528. *Application of Molecular-orbital Theory to Some Binuclear Co-ordination Compounds.*

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Molecular-orbital theory is applied to some binuclear co-ordination compounds of transition metals. For the $(Ru_2Cl_{10}O)^{4-}$ ion the theory involves ruthenium–oxygen double bonding with consequent diamagnetism of the ion. The peroxo-cobalt decammines and iron enneacarbonyl are also discussed.

We have recently used molecular-orbital theory in discussing the structure and stability of di*cyclo*pentadienyliron (ferrocene) and related compounds (Dunitz and Orgel, *Nature*, 1953, **171**, 121). Here, we apply the theory to some binuclear compounds containing transition metals, to show that, in certain cases, it provides a ready explanation of otherwise puzzling aspects of their molecular structure. We shall make considerable use of the theory of group representations and shall employ the nomenclature of Eyring, Walter, and Kimball ("Quantum Chemistry," Wiley, New York, 1944).

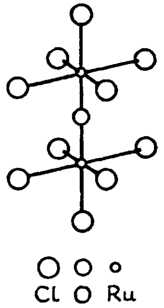


Fig. 1. *Atomic arrangement in* $(Ru_2Cl_{10}O)^{4-}$ *anion* (after Mathieson, Mellor, and Stephenson, *loc. cit.*).

Potassium Hydroxychlororuthenate, $K_4Ru_2Cl_{10}O,H_2O$.—Mathieson, Mellor, and Stephenson (*Acta Cryst.*, 1952, **5**, 185) have shown that potassium hydroxychlororuthenate contains an anion $(Ru_2Cl_{10}O)^{4-}$ with structure as in Fig. 1. Three features seem worthy of comment: (*a*) The substance is diamagnetic in spite of the fact that Ru^{IV} would be expected to have two unpaired electrons. (*b*) The arrangement of Ru–O–Ru is linear. (*c*) The Ru–O bond distance is 1·80 Å, considerably shorter than the sum of single-bond radii, 1·98 Å. The Ru–Cl distance, however, is normal, 2·34 Å. The above authors suggest, as a possible explanation of the diamagnetism, that "the spins of the unpaired electrons on each Ru^{IV} atom are antiparallel but uncoupled. Alternatively some type of electron pairing may take place." The nature of such electron pairing is not specified but a possible analogy with $Fe_2(CO)_9$ is suggested, whence it may be inferred that some type of interaction between the ruthenium atoms is postulated. In view of the long Ru · · · Ru distance, 3·6 Å, any strong direct action seems most unlikely. A footnote refers to a suggestion by Pauling that "if each ruthenium atom has seven orbitals of which two are required for bond formation with the oxygen atom, the diamagnetism would be explained," but Mathieson, Mellor, and Stephenson consider that the structure involving oxygen associated with two double bonds is improbable. We shall show that features (*a*), (*b*), and (*c*) all emerge from a qualitative molecular-orbital treatment which not only confirms Pauling's suggestion but also throws considerable light on the nature of the double bonding involved.

The symmetry of the complex anion is D_{4h} but the local symmetry of each Ru atom is only C_{4v}. In the latter point group, the relevant orbitals transform as follows:

A_1	$s, p(z), d(z^2)$
B_1	$d(x^2 - y^2)$
B_2	$d(xy)$
E	$d(xz,yz), p(x,y)$

giving a sum of representations $3A_1 + B_1 + B_2 + 2E$. The set of five σ-bonds formed by the chlorine atoms transform as $2A_1 + B_1 + E$ and the σ-bond to the oxygen atom transforms as A_1, so that B_2 and E are available for the four electrons of the Ru^{IV} atom. These orbitals correspond to the triply degenerate T_2 orbitals of the octahedral paramagnetic $(Ru^{IV}Cl_6)^{2-}$ ion, and it is just this partial breakdown of the degeneracy in the lower symmetry group which removes the paramagnetism. Considering the two ruthenium atoms, now as a pair, these atomic orbitals combine to give new molecular orbitals, transforming (in the point-group $D_{4h} = C_{4v} \times i$) as B_{2g}, B_{2u}, E_g, and E_u. The filled degenerate $p(x,y)$ orbitals of the O^{2-} ion transform as E_u. Clearly the two E_u orbitals (one from the Ru pair and one from O^{2-}) combine to give a bonding E_u^b and an antibonding E_u^a orbital. The order of energy levels is therefore :

$$(E_u^b)[(B_{2g})(B_{2u})(E_g)](E_u^a)$$

where the orbitals in the square brackets are approximately degenerate. We now have to place 12 electrons [4 from each Ru^{IV} together with the oxygen $p(x,y)$ set] and it is evident that the ground state is described by $(E_u^b)^4(B_{2g})^2(B_{2u})^2(E_g)^4(E_u^a)^0$ whence, since all electrons are in closed shells, the substance should be diamagnetic.

FIG. 2. *One of the two perpendicular components of the bonding* E_u^b *π-orbital in* $(Ru_2Cl_{10}O)^{4-}$ *anion.*

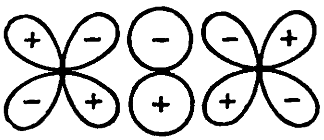
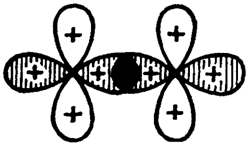


FIG. 3. *The* E_g^b *(unshaded) and* A_{1g} *(shaded) orbitals for* $Fe_2(CO)_9$ *projected on a plane.*



The E_u^b orbital may be described as a degenerate bonding π-orbital (Fig. 2) ; the actual extent of π-bonding will be sensitive to the relative electronegativities of the atoms concerned, but the observed Ru–O distance, 1·80 Å, is close to the value 1·74 Å found in RuO_4 and indicates considerable double-bond character. It is clear too that the degree of π-bonding, and hence the stability of the anion, would be diminished by any departure from linearity of Ru–O–Ru. In valence-bond terms, the situation may perhaps be described as corresponding to resonance between a number of structures of which the extremes are $(Cl_5Ru^{IV}\text{–}\overset{2-}{O}\text{–}Ru^{IV}Cl_5)$ and $(Cl_5Ru^{II}{=}\overset{2+}{O}{=}Ru^{II}Cl_5)$.

Peroxocobalt Decammines.—The peroxocobalt decammines $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]X_4$ (I) are remarkable for the ease with which they may be oxidised to $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]X_5$ (II), which have been regarded as the only compounds containing Co^{IV} (see, *e.g.*, Sidgwick, " The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 1420). The possibility that the oxidation involves removal of an electron from the oxygen rather than from the cobalt has, however, been suggested by several authors (Gleu and Rehm, *Z. anorg. Chem.*, 1938, **237**, 79 ; Malatesta, *Gazzetta*, 1942, **72**, 287 ; Thompson and Wilmarth, *J. Phys. Chem.*, 1952, **56**, 5). Our discussion of the previous section may be applied directly to the ion (I), provided it is linear, the only difference being that the oxygen has now both internally bonding $E_u(w\pi)$ and antibonding $E_g(v\pi)$ orbitals. The available orbitals, after σ-bonding, are in order of stability, $(E_u^b)[(B_{2g})(B_{2u})(E_u^a)(E_g^b)](E_g^a)$ the order within the square bracket being unknown, and there are 20 electrons, just enough to fill all available orbitals and thereby ensure diamagnetism. Since all the antibonding orbitals, as well as the bonding ones, are filled, we expect no double-bond character in either the Co–O or the O–O bonds, and the ion should not be appreciably destabilised by departure from linearity. Oxidation must involve removal of an electron from the least stable orbital which is E_g^a and presumably concentrated mainly on the O_2 group, so that the resulting cation (II) is perhaps more correctly represented as $[(NH_3)_5Co^{III}{\cdot}\overset{1-}{O_2}{\cdot}Co^{III}(NH_3)_5]$ rather than as $[(NH_3)_5Co^{IV}{\cdot}\overset{2-}{O_2}{\cdot}Co^{III}(NH_3)_5]$. We expect the O–O and Co–O distances to be slightly shorter than in (I). The O–O distance should be about the same as that, 1·28 ± 0·07 Å, in the alkali "tetroxides" M_2O_4 which have been shown to contain the odd univalent anion $[O{\cdot}O]^-$ (Kassatochkin and Kotov, *J. Chem. Phys.*, 1936, **4**, 458).

Iron Enneacarbonyl.—Iron enneacarbonyl, $Fe_2(CO)_9$, differs from the previous binuclear compounds in that direct metal-to-metal bonding is possible. Owing to the large number of orbitals of the same symmetry type, the assignment of electrons to the various orbitals cannot be made unambiguously. A simplified treatment yields quite interesting results however. After σ-bonding there are left three orbitals on each iron atom (corresponding to the triply degenerate T_2 orbitals of the octahedral group) which transform in C_{3v} as $A_1 + E$. Considering the iron atoms as a pair, we have in $D_{3h} = C_{3v} \times i$, $(A_{1g}{}^b)(E_g{}^b)(E_u{}^a)(A_{1u}{}^a)$ in order of stability. The order follows from the fact that the orbitals making up the E representations will not interact much, while the A_1 atomic orbitals will interact strongly with one another, stabilising A_{1g} and destabilising A_{1u} (Fig. 3). The ten electrons remaining after σ-bonding are assigned as $(A_{1g}{}^b)^2(E_g{}^b)^4(E_u{}^a)^4$ leading to diamagnetism and with net formation of an iron–iron bond, in accord with the observed Fe–Fe distance, 2·46 Å (Powell and Ewens, *J.*, 1939, 286).

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