,4] (and equal to $2n\beta$ for a ML_n complex ion)*, so that the first term of steric significance is that of order $S_{12}{}^4$. Consider the case of the methane molecule which we assume to have D_{2d} symmetry. The group overlap integrals are[5]:

$$\begin{aligned} S(A_1) &= 2S_\sigma(1s, 2s) \\ S(B_1) &= 2\cos\vartheta S_\sigma(1s, 2p) \\ S(E) &= \sqrt{2}\sin\vartheta S_\sigma(1s, 2p), \end{aligned}$$

where ϑ is the angle a C–H bond makes with the D_2 axis, so that $2\sum\beta S^2 = 2[4\cos^2\vartheta+2.2\sin^2\vartheta]\beta_{1s,2p}S_\sigma{}^2(1s, 2p)+8\beta_{1s,2s}S_\sigma{}^2(1s, 2s) = 8[\beta_{1s,2p}S_\sigma{}^2(1s, 2p)+ +\beta_{1s,2s}S_\sigma^2(1s, 2s)]$ which, as noted above, is independent of ϑ. It is evident that the A_1 contribution is independent of ϑ, so we neglect it in the following.

The term $2\sum\beta'S^4 = 2[16\cos^4\vartheta+2.4\sin^4\vartheta]\beta'S^4(1s, 2p)$. Since this term is a destabilizing one the favoured geometry will be that for which the factor in square brackets is a minimum. It is easily shown that this occurs at $\tan\vartheta = \sqrt{2}$ *i.e.* $\angle HCH = 109°28'$.

In Tables 1–5 we give group overlap integrals in units of S_σ (σ, d) for ML_n complexes $n = 4 \rightarrow 8$, where L is a unidentate ligand. In each table we also indicate the relative steric favourability of the various geometries by listing the number and distance of the important ligand–ligand contacts, the metal–ligand bond length being taken as unity. Overlap integrals were calculated using the general expressions we have given elsewhere[5].

TABLE 1

GROUP OVERLAP INTEGRALS AND STERIC REQUIREMENTS FOR ML_4 COMPLEXES

	Symmetry	
Metal orbital	D_{4h}	T_d
z^2	1.000	—
x^2-y^2	—	—
xz	—	1.155
yz	—	1.155
xy	1.732	1.155
ΣS^4:	10.0	5.3
Ligand–ligand distance	1.414	1.633
Number of contacts	4	6

d^n *configurations.* d electrons on the central metal atom will first be accommodated in orbitals not involved in metal–ligand bonding (if any). When these orbitals are filled the next occupied will be the lowest antibonding orbitals which will correspond to those orbitals shown with the smallest overlap integrals in the tables. Occupation of these antibonding orbitals means that we can no longer

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* Each orbital is occupied by two electrons.

TABLE 2

GROUP OVERLAP INTEGRALS AND STERIC REQUIREMENTS FOR ML_5 COMPLEXES

	Symmetry					
	D_{3h}	C_{4v}(a)[a]	C_{4v}(b)[b]	*Symmetry*	*Ligand–ligand distance*	*Number of contacts*
z^2	1.658	1.414	1.352	D_{3h}	1.414	6
x^2-y^2	1.061	1.732	1.680		1.732	3
xy	1.061	—	—	C_{4v}(a)[a]	1.414	8
yz	—	0.000	0.419	C_{4v}(b)[b]	1.393	4
zx	—	0.000	0.419		1.532	4
ΣS^4	10.1	13.0	11.4			

[a] C_{4v}(a): The metal atom is coplanar with the plane of four ligands.

[b] C_{4v}(b): The angle between lines joining the metal and one of the equivalent ligands and the metal and the unique ligand is 100°.

TABLE 3

GROUP OVERLAP INTEGRALS AND STERIC REQUIREMENTS FOR ML_6 COMPLEXES

	Symmetry					
	O_h	D_{3h}(a)[a]	D_{3h}(b)[b]	*Symmetry*	*Ligand–ligand distance*	*Number of contacts*
z^2	1.732	0.000	0.351	O_h	1.414	12
x^2-y^2	1.732	1.000	0.857	D_{3h}(a)[a]	1.155	3
xy	—	1.000	0.857		1.414	6
yz	—	1.414	1.485	D_{3h}(b)[b]	1.310	9
zx	—	1.414	1.485			
ΣS^4	18.0	10.0	10.8			

[a] D_{3h}(a): Three ligands at the corners of a face of an octahedron rotated by 60° about the three-fold axis passing through this face.

[b] D_{3h}(b): As for D_{3h}(a) but all nearest neighbour ligand–ligand distances are equal.

TABLE 4

GROUP OVERLAP INTEGRALS AND STERIC REQUIREMENTS FOR ML_7 COMPLEXES

	Symmetry					
	C_{3v}[a]	C_{2v}[b]	D_{5h}	*Symmetry*	*Ligand–ligand distance*	*Number of contacts*
z^2	1.302	1.416	1.803	C_{3v}[a]	1.253	12
x^2-y^2	1.153	0.579	1.369		1.691	3
xy	1.153	1.676	1.369	C_{2v}[b]	1.300	11
yz	1.150	0.348	—		1.506	2
zx	1.150	1.317	—	D_{5h}	1.176	5
ΣS^4	12.6	16.8	17.6		1.414	10

[a] C_{3v}: An octahedron in which an additional ligand caps one face. The structure considered is that in which the maximum number of ligand–ligand distances are equal.

[b] C_{2v}: A trigonal prism in which an additional ligand caps one rectangular face. The structure considered is that in which the maximum number of ligand–ligand distances are equal.

TABLE 5

GROUP OVERLAP INTEGRALS AND STERIC REQUIREMENTS FOR ML_8 COMPLEXES

	Symmetry				
	D_{2d}[a]	D_{4d}(a)[b]	D_{4d}(b)[c]	O_h	D_{6h}
z^2	1.041	0.000	0.316	—	1.871
x^2-y^2	—	1.155	1.283	—	1.500
xy	1.608	1.155	1.283	1.633	1.500
yz	1.472	1.633	1.517	1.633	—
zx	1.472	1.633	1.517	1.633	—
ΣS^4	19.2	17.8	16.0	21.3	22.4

Symmetry	*Ligand–ligand distance*	*Number of contacts*
D_{2d}[a]	1.220	18
D_{4d}(a)[b]	1.155	8
	1.313	8
D_{4d}(b)[c]	1.215	16
O_h	1.155	12
D_{6h}	1.000	6
	1.414	12

[a] D_{2d}: The dodecahedral arrangement. The structure considered is that in which the maximum number of nearest neighbour ligand–ligand distances are equal.

[b] D_{4d}(a): Four ligands at the corners of a face of a cube rotated by 45° about the fourfold axis passing through this face.

[c] D_{4d}(b): As for D_{4d}(a) but all nearest neighbour ligand–ligand distances are equal.

neglect the term of order S^2 in (3). As this term is probably an order of magnitude larger than the term in S^4 (*i.e.* the series is assumed to converge rapidly) we can in general, neglect the latter. In this way Table 6 in which we list those geometries which appear orbitally preferred for d^n configurations $n = 0 \rightarrow 9$, was compiled.

TABLE 6

GEOMETRIES OF TRANSITION METAL COMPLEXES PREFERRED ON THE GROUNDS OF TOTAL ORBITAL STABILIZATION. JAHN–TELLER AND π-BONDING EFFECTS ARE NEGLECTED

	ML_4	ML_5	ML_6	ML_7	ML_8
d^0	T_d	D_{3h}	D_{3h}(a)	C_{3v}	D_{4d}(b)
d^1	T_d	D_{3h}	D_{3h}(a)	D_{5h}	D_{2d}
d^2	T_d	D_{3h}	D_{3h}(a)	D_{5h}	D_{2d}
d^3	T_d	D_{3h}	O_h	D_{5h}	O_h
d^4	T_d	D_{3h}	O_h	D_{5h}	O_h
d^5	D_{4h}	C_{4v}(a)	O_h	D_{5h}	[a]
d^6	D_{4h}	C_{4v}(a)	O_h	D_{5h}	D_{6h}
d^7	D_{4h}	C_{4v}(a)	O_h	D_{5h}	D_{6h}
d^8	D_{4h}	C_{4v}(a)	O_h	D_{5h}	D_{6h}
d^9	D_{4h}	C_{4v}(a)	O_h	D_{5h}	D_{6h}
probably sterically preferred	T_d	C_4(b) (?)	O_h	C_{3v}	D_{4d}(b)

[a] ΣS^2 $(D_{6h}) = 13.75$, ΣS^2 $(O_h) = 13.33$. The difference may be of the order of magnitude of differences in the ΣS^4 terms.

In all cases where choicemay exist we have considered the low-spin arrangetment of d electrons.

π-bonding. The introduction of π-bonding would invalidate some of the steps in our arguments, in particular, the use of 2×2 determinental equations. Strictly, one would have to consider each system individually. However, there are grounds for believing that the inclusion of π-bonding would not greatly alter the data in Table 6. If one were able to treat π-bonding in the same way as σ-bonding *i.e.* set up 2×2 equations analogous to (1) then relationships similar to (3) would result. If, as is generally believed, π-bonding is of less energetic significance than σ, then in the subsequent summation the term $\sum S_\pi^2$ would be of less importance than that which we have considered, $\sum S_\sigma^2$, and similarly $\sum S_\pi^4$ etc. Although this argument is not strictly admissible it does indicate that Table 6 should certainly be correct unless extensive π-bonding is involved.

DISCUSSION

The most obvious thing about Table 6 is that it does not usually correctly predict the structures which are observed. So, for example, all ML_6 complexes are octahedral (neglecting Jahn–Teller distortions). The structures which seem to be sterically preferred, on the other hand, are those commonly observed. The inference seems clear. The geometry of transition metal complex ions is largely determined by steric interactions between the ligand molecules.

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