Conclusion

From our systematic examination of the ^{13}C nmr parameters of the phenylplatinum derivatives 2–10, we have deduced the following bonding information: (1) σ-inductive, π-inductive, and σ–π conjugative effects remain relatively constant in the phenyl rings of this series of compounds, (2) the absolute magnitude of the phenyl–platinum π interaction may be small while the absolute magnitude of the σ interaction appears to be appreciable, (3) σ–π conjugative interactions do not appear to occur.

There are several other important conclusions concerning the ^{13}C shieldings and ^{13}C–^{195}Pt coupling constants which arise from this work: (1) modifications in one- to three-bond ^{13}C–^{195}Pt coupling constants in the phenyl rings are probably dominated by platinum σ-orbital rehybridization, (2) one-bond ^{13}C–^{195}Pt coupling constants do not seem to reflect π-inductive or σ–π conjugative effects.

Idealized Polytopal Forms. Description of Real Molecules Referenced to Idealized Polygons or Polyhedra in Geometric Reaction Path Form

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Abstract: Molecules or ions in the cluster and coordination compound classes can be systematically ordered and rationalized for all x-atom families in terms of idealized geometric (polytopal) forms. With the exception of forms with cubic symmetry, explicit descriptions of polyhedra require information on symmetry *and* shape parameters. It is sometimes difficult to distinguish between reference idealized models for a real molecule in the condensed physical states. Most precise data are derived from X-ray studies of the crystalline state where the molecule departs to varying degrees from idealized models. A comprehensive and quantitative measure of shape in such aggregates can be readily obtained from the dihedral angles formed by the normals to adjacent polytopal faces. This measure is presented in terms of reaction paths that interrelate probable idealized geometries. It is recommended that these dihedral angle data be reported in structure investigations not only for a guide to pictorialization of the molecular geometry but also for the generation of extensive data that may bear on intramolecular rearrangements of the molecules (or ions) in the liquid, solution, or gaseous state.

An irksome phrase, encumbered with imprecise English and often[2] encountered in structural papers, is "the molecule is a distorted trigonal bipyramid" or octahedron, square plane, etc. Certain atoms in a molecule may describe *precisely* the vertices of a *regular* tetrahedron or *may nearly* describe the vertices of some idealized polygon or polyhedron. Such descriptions, properly phrased and soundly based, are of great value to the follower of structural chemistry. A more objective and quantitative assessment of shape referenced to common or readily visualized geometric forms would further assist the casual and the serious reader in a substantive fashion. There are many examples in present-day crystallographic papers where a sensible measure of shape cannot be gained from the impressive tabulations of data and structural parameters short of construction of a model from the table of positional parameters or from the distance–angle parameters for the molecule. We propose a procedure, which is an extension and generalization of a specific application made by Porai-Koshits and Aslanov,[3] that leads to a quantitative measure of polytopal shape referenced to idealized geometries and that imposes little additional burden on the crystallographer. This measure of shape, couched in terms of geometric reaction paths, should be of general value to those scientists interested in or studying intramolecular rearrangements[4–14] in molecular systems.

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(2) We both admit to having used such phraseology.

A Uniform and Quantitative Description of Shape in Coordination and Cluster Compounds

There is a surprising consistency of shape for a variety of chemical classes.[7,9,14] In coordination compounds, ML_x, and in clusters, M_xL_y, the x ligand atoms[15a] or the x cluster atoms will generally describe a polytope in which all faces are equilateral triangles or nearly equilateral triangles.[7,9,14] The fully triangulated form is the favored one in all x-atom classes, e.g., four-regular tetrahedron, five-trigonal bipyramid, six-regular octahedron, and 12-regular icosahedron. In each family, exceptions are found, especially the five-, seven-, and eight-atom families. However, the exceptional forms are generally closely related to the normal triangulated ones.[4,7,9] They usually possess a maximum of triangular faces and one or two square faces and can be readily generated from the fully triangulated form by minor bending–stretching modes. In these instances, the exceptional forms or more properly alternative forms have energies only slightly higher than the fully triangulated forms. Classic examples are the square pyramid (five atom) with one square face,[5–7,10,15b] the square antiprism (eight atom) with two square faces,[11,12,16] and the C_{4v}-monocapped square antiprism (nine atom) with one square face.[7,17] Such alternative geometries are not only found for real molecular aggregates but often serve as intermediates, or transition states, in intramolecular rearrangements. Geometries ostensibly intermediate between the favored and alternative forms have been reported for ML_x or M_xL_y complexes in the crystalline state. The immediate questions to be posed for such cases are the following. (1) Can the "nondescript" geometry be quantitatively related to limiting or idealized polytopal forms? (2) Can an idealized geometric reaction path between the favored polytope and an alternative, or a cyclic path traversing the favored polytope and two or more alternatives, be effectively utilized to describe real molecules?

We believe that these questions can be answered in the affirmative and that a singular conceptual model serves for all x-atom families. We further note that the reaction path description of shape can be effectively applied to solid-state structures. Distortions in the solid state reflect a compromise between optimal packing or lattice energy and optimal shape for the molecule. Should molecular polyhedra deform in a relatively prescribed fashion to achieve maximal lattice energy; i.e., do the observed departures from an idealized form follow well-defined paths or are the departures desultory? For the most part, we find that the departures follow explicit geometric reaction paths. There appears to be nothing capricious in solid-state packing; deformations follow paths of least resistance which, in principle at least, can be discerned theoretically from molecular orbital studies, semitheoretically from electrostatic or nonbonding models, or empirically from force constants associated with internal vibrations.

The proposed method of describing molecular geom-

(15) (a) If the metal atom is not within a polyhedron described by the ligand atoms (e.g., a pyramidal ML_3 molecule), the metal and the ligand atom positions are used to define the polyhedron. (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966)
(16) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).
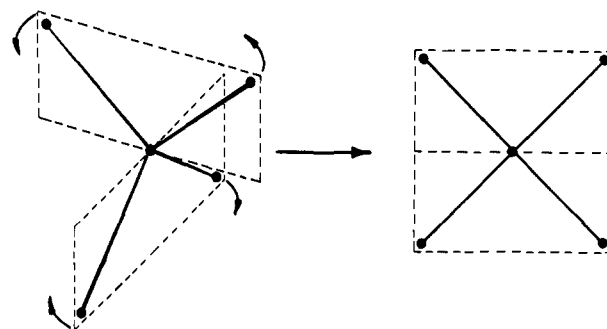(17) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

Figure 1. Digonal twist mechanism for correlating four-coordinate tetrahedral and square planar polyhedral forms. A strict digonal twist converts the regular tetrahedron to a D_{2h} rectangle. If all angles are allowed to change from 109.5 to 90°, then the digonal twist and the tetrahedral compression mechanisms are equivalent and indistinguishable.

etry relates the favored polytope, all faces equilateral triangles or nearly so, and an alternative (or alternatives) using a stylized or idealized physical rearrangement mechanism wherein one or more pairs of adjacent triangular faces of the favored form are converted to square faces.[4] The favored form is the reference form for shape parameters. The shape parameters are the dihedral angles formed by the normals to adjacent faces. These are referenced to edges of the polygon or polyhedron. In the stylized conversion of the favored to the alternative form, these dihedral angles change uniformly and some become zero, i.e., they become diagonals in the square faces, in the alternative form. An alternative approach in analyzing molecular point symmetry and reaction paths relating polytopes is the use of symmetry coordinates as in vibrational theory. However, this usually implies some prior assumptions as to point symmetry of the real and idealized polytopes and is not as easy to apply in the general case as the dihedral angle approach which involves no assumptions and uses the atomic coordinates directly.

There is an important distinction between a coordination description focused on the central atom (and the angles subtended there by the ligands) and a description focused on the polyhedron formed by the ligand atoms (characterized by the normals to the polyhedral planes). The two descriptions are in a sense inverses; however, they do have the same inherent point symmetry. The usual central atom focused description is useful in, say, establishing the effective coordination number and the point symmetry, particularly if an accurate model is available. The advantage of the description focused on the ligand polyhedron is that it immediately identifies the circumstance where two triangular faces are approaching a square face. This fact can be very useful in making fine distinctions in molecular point symmetry and in establishing geometric reaction paths.

Consider the trivial case of a four-atom coordination complex where the regular tetrahedron is the favored form although the square plane is found in some transition metal (especially d^8, d^9) complexes. For the regular tetrahedron, there are six edges, a_1–a_6, and six associated dihedral angles δ of 109.5°. Assume that the stylized reaction path interrelating the two forms is a digonal twist (Figure 1). The digonal twist is equiv-
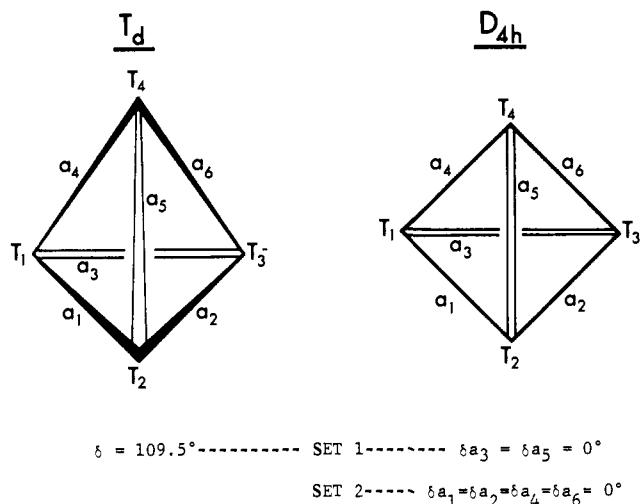
Figure 2. Four-atom family shape characteristics for limiting forms. The double lines denote the reference edges for the shape-determining δ' angles. Mechanistically, the interrelationships of the two forms may be more readily apparent if the set 2 angles are described as 180° rather than 0°.
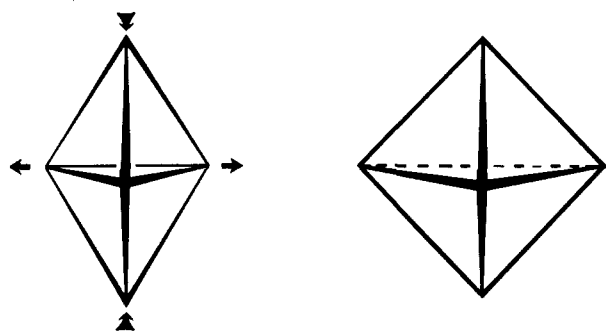

Figure 3. Berry rearrangement mechanism for interconversion of D_{3h} and C_{4v} geometries in ML_5 complexes.
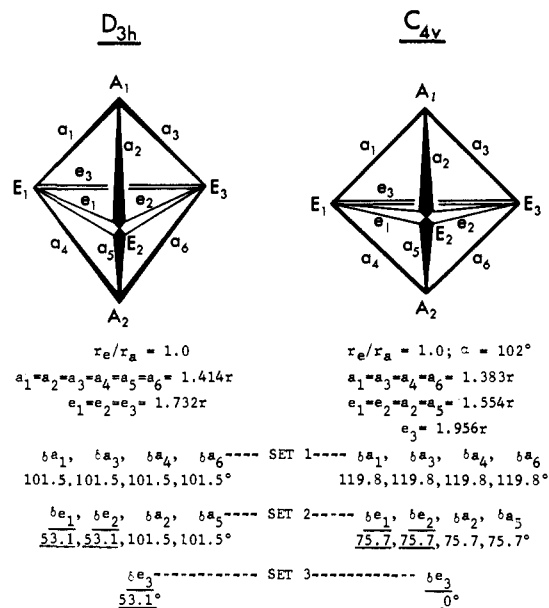

Figure 4. Five-atom family shape characteristics; underlined angles are those dihedral angles that enclose the edge represented as double lines (see text in the figure).

Table I. Dihedral Angle (deg) for $CuCl_4^{2-}$ Data

	δ' angles[a]	Other δ angles
Cs_2CuCl_4[b]	86.4, 87.9	121.3, 121.3, 122.0, 122.0
$(CH_3NC_5H_4)_2CuCl_4$[c]	87.1, 87.1	121.3, 121.7, 121.7, 122.2
$[C_6H_5CH_2N(CH_3)_3]_2CuCl_4$[d]	82.8, 83.5	123.6, 123.9, 124.3, 124.3

[a] The δ' angles are associated with the double lines of Figure 2. [b] J. A. McGinnety, J. Amer. Chem. Soc., 94, 8406 (1972). [c] J. H. Russell and S. C. Wallwork, Acta Crystallogr., Sect. B, 25, 1691 (1969). [d] M. Bonamico, G. Dessy, and A. Vaciago, Theor. Chim. Acta, 7, 367 (1967).

alent to a compression along the S_4 (4) axis if in the digonal twist the 109.5° angles between cis ligands are allowed to go to 90° maintaining local S_4 point symmetry. At the planar limit then, all the corresponding angles are obviously 0° (or 180° depending on the direction taken for the plane normals). A subset of two dihedral angles, δ' (see discussion of five-atom family below), is employed for characterization of the polyhedron; these angles are associated with edges identified by double lines in Figure 2. This subset suffices to provide a good quantitative measure of if and where a real four-coordinate molecule would be along the reaction path between the T_d and D_{4h} limits.

ML_4 molecules or ions are clustered around the limiting T_d and D_{4h} forms. For example, d^{10} $ZnCl_4^{2-}$ has interbond angles ranging only from 101 to 118°, depending on the solid-state environment. However, the range in the exceptional d^9 $CuCl_4^{2-}$ is far more extensive, 100–131°. The corresponding dihedral angles are given in Table I. Note that in each case there is a pairing of δ' angles, and the other four δ angles are equivalent within experimental errors. All intermediate structures have near D_{2d} symmetry; hence, the pairwise bending path of D_{2d} is followed. Intermediate geometries are often obtained in four-coordinate chelate structures but there the ligand constraints may be structure determining.

Structurally, most interesting are the five-, seven-, eight-, nine-, 10-, and 11-atom families of which three are discussed below to illustrate the application.

Five-Atom Family. One of the more subtle structural problems is found in the five-atom family. Here the dominant polytope is the D_{3h} trigonal bipyramid with the C_{4v} square pyramid occasionally appearing for ML_5 complexes.[7,15,18] These two forms are most simply and symmetrically related by the Berry[19] rearrangement process (Figure 3) with the trigonal bipyramid as the reference form; the correlation is shown with the square pyramid. Although the limiting polyhedra are related by minor bending–stretching modes, the resultant distribution of dihedral angles is quite different. Clearly not all dihedral angles for any polyhedron are independent, and a subset of these is usually sufficient to characterize the polyhedral shape. Here, as with the other polyhedral families, we identify a subset of angles which characterize the polyhedron for most purposes. Our subsets are not unique from a theoretical point of view; they were chosen because they define the shape and correlate between limiting forms and are usually structurally recognizable features. These shape determining angles are underlined and the associated edges are identified in the figures by double lines.

(18) J. S. Wood, Progr. Inorg. Chem., 16, 227 (1972).
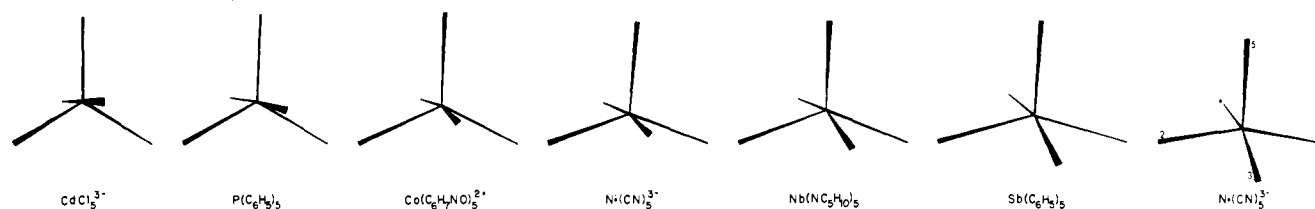(19) R. S. Berry, J. Chem. Phys., 32, 933 (1960).

Figure 5. Real five-coordinate structures illustrating population of the D_{3h} (left) to C_{4v} (right) reaction pathway. Note that the two Ni-$(CN)_5{}^{3-}$ polyhedra are present in the unit cell for the crystalline $Cr(en)_3{}^{3+}$ salt.

To calculate dihedral angles for the idealized models, certain shape parameters must be assumed. In the D_{3h} trigonal bipyramid, the ratio of edges (a to e) or of ML_a (r_a) to ML_e (r_e) bond lengths must be set. In real molecules, the ratio of r_a to r_e is usually unity or slightly larger for d^0 and d^{10} complexes and less than unity for d^8 and d^9 complexes. The actual range is ~0.96–1.07.[15b,18] We assume a ratio of unity, because this approximation does not affect the model analysis in a significant fashion. Two parameters are required for the C_{4v} model, the bond length ratio and the L(axial)–M–L-(basal) angle. The former is set at unity (the observed range is 0.97–1.17) and the latter at 102° (observed and calculated values range from 100 to 104°).[15b,18] The δ angles for the limiting polytopes are shown in Figure 4. The constraint of the Berry mechanism is

Table II. Ideal and Observed Angles (deg) for ML_5 Complexes

Complex	Shape determining δ' angles (e_3, e_1, and e_2)	δ angles (a_2 and a_5 and remaining angles)
Ideal trigonal bipyramid	53.1 53.1, 53.1	101.5, 101.5, 101.5, 101.5, 101.5, 101.5
CdCl$_5{}^{3-}$ [a]	53.8 53.8, 53.8	101.1, 101.1, 101.1, 101.1, 101.1, 101.1
Ni[P(OC$_2$H$_5$)$_3$]$_5{}^{2+}$ [b]	50.8 54.2, 57.3	98.0, 98.9, 100.9, 101.8, 102.9, 103.3
(C$_6$H$_5$)$_5$P^c	45.7 51.8, 52.3	101.3, 101.4, 102.5, 104.0, 105.4, 106.2
Co(C$_6$H$_7$NO)$_5{}^{2+}$ [d]	37.8 54.5, 58.5	93.4, 98.6, 105.9, 105.9, 106.7, 110.0
Ni(CN)$_5{}^{3-}$ [e]	32.2 62.7, 68.6	87.4, 88.2, 106.3, 106.4, 108.3, 110.3
Nb(NC$_5$H$_{10}$)$_5$(Nb2)^f	23.2 65.4, 67.0	85.7, 87.0, 109.3, 111.7, 112.0, 112.5
Nb(NC$_5$H$_{10}$)$_5$(Nb1)^f	15.8 68.6, 70.6	82.6, 82.8, 112.8, 113.2, 114.3, 115.2
Nb(NMe$_2$)$_5{}^f$	15.6 70.2, 70.2	83.0, 83.0, 113.2, 113.2, 113.7, 113.7
(C$_6$H$_5$)$_5$Sb^g	14.4 68.5, 69.2	79.7, 82.0, 114.8, 115.5, 115.9, 116.9
Ni(CN)$_5{}^{3-}$ [e]	0.3 75.0, 79.4	78.2, 78.5, 115.6, 115.7, 118.4, 119.6
Ideal tetragonal pyramid	0.0 75.7, 75.7	75.7, 75.7, 119.8, 119.8, 119.8, 119.8

[a] E. F. Epstein and I. Bernal, *J. Chem. Soc. A*, 3628 (1971). [b] E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, **4**, 407 (1970). [c] P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964). [d] B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, **9**, 767 (1970). [e] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968). Since completing this work we have learned of two other structures having Ni(CN)$_5{}^{3-}$ anions nearly identical with the C_{4v} anion in this table; the new structures are [Cr(NH$_2$CH$_2$CH$_2$CH$_2$NH$_2$)$_3$][Ni(CN)$_5$]·2H$_2$O and [Cr(NH$_3$)$_6$][Ni(CN)$_5$]·2H$_2$O: F. A. Jurnak and K. N. Raymond, private communication. [f] Coordinates received from Professor Hursthouse (private communication); see also C. Heath and M. B. Hursthouse, *Chem. Commun.*, 143 (1971). [g] A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6675 (1968).
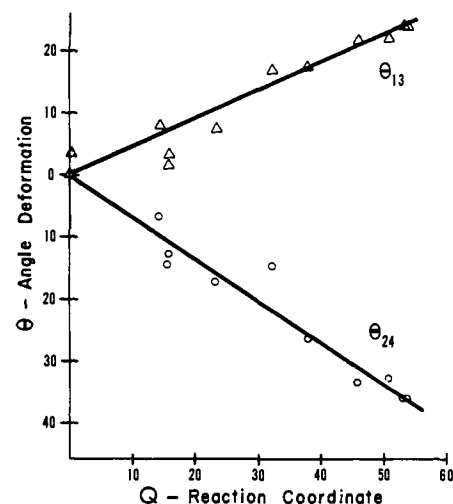

Figure 6. Reaction coordinate plots for five-coordinate complexes. For each structure in Table II, the reaction coordinate (abscissa) was taken as the smallest δ' angle; the θ angles (ordinates), as identified on the right of Figure 5 (NiCN$_5{}^{3-}$ model), were calculated or taken from the literature. Since these systems follow the C_{2v} Berry pathway, either of the θ angles subtended at the central metal may also be used as reaction coordinates. Note that the rate of change of these two angles differs by a factor of 1.5. The ordinate zero was taken for the tetragonal pyramid where θ_{13} and θ_{24} are equal; the deformations are from the C_{4v} model. Thus $\theta_{13} = |(\angle_{13}(\text{observed}) - 156)°|$ and $\theta_{24} = |(156° - \angle_{24}(\text{observed}))°|$.

that all points on the surface have minimally two mirror planes (C_{2v} symmetry constraint). If a real molecule lies on or near this path, there should be within experimental error a pairing of dihedral angles δe_1 with δe_2, δa_2 with δa_5, and δa_1, δa_3, δa_4, and δa_6 should be equivalent. The δ criterion is a measure of whether the Berry pathway is followed and of the point where the polyhedron lies on the $D_{3h} \leftrightarrow C_{4v}$ geometric reaction path.

Dihedral angles are presented in Table II for the two idealized polytopes and for a series of five-coordinate molecules or ions for which accurate positional parameters have been published. Inspection of the angle data especially for molecules of intermediate structures, e.g., Sb(C$_6$H$_5$)$_5$, Ni(CN)$_5{}^{3-}$, and P(C$_6$H$_5$)$_5$, alone shows that the requisite angle pairing (δe_1 with δe_2 and δa_2 with δa_5) for a Berry reaction path is satisfied throughout this group of molecules. Precision models incisively illustrate the smooth transition from D_{3h} to C_{4v} for this group. This is illustrated by computer generated line drawings of actual structures shown in Figure 5; the perspective was established for the trigonal bipyramid and maintained for the other structures. Coordinates for any atom or group of atoms change continuously along the C_{2v} Berry reaction path as quantitatively documented in Figure 6 where two shape

Table III. Ideal and Observed Angles (deg) for ML_6 Complexes[a]

Complex	δ's at b_1	δ's at b_2	Remaining δ's	ϕ[b]
Ideal octahedron	70.5, 70.5, 70.5	70.5, 70.5, 70.5	70.5, 70.5, 70.5 70.5, 70.5, 70.5	60
$Fe(O_2C_5H_7)_3$[c]	63.6, 65.0, 66.0	74.3, 75.6, 76.4	69.0, 69.0, 70.5 72.1, 72.6, 73.0	54
$Cu(NH_2CH_2CH_2NH_2)_3SO_4$[d]	62.7, 62.7, 62.7	80.3, 80.3, 80.3	69.8, 69.8, 69.8 69.8, 69.8, 69.8	49
$Al(O_2C_7H_5)_3$[e]	60.2, 60.2, 63.5	78.5, 80.8, 80.8	68.6, 68.6, 70.2 70.2, 73.2, 73.2	48
$Sc(O_2C_5H_7)_3$[f]	58.1, 60.2, 62.3	79.7, 81.3, 81.5	68.2, 68.5, 70.1 72.2, 73.1, 73.2	47
$Co[S_2CN(C_2H_5)_2]_3$[g]	58.8, 58.8, 58.8	84.7, 85.0, 85.0	69.5, 69.5, 69.9 69.9, 70.1, 70.1	44
$Co(O\text{-ethyl xanthate})_3$[h]	58.3, 58.3, 58.3	85.1, 85.1, 85.1	69.9, 69.9, 69.9 70.0, 70.0, 70.0	43
$Fe(tert\text{-}C_4H_9SCS_2)_3$[i]	56.8, 56.9, 59.2	85.0, 86.1, 86.8	68.6, 68.8, 69.6 70.1, 71.1, 71.5	42
$Fe(S_2CNMePh)_3$[j]	54.4, 55.2, 57.2	86.6, 86.7, 87.2	67.6, 68.4, 70.0 70.6, 73.0, 74.2	41
$V[S_2P(OEt)_2]_3$[k]	53.1, 53.5, 53.5	84.2, 84.9, 84.9	71.5, 71.5, 73.2 73.2, 73.8, 73.8	42
$Fe[S_2CN(CH_2)_4]_3$[j]	50.0, 51.3, 53.8	87.0, 89.5, 90.3	68.1, 70.4, 72.8 73.1, 73.1, 73.5	37
$Mn(S_2CNEt_2)_3$[l]	48.9, 56.6, 63.2	86.4, 88.6, 89.2	64.5, 66.1, 68.8 71.5, 73.2, 74.9	35, 40, 46
$Fe[S_2C_2(CF_3)_2][S_2CNEt_2]_2$[m]	46.2, 48.6, 48.6	88.4, 89.1, 89.1	71.7, 71.7, 74.5 74.5, 75.8, 75.8	34 (S_2CNEt_2) 42 ($S_2C_2(CF_3)_2$)
$In(S_2CNC_5H_{10})_3$[n]	44.4, 49.6, 51.4	92.1, 92.7, 93.9	66.9, 68.2, 72.6 73.5, 74.2, 76.4	33
$Fe(O_2N_2C_6H_3)_3$[o]	34.3, 48.2, 50.2	92.0, 92.0, 94.4	64.9, 65.4, 76.1 78.1, 80.5, 82.2	28, 29, 39
Ideal trigonal prism	0, 0, 0	120, 120, 120	90, 90, 90 90, 90, 90	0

[a] Observed structures involve bidentate ligands. [b] The twist angles were calculated by taking the average of the projection angles in the M–Cen direction, where Cen is the centroid of the top and bottom triangles on the C_3 axis. The three twist angles were averaged except where a significant spread was observed. [c] J. Iball and C. H. Morgan, *Acta Crystallogr.*, 23, 239 (1967). [d] D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 9, 1858 (1970). [e] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 8046 (1972). [f] T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 12, 927 (1973). [g] Two structure determinations (coordinates taken from first reference): S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968); T. Brennan and I. Bernal, *J. Phys. Chem.*, 73, 443 (1969). [h] S. Merlino, *Acta Crystallogr., Sect. B*, 25, 2270 (1969). [i] D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 11, 823 (1972). [j] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972). [k] C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970). [l] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972). [m] D. L. Johnson, W. L. Rohrbaugh, and W. D. Horrocks, *Inorg. Chem.*, 10, 1474 (1971). [n] P. J. Hauser, J. Bordner, and A. F. Schreiner, *Inorg. Chem.*, 12, 1347 (1973). [o] D. Van DerHelm, L. L. Merritt, Jr., H. Degeilh, and C. H. MacGillavry, *Acta Crystallogr.*, 18, 355 (1965).

functions are plotted for the idealized polyhedron and real molecules; we have used straight lines to fit the shape functions, but it is certainly not necessary that the reaction coordinate be linear, although that is a good approximation for this case. Deformations in the solid state that may represent a compromise between optimal packing and optimal shape in fact follow an explicit reaction path in ML_5 molecules. For established ML_5 structures, there is a continuum between D_{3h} and C_{4v} along a C_{2v} path. That one reaction path suffices here gives convincing support to the postulated Berry physical mechanism for intramolecular rearrangement in five-coordinate molecules (see Meakin, *et al.*,[10] for limitations in applying this physical mechanism to real molecules). This analysis may be extended to ML_5 species in which the ligand atoms or groups are different but where bond distances vary substantially; the "idealized" dihedral angles should be renormalized in the two limiting forms to account for such differences. Burgi[20] has recently used geometric reaction coordinates for five-coordinate cadmium ML_3X_2 {L = S; X = S, I, or O} complexes to study a ligand exchange reaction. Chelate ligands can introduce substantial constraints in a rearrangement reaction

(20) H. B. Burgi, *Inorg. Chem.*, 12, 2321 (1973).

and might also favor significant departures from idealized models. Accordingly, the class of five-coordinate chelates are not ideally suited to the δ analysis; there may well be a family of reaction paths with coordinate proscriptions defined by the intrinsic conformational and dynamic twisting-torsional characteristics of the chelate ligand(s).

Six-Atom Family. Following the idealized shape analysis, the regular octahedron is the reference in the six-atom family. An alternative of experimental relevance in the dynamic chemistry of chelates is the D_{3h} trigonal prism. No discrete ML_6 molecule has trigonal prismatic geometry. Most ML_6 molecules that *ostensibly* undergo some distortion in the solid state as a compromise to packing factors or to the Jahn–Teller effect do so in a fashion that really does not relate to intramolecular rearrangements, *e.g.*, compression (elongation) along a two-, three-, or fourfold axis. Six-coordinate tris chelates display a shape that essentially preserves threefold symmetry with a reaction path that connects the D_{3d} trigonal antiprismatic and the D_{3h} trigonal prismatic forms. In Figure 7, the dihedral angle criterion is applied to the $O_h(D_{3d})$–D_{3h} reaction couple. A single, alternative parameter previously employed for this couple is the twist angle
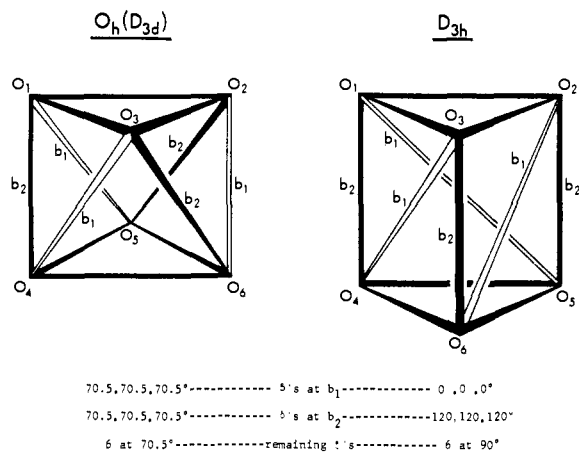
Figure 7. Six-atom family shape characteristics.

Figure 8. Twist angle in six-coordinate complexes.

illustrated in Figure 8. Dihedral angles have been calculated for a series of chelates of intermediate geometry and these data are compared with the twist angle criterion in Table III. The tabulated data incisively establish that all these chelates lie on or near the $D_{3d} \leftrightarrow D_{3h}$ reaction path. Because of the C_3 constraint in this interrelationship, the dihedral angle and the twist angle criteria might be presumed to be equivalent; the data in Table III clearly show the relationship between δ and ϕ but these parameters are not equivalent.

The dihedral angles for the six-coordinate tris chelates illustrate an interesting point. The usual combinations of attractions and repulsions are constrained here by the characteristics of the bidentate ligands, especially the ligand bite (separation of ligating atoms). The bite size leads quite naturally to elongations and compressions of the coordination polyhedra, compressions being the most common. These perturbations also necessarily affect the dihedral angles. They lead to a quantitative difference in the ϕ and δ criteria for describing six-coordinate tris chelates. A very compressed polyhedron can have a small ϕ (defining it as being closer to a trigonal prism) and yet rather large shape defining δ' angles (defining it as being closer to a D_{3d} octahedron). An actual case illustrating this is $In(S_2CNC_5H_{10})_3$ where the ϕ is 33° (near the midpoint of the D_{3d}–D_{3h} couple)[21] but the δ' angles are closer to a D_{3d} octahedron (44.4, 49.6, 51.4°). Is the δ or the ϕ criterion a better measure of the reaction coordinate in the $D_{3d} \rightleftharpoons D_{3h}$ couple? The dihedral angles provide a more comprehensive measure of polyhedral shape, and accordingly it might be argued that this criterion is the better quantitative measure of the reaction path. However, there is one deficiency in this parameter for certain limiting polyhedra. The trigonal prism is one in which all dihedral angles are defined only by symmetry and are insensitive to the shape of faces which may be square or rectangular (all known trigonal prismatic $M(chel)_3$ complexes do have square faces). For this reason, Stiefel and Brown[22] introduced the parameter, the compression ratio, which is the ratio of intertriangle separation (h) and the edge length (s) of the triangle, 1, with an assumption about the ratio for the D_{3h} and D_{3d} limits using data for known complexes.

This assumption may be valid or it may be flawed in a general application.[23] The basic problem is that there are no data that relate any of these parameters to the energy associated with the $D_{3d} \rightarrow D_{3h}$ traverse. Furthermore, there will be no one potential energy curve for this class of chelates but rather a family of curves irrespective of the shape parameter employed. Despite all these qualifications we suggest that the dihedral angle criterion is the best direct measure of the geometric reaction path in the $D_{3d} \rightleftharpoons D_{3h}$ couple.

With the exception of about six tris-dithiolate complexes that are at or close to the D_{3h} limit, all structurally established tris chelates have D_3 or near D_3 symmetry and they are at or near the D_{3d} limit or along the $D_{3d} \rightleftharpoons D_{3h}$ reaction path. However, the reaction path is only represented by actual examples from the D_{3d} limit to close to the midpoint of the path with the number of real structures of a specific reaction-coordinate-set value falling sharply in going from the D_{3d} (D_3) limit to the reaction path midpoint. Absence of real examples for the other half of the reaction path (exclusive of the unique dithiolates) reflects either a lack of synthesis studies with appropriate bidentate ligands or an important facet about the generally, relatively high-energy trigonal twist process.

Seven-Atom Family. The seven-atom family is the most difficult to parameterize at this point due primarily to the paucity of available structural data. There are few X-ray structures of any import available for ML_7 complexes and even fewer are of ordered molecular-type complexes. Most available data are on extended lattice, solid-state-type structures further complicating the development of systematics. Nevertheless, the criteria we have been developing apply equally well here for differentiating between polyhedra.

We take for convenience the C_{3v}-capped octahedron as the reference polyhedron. The other polyhedra of importance in this family are the D_{5h} pentagonal bipyramid and the C_{2v} monocapped trigonal prism. These three polyhedra describe a reaction cycle (Figure 9) illustrating the idealized relationships based on edge stretching. We have used the data from Thompson and Bartell[24] to generate ideal coordination geometries

(21) We calculated ϕ values of 31, 32, and 36° for the individual ligands in contrast to the reported value of 25° (n, Table III).
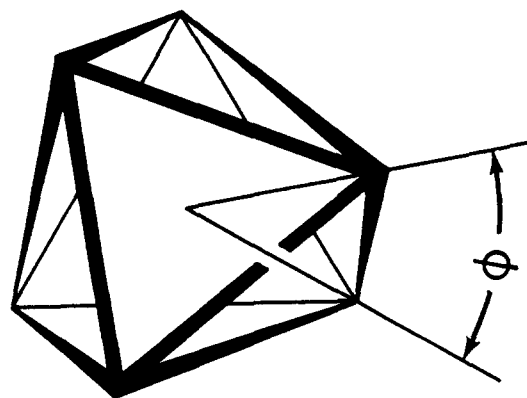(22) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

(23) Footnote e, Table III.
(24) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, 7, 488 (1968).
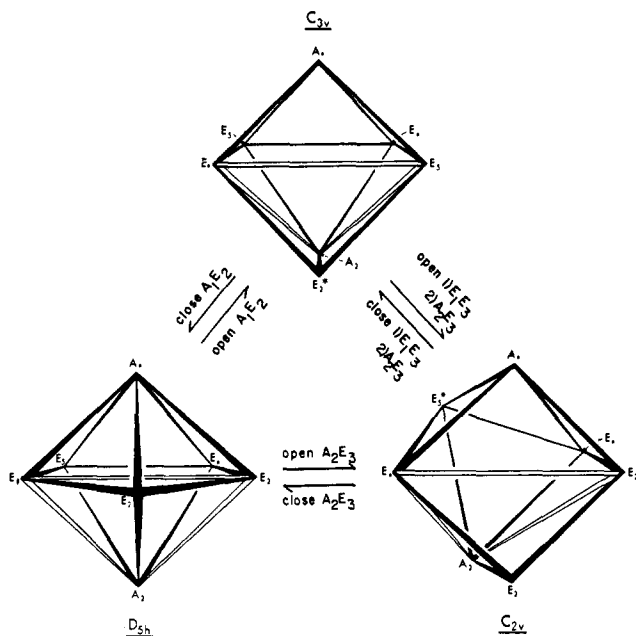
Figure 9. Reaction pathways for seven-coordinate complexes.
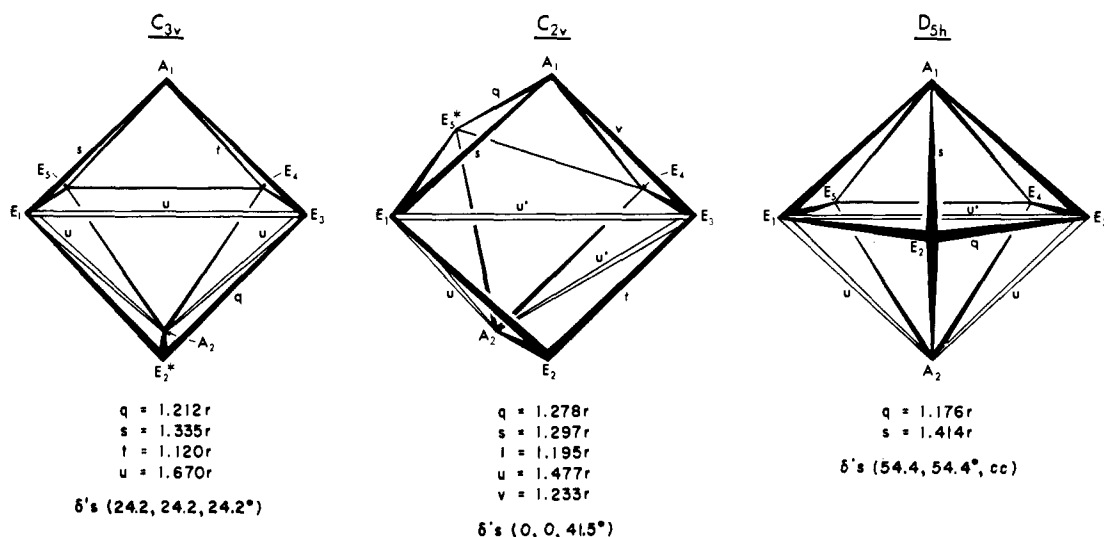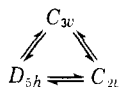
slight distortions to C_s or C_2 point symmetry models. We will ignore these here; in fact, they are virtually indistinguishable from the C_{2v} model in the $n = 6$ approximation.

The angle data for the ideal and observed ML_7 structures are given in Table IV. We notice first of all that there are no good observed C_{3v}-type structures. The most interesting data perhaps are for $Rb_5Zr_4F_{21}$ where there are two independent ZrF_7 polyhedra. Both have the same structure which is midway between C_{3v} and D_{5h} structures. Also, these two polyhedra appear to be close to a special C_s-type structure obtained by the slight puckering of one ligand position of the equatorial plane of a pentagonal bipyramid. Other complexes which are close to the pentagonal bipyramidal structure are $ZrF_7{}^{3-}$ (disordered X-ray structure),[25] ReF_7 (electron diffraction structure),[26] IF_7 (electron diffraction structure),[27] and $V(CN)_7{}^{4-}$ (communication of an X-ray structure).[28] We have looked at the data for K_3UF_7[29] and β-UF_5,[30] which have UF_7 structures but have excluded the data here because of uncertain accuracy in the F atom positions as derived from X-ray powder data.

Figure 10. Seven-atom family shape characteristics. The δ' angles listed are associated with edges identified by double lines. There are only two δ' angles for the D_{5h} model; the edge at μ' is concave and is not an exterior polyhedral edge.

based on the "hard sphere model" and the $n = 6$ exponent for the repulsive potentials ($\Sigma_{i \neq j} R_{ij}{}^{-6}$). We then get the shape parameters for seven-coordinate polyhedra listed in Figure 10. Note that in minimizing repulsions the trigonal prism in the C_{2v} model is not maintained precisely (t vs. s edge lengths). The D_{5h} model results from minor stretching–bending modes involving the expansion of one of the shape-defining edges of the C_{3v} model while the C_{2v} model results from the expansion of two shape-defining edges setting up the reaction cycle mentioned above.

$$C_{3v}$$
$$D_{5h} \rightleftharpoons C_{2v}$$

The corresponding (stylized) rearrangement modes are illustrated in Figure 9. It is worth pointing out here that the C_{2v} model can be broken down further by very

The structural data show a model of C_s symmetry but of a specialized form as found in the complex $Zr_4F_{21}{}^{5-}$ aggregates. This model is midway between C_{3v} and D_{5h} idealized forms. There is a triangular base and then orthogonally staggered sets of two and two ligand atoms. We suggest that this "intermediate" C_s-3:2:2 form may prove relatively common in seven-atom structures and illustrate the specific model in a "points on a sphere" form in Figure 11. It is interesting to note the absence of a real ML_7 complex with a geometry close to the idealized C_{3v} model, a model identified as a low energy form in all "points on a sphere" calculations.

(25) H. J. Hurst and J. C. Taylor, *Acta Crystallogr., Sect. B*, **26**, 417 (1970).
(26) E. J. Jacob and L. S. Bartell, *J. Chem. Phys.*, **53**, 2235 (1970).
(27) W. J. Adams, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **53**, 4040 (1970).
(28) R. L. R. Towns and R. A. Levenson, *J. Amer. Chem. Soc.*, **94**, 4345 (1972).
(29) W. H. Zachariasen, *Acta Crystallogr.*, **7**, 792 (1954).
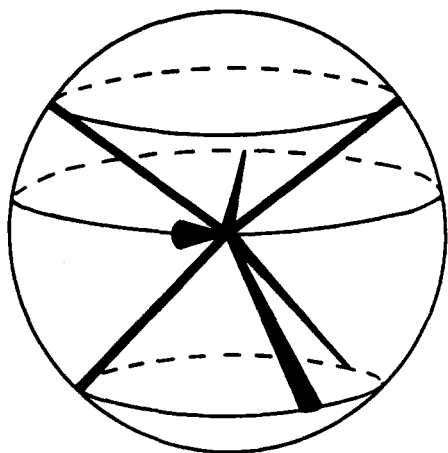(30) W. H. Zachariasen, *Acta Crystallogr.*, **2**, 296 (1949).

Figure 11. C_s-3:2:2 model for seven-coordinate complexes as idealized in a "points on a sphere model."

Table IV. Ideal and Observed Angles (deg) for ML_7 Complexes[a]

	δ' angles
C_{2v} model	0, 0, 41.5
$Na_5Zr_2F_{13}$[b]	0.0, 0.0, 38.3
K_2NbF_7[c]	0.8, 6.1, 36.7
C_{3v} model	24.2, 24.2, 24.2
$Rb_5Zr_4F_{21}$ (polyhedron 1)[f]	(a) 31.1, 50.0
	(b) 33.5, 38.9
$Rb_5Zr_4F_{21}$ (polyhedron 2)[f]	(a) 31.4, 48.0
	(b) 35.0, 38.8
$PaCl_5$[d]	(a) 48.4, 50.9
	(b) 48.4, 50.9
D_{5h} model	54.4, 54.4[e]

[a] (a) and (b) are the results of separate calculations of μ edge angles (Figure 10) for the upper and lower parts of the observed polyhedra based on pentagonal bipyramidal geometry. [b] R. M. Herak, S. S. Malcic, and L. M. Manojlovic, *Acta Crystallogr.*, **18**, 520 (1965). [c] G. M. Brown and L. A. Walker, *Acta Crystallogr.*, **20**, 220 (1966). [d] R. P. Dodge, G. S. Smith, Q. Johnson, and R. E. Elson, *Acta Crystallogr.*, **22**, 85 (1967). [e] There are only two angles here since the third edge (μ', D_{5h} model Figure 10) is not an exterior polyhedral edge for this model, although it is for the C_{3v} and C_{2v} models. [f] G. Brunton, *Acta Crystallogr.*, *Sect. B*, **27**, 1944 (1971).

Eight-Atom Family. One of the most interesting x-atom families for analysis is the eight-atom family. Our treatment here is an amplification of the Porai-Koshits and Aslanov[3] analysis. The reference polyhedron is taken as the D_{2d}-dodecahedron (Figure 12). Two alternative polyhedra, the D_{4d}-square antiprism and the C_{2v}-bicapped trigonal prism, can be generated from the dodecahedron by the stretching of one and two b edges, respectively, as shown in Figure 12. Also, the D_{4d} and C_{2v} forms are interrelated by a simple edge stretching (Figure 12). Thus, we have a reaction cycle, **2**, and, as shown by Porai-Koshits and Aslanov,[3] the

$$
\begin{array}{ccc}
 & D_{2d} & \\
 & \diagup \diagdown & \\
D_{4d} & \rightleftarrows & C_{2v} \\
 & \mathbf{2} &
\end{array}
$$
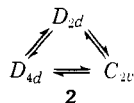
points along the reaction path where real molecules may lie may be described by the dihedral angle criterion.

A dodecahedron is also characterized by the intersection of two orthogonal trapezoids. Distortions from the dodecahedral shape lead to a twisting of these trapezoidal planes. This nonplanarity of the trapezoi-
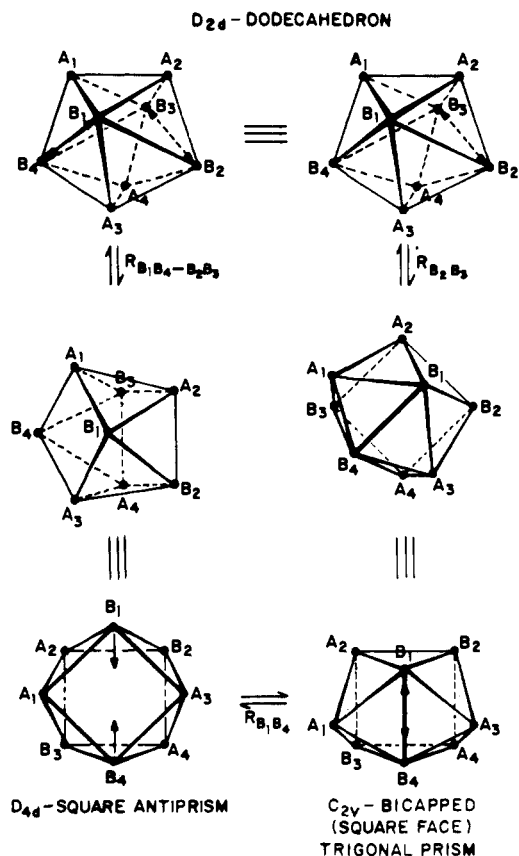
D_{2d} – DODECAHEDRON

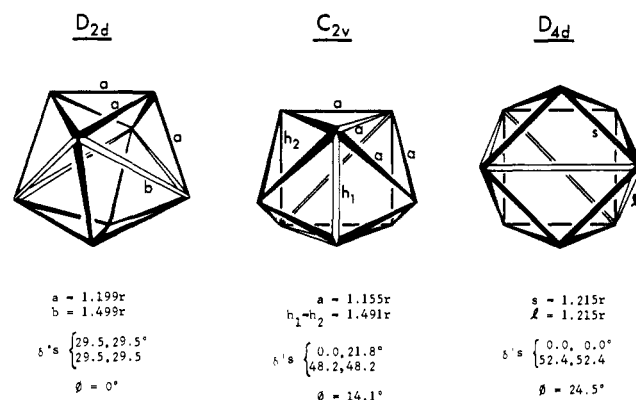Figure 12. Reaction pathways for eight-coordinate complexes.

Figure 13. Eight-atom family shape characteristics; δ' angles are associated with double lines and ϕ's are identified in text.

dal-type atoms (ϕ) is another useful parameter for characterizing eight-atom polyhedra. We calculated ϕ as did Porai-Koshits and Aslanov[3] by taking the dihedral angle between two triangles constructed from the trapezoidal atoms; *i.e.*, ϕ is the angle between the dotted and dashed triangles for the trapezoidal atoms BAAB, **3**. The pertinent structural parameters for the

3
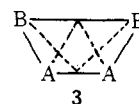
eight-atom family are summarized in Figure 13. Note that the C_{2v} model here was constrained to be on the surface of a sphere, but the prism was also constrained to be trigonal ($h_1 = h_2$). A true "hard sphere model"

in the R_{ij}^{-6} approximation would lead to a distribution of edge lengths with h_1 slightly larger than h_2 (similar to the C_{2v} model in the seven-atom family).

We have calculated the pertinent dihedral angles and ϕ's for ML_8 complexes and the results along with the ideal values are listed in Table V. All but the Na_3W-

Table V. Ideal and Observed Angles (deg) for ML_8 Complexes

Complex	δ' angles	ϕ's
Ideal dodecahedron	29.5, 29.5	0
	29.5, 29.5	
Ideal bicapped trigonal prism	0.0, 21.8	14.1
	48.2, 48.2	
Ideal square antiprism	0.0, 0.0	24.5
	52.4, 52.4	
$Mo(CN)_8^{3-}$ [a]	29.4, 29.4	1.0
	33.1, 33.1	
$H_4W(CN)_8 \cdot 6H_2O$ [b]	0.0, 2.9	22.7
	48.7, 48.7	
$Na_3W(CN)_8 \cdot 4H_2O$ [c]	2.7, 9.6	18.5, 19.3
	45.7, 48.2	
$H_4W(CN)_8 \cdot 4HCl \cdot 12H_2O$ [d]	5.2, 5.2	22.0
	46.3, 52.5	

[a] B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970). [b] S. S. Basson, L. D. C. Bok, and J. G. Leipoldt, *Acta Crystallogr., Sect. B*, **26**, 1209 (1970). [c] L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *ibid.*, **26**, 684 (1970). [d] L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Z. Anorg. Allg. Chem.*, **392**, 303 (1972).

$(CN)_8 \cdot 4H_2O$ polyhedron can be accurately described as square antiprismatic or dodecahedral. The exception is an interesting one because visual inspection of a precision model, unless done very critically, will lead to the conclusion—as reported in the literature—that it is square antiprismatic. However, it is not square antiprismatic; it lies essentially at the midpoint of the reaction path interconnecting the square antiprism and the bicapped trigonal prism. Porai-Koshits and Aslanov have applied[3] these criteria to the description of eight-coordinate chelate structures and show that some previously described as "distorted" square antiprisms are fair approximations of the bicapped trigonal prism.

Procedure for Using δ Criterion

In general we follow the Porai-Koshits and Aslanov method,[3] but a few specific qualifying comments are in order. The goal, of course, for a given polyhedron is to calculate the δ angles for the shape-determining edges as described for each family. In practice, the shape-determining edges are sometimes easy to establish, as when the polyhedron is obviously close to a limiting form or when there is imposed point group symmetry. In these cases the appropriate δ angles can be calculated directly. However, in practice it is commonly not easy to establish the shape-determining edges from a list of distances and angles or even from a picture. In these cases the best procedure is to calculate all the dihedral angles and then sort out the smallest δ (or δ') angles which will serve to identify the primary shape.

The other shape determining edges can then be identified as shown above for each family. In some cases, however, where there are essentially equivalent edges along the periphery of the polyhedron (for example, D_{4d} in the eight-, D_{3d} and D_{3h} in the six-, and C_{4v} in the five-atom family), there is a choice as to which pair of edges along the periphery will be chosen as shape determining. In these cases we selected the pair with the smallest average δ consistent with the twofold (for five- and eight-atom families) or threefold (for the six-atom family) symmetry about the principal axis. In the five- and eight-atom families the remaining δ or δ' angles connect the chosen pair of edges.

Care should be taken in these calculations that all atoms chosen are in the same polyhedron and that any space group imposed point symmetry is handled correctly in filling out a polyhedron from a subset of symmetry independent atoms. We have found it useful in our program for doing these calculations to do interatomic distance calculations with all δ calculations to ensure that all atom positions for a given polyhedron are included correctly. We calculated the plane normals by taking the cross product of two vectors defining the triangular face so that the normal is directed out from the polyhedron.

Reference or idealized models may be based on averages of established structures or may be calculated from a points on a sphere model. The dihedral angle criterion for assessing shape is relatively insensitive to the nonsymmetry-defined shape parameters employed in the idealized model. The dihedral angles are most sensitive to symmetry; the very probe we seek in assessment of geometry.

Conclusion

A general, quantitative procedure has been developed from Porai-Koshits and Aslanov's procedure for the description of polyhedra in coordination complexes, polyhedral boranes and metal clusters. This procedure if followed will remove ambiguous terminology from the literature for descriptions of molecular shape. The generality of the applications does in our view provide an incentive for using this criterion for describing real molecules or ions that do not have defining point group symmetry. Furthermore, we believe that the development of further structural data characterized in such stylized reaction path form will provide substantive information about intramolecular rearrangements. Criteria were not developed here for the 9-, 10-, 11-, and 12-atom families in the interests of brevity and because the 4–8-atom families are more commonly encountered.[31] The procedure outlined here is also applicable for analyzing the conformations in cycles (for example, cycloalkanes), but we see no need for such an extension since the well-established torsion angle scheme is similar to that set forth in this article.

(31) A separate analysis of the nine-atom family will be presented.