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A Graph-Theoretical Interpretation of Stereochemically Nonrigid Coordination Structures

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Sir:

In 1956 Günthard and Primas¹ demonstrated the connection between graph theory and MO theory in the Hückel treatment of conjugated systems. Subsequently Schmidtke^{2,3} showed that similar graph-theoretical methods could also be used for the LCAO treatment of directed valency in ML_n complexes. This communication shows how an extension of Schmidtke's methods can immediately provide information on the stereochemical nonrigidity of certain ML_n structures. Such information is not accessible from the standard treatment⁴ of directed valency based solely on the hybridization of atomic orbitals.

Schmidtke has shown^{2,3} that the usual secular equation $|\mathbf{H} - E\mathbf{S}| = 0$ can be converted to the equation $|\mathbf{A} - \rho\mathbf{I}| = 0$ where \mathbf{A} is the adjacency matrix⁵⁻⁹ of the graph representing the nearest-neighbor interactions, ρ corresponds to the usual Hückel numbers for the energy eigenvalues by the relationship $E = (\alpha + \rho\beta)/(1 + \rho S)$, and \mathbf{I} is the unit matrix. For ML_n complexes we therefore consider first the ligands L and introduce a graph representing nearest-neighbor repulsive interactions. The spectrum of this graph,⁵⁻⁹ which corresponds to the ρ values in the solution of $|\mathbf{A} - \rho\mathbf{I}| = 0$, is now used to determine the resulting energy levels of the set L_n of the n interacting ligands L .

In the LCAO treatment of ML_n complexes the energy levels of the set L_n must be matched with the relative energy levels of the bonding atomic orbitals of the central atom M . The n M - L bonds arise from linear combinations of the type $\psi = \phi_L + \phi_M$ where the ϕ_L have the energy levels of the set L_n and the ϕ_M have the energy levels of the atomic orbitals of M . The energies of these bonds are minimized if ϕ_L and ϕ_M have the same energies. For this reason favorable coordination graphs of ML_n structures which represent relatively deep minima of energy hypersurfaces will be those in which the energy levels of the spectra of the graphs from the L_n set match those of the available bonding orbitals of M . Mismatch of the spectra of the L_n graphs with the energy levels of the bonding orbitals of M will lead to a relatively flat energy hypersurface. Such a relatively flat energy hypersurface will have shallow minima and a low activation energy for the interconversion of

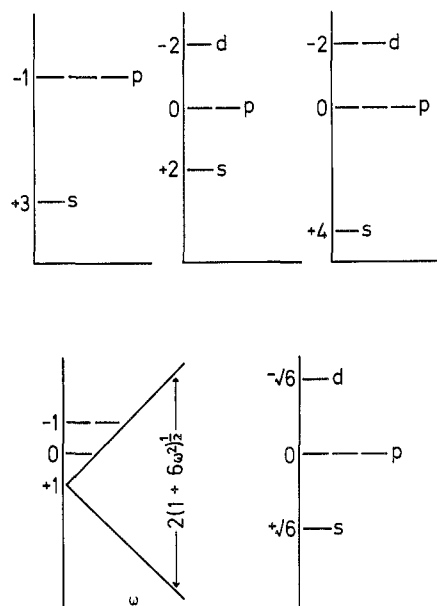


Figure 1. Eigenvalue patterns of the various graphs used to represent coordination structures: (a) the tetrahedron; (b) the square; (c) the octahedron; (d) the trigonal bipyramid, where ω represents the interactions of the apical-equatorial edges relative to the equatorial-equatorial edges; (e) the bipartite graph $K_{2,3}$.

equivalent structures thereby leading to stereochemical nonrigidity.

The coordination numbers of 4 and 6 are known to lead to stereochemically rigid structures. We start by illustrating our method for these structures. The spectrum of the K_4 graph,⁹ i.e., that of the tetrahedron (Figure 1a), has one eigenvalue at +3 and three degenerate eigenvalues at -1. These four eigenvalues correspond respectively to the energies of the one s and three p atomic orbitals of M . Thus the tetrahedron will be the stereochemically rigid¹⁰ graph for coordination number 4 in the usual cases where all three p orbitals of M can participate in the M - L bonding. Similarly, the eigenvalues of the C_4 graph,⁹ i.e., that of the square (Figure 1b), are +2, 0, 0, and -2 corresponding, respectively, to one s orbital, two p orbitals, and one d orbital of M . The square will thus be the graph for systems where only two of the p orbitals of M are available for bonding to the ligands. The H_3 graph of the octahedron has eigenvalues of +4, 0, 0, 0, -2, and -2 (Figure 1c) corresponding directly to the single s orbital, the three p orbitals, and the two d orbitals of M involved in octahedral bonding. This is consistent with the occurrence of the octahedron as the usual and stereochemically rigid¹⁰ graph for coordination number 6. In all of these four- and six-coordinate systems, the graph for the coordination is thus identical with the coordination polyhedron usually considered.

The situation changes drastically, however, when the coordination number 5 is considered. In order to match the energies of the sp^3d hybrids used in this coordination a five-vertex graph is required having only three distinct eigenvalues, where the lowest and highest eigenvalues are unique and the middle one is triply degenerate; i.e., a 1, 3, 1 eigenvalue pattern is required. The five eigenvalues of the Π_3 graph, i.e., that of the trigonal bipyramid, are $1 \pm (1 - 6\omega^2)^{1/2}$, 0, -1, and -1, where ω is a weighting factor for the equatorial-equatorial and equatorial-axial interactions. As illustrated schematically in Figure 1d, there are no reasonable values of ω giving the desired 1, 3, 1 eigenvalue pattern. Similarly the eigenvalues of the W_4 graph, i.e., that of the square pyramid, are $1 \pm (1 - 4\omega^2)^{1/2}$, 0, 0, and -2, where ω is again a weighting factor for the basal-basal and apical-basal interactions. The desired 1, 3, 1 pattern can be attained for the square pyramid only

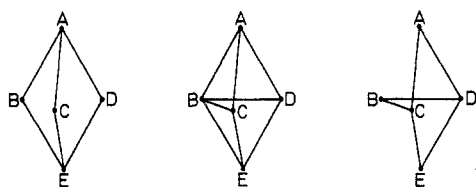


Figure 2. The bipartite graph $K_{2,3}$ (a) in the Berry pseudorotation mechanism for ligand exchange in five-coordinate systems.

with the absurd ω value of zero. Thus neither the trigonal bipyramid nor the square pyramid represents a favorable graph for the coordination number 5.

The desired 1, 3, 1 eigenvalue pattern for coordination number 5 may be obtained by use of the $K_{2,3}$ bipartite graph shown in Figure 2a. The eigenvalues of this graph are $+6^{1/2}$, 0, 0, 0, and $-6^{1/2}$ (Figure 1e). The $K_{2,3}$ graph is planar, has the D_{3h} automorphism group, and can thus mimic the trigonal bipyramid. Indeed, it differs from the trigonal bipyramid only in that the equatorial-equatorial interactions are taken to be negligible relative to the equatorial-axial interactions. This is not unreasonable since the equatorial-equatorial bond angles are 120° whereas the equatorial-axial bond angles are only 90° . Furthermore, if a $K_{2,3}$ graph is visualized in three-dimensional space with vertices of like charge, minimization of its repulsion energy will cause the vertices to form a trigonal bipyramid.

By recognizing that the graph representing the energy minimum for a five-coordinate system is the $K_{2,3}$ bipartite graph of Figure 2a, we have accounted for the stereochemical nonrigidity of five-coordinate systems as compared to the relative rigidity of four- and six-coordinate systems. The $K_{2,3}$ graph has a very flexible shape and considerable freedom of motion without any change of the bond lengths. Moreover, the Berry pseudorotation mechanism^{11,12} can be represented using $K_{2,3}$ graphs as in Figure 2. For example, flexing of the $K_{2,3}$ graph of Figure 2a such that new edges BC and BD are formed gives the square pyramid, Figure 2b. Rupture of the edges BA and BE of this square pyramid gives the new $K_{2,3}$ bipartite graph of Figure 2c, where C and D are now the vertices of order 3. Repetition of this process makes the five ligands in a five-coordinate system equivalent on an appropriate time scale.¹³

The situation is still different with coordination numbers 7 and 8, which require respective eigenvalue patterns of 1, 3, 3 and 1, 3, 4. These patterns are impossible¹⁴ in a relatively symmetrical graph which can be inscribed in a sphere without its edges crossing, i.e., in a planar graph.¹⁵ Only by taking a relatively unsymmetrical graph with at least two edge orbits and varying their relative weights can the appropriate eigenvalue patterns for the coordination numbers 7 and 8 be attained. Eigenvalue patterns obtained in this fortuitous manner represent unstable equilibria which should lead to inherently nonrigid stereochemical systems.

In summary, our analysis indicates the following possibilities for coordination numbers from 4 to 8 inclusive, when use is made of sp^3d^m ($0 \leq m \leq 4$) hybridization for the central atom: (1) structures for coordination numbers 4 and 6 should be relatively rigid and have a stable symmetry-determined equilibrium; (2) structures for coordination number 5 should be flexible and nonrigid and have a stable symmetry-determined equilibrium; (3) structures for coordination numbers 7 and 8 should be nonrigid and have an unstable equilibrium which is not determined by symmetry. We also note that the octahedron is the graph having the largest number of vertices which can be formed for sp^3d^m hybrids and that this graph has the appropriate eigenvalue pattern for an sp^3d^m system. These facts may account for the predominance and stability of the octahedron in many areas of coordination chemistry.

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The Radiofrequency Plasma as a Synthetic Method. Preparation of Tris(trifluoromethyl)bismuth

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Sir:

Recently we have reported¹ a new preparative route to organometallic compounds which are highly or fully substituted with CF_3 groups. The first successful synthesis of, e.g., $Te(CF_3)_2$, $Sn(CF_3)_4$, and $Ge(CF_3)_4$ from the metal halides and CF_3 radicals produced by the glow discharge of C_2F_6 indicates that the plasma technique may be of general utility for the preparation of other new compounds not readily accessible through standard thermal routes. The species produced in these low-pressure discharges are vibrationally and electronically excited, but almost in thermal equilibrium with the surroundings ($T_g \approx 40^\circ C$). Thus the trifluoromethyl radical is very reactive, but any molecules synthesized by interaction with a second substrate are formed at or near room temperature. Consequently, these products are less likely to undergo unimolecular decomposition than if produced by methods which employ higher temperatures.

The fully substituted trifluoromethyl derivative of bismuth, $Bi(CF_3)_3$, which is currently unknown, provides a particularly interesting case; each of the group 5A trisubstituted analogues $N(CF_3)_3$,² $P(CF_3)_3$,³ $As(CF_3)_3$,⁴ and $Sb(CF_3)_3$ ⁵ has been characterized and many have been prepared by a variety of methods. Representative reactions⁵⁻⁷ which yield the trisubstituted derivatives of the lighter members of group 5 are shown in eq 1-3. However, in each case, either the corresponding reaction of bismuth is reported to fail⁷ or the required reagent is also unknown.

Additionally, in the related reaction of a metallic bismuth mirror with CF_3 radicals produced by the pyrolysis of hex-