715. *Double Bonding in Chelated Metal Complexes.*

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The effect of double bonding in chelated octahedral metal complexes is discussed and it is shown that the degeneracy of the t_{2g} orbitals can be removed in certain circumstances. It is suggested that the diamagnetism of tris-*o*-phenanthrolinetitanium is due to this splitting of the t_{2g} orbitals.

THE effect of π bonding on the electronic structure of octahedral transition-metal complexes has been considered by a number of authors. It has been shown that the metal $d(e_g)$ orbitals are unable to combine with π orbitals of the ligands and that although the $d(t_{2g})$ do combine there is no breakdown of their degeneracy so long as the complex has cubic symmetry.[1]

Complexes with axially symmetric ligands, for example hexahalides and hexacyanides, do usually have cubic symmetry, but complexes with less symmetrical ligands such as water, pyridine, or ethylenediamine do not. Here we discuss the way in which the degeneracy of the t_{2g} orbitals is broken down in complexes of planar, conjugated, bidentate ligands such as 1,1'-bipyridyl or the acetylacetonate anion. This discussion leads to a novel explanation of the diamagnetism of tris-1,1'-bipyridyltitanium.[2]

The d *Orbitals of Trichelated Octahedral Complexes.*—We consider a trichelated metal complex MX_3 where M is a transition-metal ion (or atom) and X is a symmetrical bidentate ligand such as ethylenediamine, 1,1'-bipyridyl, or the acetylacetonate anion. We suppose the complex ion to have the maximum symmetry consistent with its composition, namely D_3 symmetry (Fig. 1). Symmetry arguments, independent of any model of the interaction between metal and ligands, show that the d orbitals split into two degenerate pairs belonging to the e representation of the group and one non-degenerate a_1 orbital. These arguments do not indicate the relative energies of the orbitals.

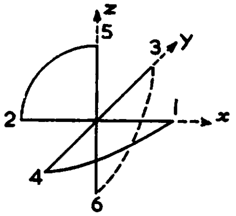

FIG. 1. *The structure of trichelated complexes.*

We may identify the a_1 orbital with one of the t_{2g} orbitals of an octahedral complex and, providing the bond angles do not deviate greatly from those for an octahedral complex, we may, to a first approximation, associate the e orbitals with the remaining t_{2g} and e_g orbitals as shown in Table 1. More complete calculations show that the e orbitals may become mixed together and hence that the forms indicated in the Table are only approximately correct.

Elementary electrostatic arguments show that if we can represent the ligands as point charges or point dipoles the a_1 orbital is lowest in a flattened D_3 arrangement while the e orbital is lowest if the octahedron is elongated. The situation is less clear-cut if σ bonding is taken into account, but it is fairly certain that the above conclusions remain valid. If we neglect π bonding, it follows that the order of the lowest a and e orbitals is likely to be determined by geometrical considerations and that a large splitting between these orbitals is unlikely unless the trigonal distortion of the bond directions is large. We shall show that this conclusion is no longer valid when π bonding is taken into account.

In a symmetric conjugated system such as 1,1'-bipyridyl the π orbitals may be classified

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[1] Orgel, *Proceedings 10th Solvay Conference, Brussels,* 1956.

[2] Herzog and Taube, *Angew. Chem.*, 1958, **70**, 469.

TABLE 1. *The d orbitals in octahedral and D_3 complexes.*

Octahedral	D_3	Symmetry
$d_{(x^2-y^2)}$	$d_{(x^2-y^2)}$	E
d_{z^2}	d_{z^2}	
d_{xy}	$\frac{1}{\sqrt{3}}(d_{xy} + d_{xz} + d_{yz})$	A_1
d_{xz}	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$	E
d_{yz}	$\frac{1}{\sqrt{6}}(2d_{xy} - d_{xz} - d_{yz})$	

according to their symmetry with respect to reflection in the symmetry plane perpendicular to the plane of the molecule. We shall designate the π molecular orbitals as ψ and χ orbitals depending on whether they remain unchanged or change sign under this symmetry operation. It can then be shown by group theoretical arguments, or seen by inspection, that ψ orbitals combine only with the metal e orbitals while χ orbitals combine with both metal a_1 and e orbitals.

To obtain quantitative results we must specify the nature of the combining orbitals more fully. Let us concentrate first on any ligand ψ orbital, which we may suppose to have the form

$$\psi = \sum_i c_i\phi_i$$

where ϕ_i is the $2p_\pi$ orbital on the i'th atom of the conjugated system. We denote by c_L the particular coefficient in this expansion which refers to the atoms linked to the metal. Finally we denote by ψ_A, ψ_B, and ψ_C the ψ orbitals of the ligand molecules which occupy positions 1, 3, and 5, respectively, in the co-ordination sphere.

Then it is readily shown that the appropriate linear combinations of metal orbitals and ligand ψ orbitals (apart from sign) which can combine together are as shown at the top of Table 2. At the bottom of the Table we give the corresponding linear combinations for χ orbitals.

We now discuss the combination of ligand and metal orbitals from the point of view of elementary LCAO molecular-orbital theory. We suppose that there is a single resonance integral β_{ML} given by

$$\beta_{ML} = \int d(t_{2g})\, H\, \phi_L\, d\tau$$

corresponding to all the equivalent interactions between t_{2g} orbitals of the metal and suitably oriented p_π orbitals on the ligands, for example between the d_{xy} orbital and the

TABLE 2. *Symmetry orbitals and interaction energies for D_3 complexes*

	Metal	Ligand	Interaction matrix element
A_1	$\frac{1}{\sqrt{3}}(d_{xy} + d_{xz} + d_{yz})$	—	—
E	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$	$\frac{1}{\sqrt{6}}(2\psi_A - \psi_B - \psi_C)$	$\sqrt{3}c_L\beta_{ML}$
	$\frac{1}{\sqrt{6}}(2d_{xy} - d_{xz} - d_{yz})$	$\frac{1}{\sqrt{2}}(\psi_B - \psi_C)$	
A_1	$\frac{1}{\sqrt{3}}(d_{xy} + d_{xz} + d_{yz})$	$\frac{1}{\sqrt{3}}(\chi_A + \chi_B + \chi_C)$	$2c_L'\beta_{ML}$
E	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$	$\frac{1}{\sqrt{2}}(\chi_B - \chi_C)$	$c_L'\beta_{ML}$
	$\frac{1}{\sqrt{6}}(2d_{xy} - d_{xz} - d_{yz})$	$\frac{1}{\sqrt{2}}(2\chi_A - \chi_B - \chi_C)$	

p_x orbital on the ligand atom at position 3 in the co-ordination sphere. Then the corresponding interaction integrals for symmetry orbitals are as given in column 3 of Table 2.

We shall use these results to discuss only one of the many groups of compounds to which they are relevant, namely the tris-1,1′-bipyridyl derivatives of the transition metals in their lowest valencies. By limiting our discussion to these compounds we are able to neglect all π-electron interactions except those between filled orbitals of the metal and empty orbitals of the ligands.

The first four unoccupied π orbitals of biphenyl are shown in Fig. 2. The corresponding orbitals of 1,1′-bipyridyl may be somewhat different in detail but their general form should be similar; in particular the lowest unoccupied orbital should be a ψ orbital. Since the orbital interacts with and stabilizes the metal e orbital but does not interact with the a_1 orbital it seems plausible that the former might be depressed below the latter by double-bonding. However this effect must be small and hence might be obscured by splitting due to electrostatic forces, σ bonding and d–s mixing, unless the ψ orbital and the e orbital have similar energies.

FIG. 2. *The first four unoccupied orbitals of biphenyl* (Brickstock, Thesis, Cambridge, 1954).

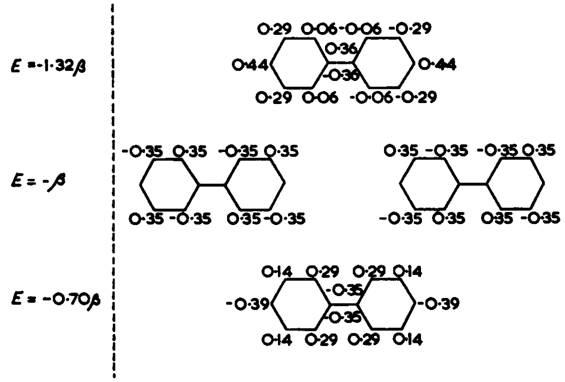
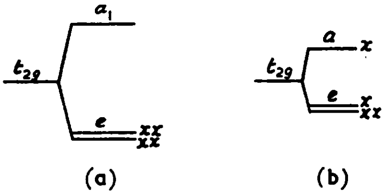


FIG. 3. *Possible electron arrangements for* $(t_{2g})^4$ *systems in trigonal fields.*



(a) *low spin*; (b) *high spin.*

The study of the charge-transfer spectra of 1,1′-bipyridyl complexes of bi- and tervalent metals such as iron shows that for these the metal d orbitals are at least 2—3 ev more stable than the empty ligand orbitals,[3] so that in these the d orbital splitting due to π bonding is probably small. However, in the case of neutral titanium or hafnium atoms the reducing power must be extreme and there can be little doubt that they would reduce bipyridyl if they did not form complexes with it. It is extremely plausible then that in such complexes of very low-valency metals extensive delocalization of metal electrons occurs and is associated with a significant depression of the metal e orbital below the a_1 orbital. We suggest that this is the main source, or at least one of the most important sources, of the energy separation between a_1 and e orbitals which is required to account for the spin-pairing and diamagnetism of tris-1,1′-bipyridyltitanium (Fig. 3).[4] The lesser importance of π bonding and the larger size of the Slater–Condon parameters in the $[V(1,1'\text{-bipyridyl})_3]^+$ ion would then account for its quite different magnetic properties which indicate the presence of two unpaired electrons (Fig. 3).

It should be noted that while a description in terms of metal d electrons more or less spread on to the ligands is usually adequate in describing metal complexes, this is not necessarily true for the compounds of metals in their very lowest valencies. Thus it may be that some of these compounds are better regarded as chelate complexes of the 1,1′-bipyridyl anion radical. It seems very probable that this is so for the lithium derivative

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[3] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 166.

[4] Perthel, *Z. phys. Chem.* (*Leipzig*), 1959, **211**, 74.

and it may well be that the ligands carry a very considerable negative charge in some of the transition-metal compounds also. Nuclear resonance and paramagnetic resonance experiments should throw much light on the details of the electron distribution in the paramagnetic compounds.

Finally we remark on the utilization of metal *s* electrons in these compounds, for *s* orbitals are quite stable in transition-metal atoms. In the group D_3 the *s* orbitals transform as a_1 and hence can become mixed with the a_1 *d* orbital, resulting in new orbitals respectively more and less stable than the *d* and *s* orbitals themselves. It seems unlikely that the *s* orbital is utilized in the titanium compound for then the diamagnetism could only be accounted for if the electron configuration were $s(a_1)^2\, d(a_1)^2$. It is hard to see how both a_1 orbitals could be below the *e* orbital. In the aluminium compound [5] [Al(1,1′-bipyridyl)$_3$]^0 the situation is quite different and it is possible that the 3*s* orbital is indeed occupied.

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[5] Herzog, Abs. of paper presented at Symp. Co-ordination Chem., Prague, Sept. 1960.