in the metal–oxygen σ bonds.[10] Although we can account for a considerable reduction in Q' by taking covalency into account, the experimental values are still much lower than the smallest ones we compute, a fact which suggests that the charge distribution near the copper nucleus in a covalent complex is much closer to spherical than the usual simple crystal field or molecular orbital picture would lead us to expect.

Acknowledgment. The work was supported by ARPA SD-131 through the Materials Research Laboratory at the University of Illinois.

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Trigonal Prismatic Cobalt(II) in a Polynuclear Complex

Sir:

There are several reports[1-4] in the literature of polynuclear cations containing cobalt and 2-aminoethanol; a trinuclear cation was formulated[1] as a cobalt(II) complex, but has more recently been reported[4] to contain a central cobalt(II) ion coordinated to two tris(2-aminoethoxido)cobalt(III) complexes. A structure with octahedral coordination of the central cobalt(II) through face-sharing of oxygens with the cobalt(III) octahedra was proposed.[4] Analogous trinuclear complexes, $[M(Co(chelate)_3)_2]^{m+}$, with 2-aminoethanethiolate as the chelate ligand and with cobalt(III), zinc(II), and nickel(II) as the central metal, M, have been studied;[5,6] the same structure has been assumed for these complexes.

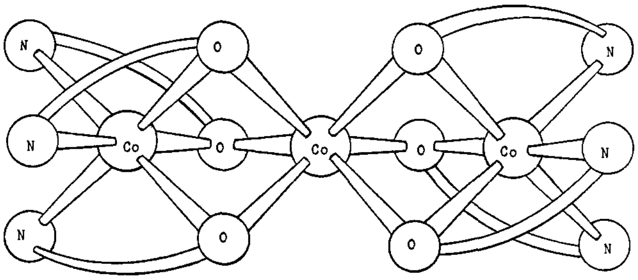

Figure 1.

We prepared the acetate salt of the trinuclear cation, $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$; unlike the previously prepared salts, which were isolated as unstable hydrates, the acetate crystallized from methanol as the anhydrous salt. The compound crystallized as dark red crystals which were roughly octahedral in shape. Precession photographs (Zr-filtered Mo radiation) indicated that the crystals were monoclinic with a = 14.98 (3) Å, b = 8.61 (2) Å, c = 11.28 (3) Å, and β = 116.7° (1);[7] the density calculated for $Z = 2$, 1.68 g/cm^3, agreed well with the experimental value, 1.66 g/cm^3, obtained by the flotation method. Systematic extinction of the hkl reflections for $h + k = 2n + 1$ was consistent with space groups C2 and C2/m. Although both space groups have twofold positions, the 2/m symmetry of the twofold positions of C2/m was not consistent with any reasonable structure for the trimer; C2 was, thus, assumed to be the correct space group and the subsequent refinement was verified this choice.

The same crystal as used for the space group determination was used to collect intensity data on a Picker four-circle automated diffractometer; a total of 830 unique reflections above background were collected in the 2θ scan mode; unfiltered Mo radiation was used.

Since the origin in the y direction of space group C2 is not fixed by symmetry, the cobalt of the twofold set (2a) was placed at the origin of the unit cell; from a Patterson synthesis, coordinates for the cobalt of the fourfold general set (4c) were obtained. Successive structure factor and Fourier calculations were used to locate the remaining nonhydrogen atoms of the structure; the oxygen atoms of the acetate appear to be disordered. The present conventional R value of 0.11 was obtained with all reflections weighted at unity, isotropic temperature factors, and no correction for the f'' component of anomalous dispersion; further refinement is in progress.

The main features of the structure are, however, apparent from the present stage of refinement. As suggested by previous workers,[4] the trimer consists of two tris(2-aminoethoxido)cobalt(III) complexes, each sharing three oxygens with a central cobalt(II); the twofold site symmetry relates the two tris chelates and requires that the two be of the same optical configuration.

The coordination of the central cobalt(II), Figure 1, is unusual; the oxygens are arranged at the corners of an almost perfect trigonal prism with Co–O distances of 2.03 (2), 2.03 (2), and 2.05 (2) Å. The triangular faces are almost perfect equilateral triangles with O–O distances of 2.59 (3), 2.61 (3), and 2.64 (3) Å and angles of 61 (1), 59 (1), and 60° (1); between the triangular faces there are two O–O distances of 2.75 (3) and one of 2.72 (3) Å. The best least-squares plane for the group of four oxygens comprising each rectangular face of the trigonal prism was calculated, the distance of each atom from the plane was calculated, and the dihedral angle between each pair of adjacent faces was calculated; no atom was more than 0.05 Å out of the plane of its face, and the dihedral angles between faces were 117.9° (1.3) for one pair and 120.9° (7) for the other two pairs.

Construction of models of the structure found and the postulated structure with octahedral coordination about cobalt(II) indicates that the hydrogen atoms of the methylene groups adjacent to the oxygens may be responsible for the unusual coordination; hydrogens of the two tris chelates appear to approach to less than the sum of their van der Waals radii in the octahedral complex but are less crowded in the trigonal-prismatic complex. On the basis of models, octahedral coordina-

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(1) W. Hieber and E. Levy, *Ann.*, 500, 14 (1932).
(2) W. Hieber and E. Levy, *Z. Anorg. Chem.*, 219, 225 (1934).
(3) H. Brintzinger and B. Hesse, *ibid.*, 248, 345 (1941).
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(7) Figures in parentheses here and elsewhere in this paper represent the estimated error in the least significant digit.

tion would give less crowding of the hydrogens in the inactive complex in which the cobalt(II) is coordinated to one *d* and one *l* tris chelate; work on that structure is in progress.

This complex represents the first example of a trigonal-prismatic complex with a coordination sphere of oxygen atoms; all previous examples[8] of discrete, trigonal-prismatic complexes have been based on the dithiolate ligand.

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(8) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

(9) Alfred P. Sloan Research Fellow, 1966–1968.

(10) National Science Foundation Faculty Research Participant, 1968.

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On the Application of Orbital Symmetry Arguments to the Reactions of Transition Metal Complexes

Sir:

A recent paper[1] describes the application of the principles of orbital symmetry conservation[2] to some reactions of transition metal complexes. In this communication, we wish to amplify the conclusions of that paper, using a more rigorous method, and to point out certain very general limitations on the application of this approach to chemical problems.

The method of Woodward and Hoffmann involves the construction of orbital correlation diagrams for the one-electron energy levels of starting material and product, the correlations being made according to the symmetries of the activated complexes of two separate pathways. If these correlations predict substantial electronic destabilization of one transition state relative to the other, then the corresponding mechanism is disallowed; otherwise, it is allowed. A correctly constructed correlation diagram gives information concerning the energy of the activated complex of a reaction.

Merely correlating the orbitals of the starting material and the product without regard to the symmetry of the activated complex (the procedure followed by Eaton[1]) does not guarantee that this type of information will be obtained. The problems which can arise are illustrated by the treatment of the isomerization reactions of four-coordinate d^8 species given in ref 1, where it was concluded that square-planar to tetrahedral reactions are allowed, but that square-planar *cis–trans* isomerizations are disallowed. These two statements are contradictory, since attainment of tetrahedral geometry assures an allowed pathway for *cis–trans* isomerization. One reason for the contradiction is that the symmetry of the activated complex for the isomerization reaction (assumed to involve tetrahedral geometry) is higher than either the starting material or the product. The resulting increase in orbital degeneracy makes the correlation drawn in ref 1 of questionable value.[3] It is more informative in this case to look at the orbital correlation between the square plane and the tetrahedron.

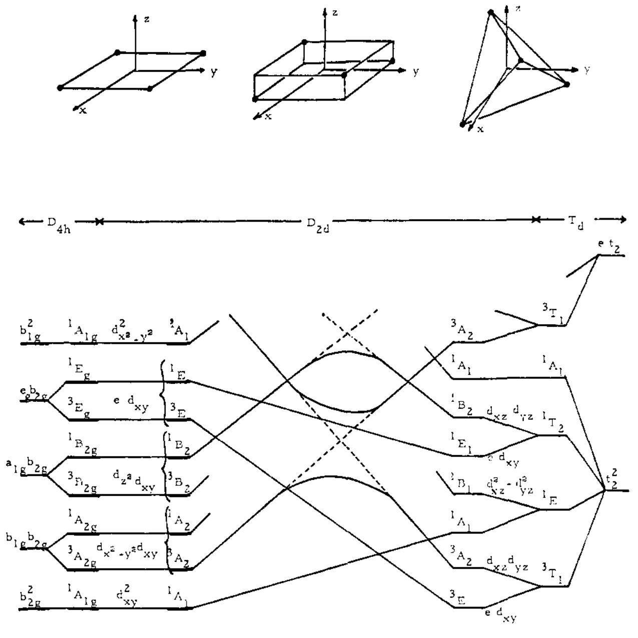

Figure 1. State correlation diagram for the isomerization of a square-planar to a tetrahedral d^8 complex. The symbol e stands for the degenerate set of orbitals (d$_{xz}$, d$_{yz}$). The orbital labels show the distribution of holes among the d orbitals for each state.

As pointed out by Longuet-Higgins and Abrahamson,[4] and acknowledged by Eaton,[1] a more elegant approach to this problem is to construct a state correlation diagram of the type shown in Figure 1.[5] Consideration of this diagram, which shows some of the correlations produced by the change of geometry for a d^8 system, leads to several conclusions. (a) Isomerization of a triplet tetrahedral complex to a square-planar complex is "disallowed," in the sense that the ground state of the tetrahedron correlates with an excited state of the square plane.[8] (b) The reverse reaction is "disallowed"

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(1) D. R. Eaton, *J. Am. Chem. Soc.*, **90**, 4272 (1968).

(2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 4389 (1965); see also R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(3) In particular, the distinction between the d_{xy}, d_{xz}, and the d_{yz} orbitals disappears in T$_d$ symmetry. The d_{xy} orbital of one isomer cannot, therefore, be correlated uniquely with the d_{xy} orbital of the other.

(4) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(5) This diagram is similar to those used by Ballhausen, *et al.*,[6] and Martin, *et al.*,[7] to explain certain features of the spectra of square-planar compounds.

(6) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

(7) D. S. Martin, M. A. Tucker, and A. J. Kassman, *ibid.*, **4**, 1682 (1965).

(8) This definition of the term "disallowed" differs from that used in ref 1 or ref 4. In organic systems, where the ground states of starting material and product are almost always ^1A, a correlation of a ground with an excited state implies the existence of a crossing of states of the same symmetry, and the occurrence of such a crossing is used as the basis for the previous[4] definition. In inorganic systems, where ground states are not always totally symmetric singlets, a correlation of a ground with an excited state does not always produce this type of crossing. The extension of the definition of "disallowed" to cover any ground-state–excited-state correlation seems justified *conceptually* because such a correlation implies a barrier to reaction beyond that resulting from a difference in thermodynamic stability of starting material and product. Of course, as pointed out later, no definition has *experimental* meaning without a parallel "allowed" pathway for comparison.