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POLYTOPAL FORM AND ISOMERISM

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Abstract—A thesis is developed that accurate structural data for molecules in the solid state can be utilized to derive direct information about the geometric parameters for solution reaction mechanisms. This is specifically illustrated for intramolecular rearrangements but the basic approach should be applicable to bimolecular reactions. A dihedral angle criterion is employed to quantitatively assess shape parameters for polyhedra found in coordination compounds and cluster molecules. These data are expressed in reaction coordinate form whereby a real structure is related to two idealized polyhedra (a reaction path) or to three or more idealized polyhedra (a reaction cycle or chain). It is demonstrated through an analysis of structural data for five coordinate complexes that the Berry type of rearrangement is the lowest energy physical pathway for rearrangements in ML_5 molecules or ions. Solvents may alter the relative energies of ground and excited state forms but should not significantly alter the physical character of the rearrangement process unless the solvent strongly interacts with the molecules. This feature is discussed with respect to polytopal polymorphism in clusters, e.g., $B_8H_8^{2-}$.

INTRODUCTION

Despite the diversity of chemical constitution, the shapes of molecules may be ordered through relatively simple systematics that to a first approximation are set forth in terms of idealized polygons and polyhedra.[1-6] The shape of a molecule may be described in terms of a polygon or a polyhedron where the peripheral or near peripheral atoms in the molecules define the vertices of the geometric figure. These peripheral atoms are the ligand (L) atoms† in a coordination compound‡ ML_x and those of the cluster or ligand§ atoms in a cluster compound M_xL_y. It has been found that the shape generally expressed by molecules or ions is a polytope[1] with all faces equilateral triangles or nearly equilateral triangles.[2,4] Notable polygons or polyhedra are the equilateral triangle and the regular tetrahedron, octahedron and icosahedron for 3-, 4-, 6- and 12-atom cases where shape is fully defined in these regular forms. In the other x-atom systems, shape is not fully defined by the polyhedron as in the D_{3h}-trigonal bipyramid where the ratio of lengths in the two types of edges may vary without loss of D_{3h} point group symmetry.

There are exceptions to these structural systematics; and the alternative forms, most commonly found in the 5-, 7-, and 8-atom families, are closely related to the normal fully triangulated forms. In these alternative forms, the polyhedron has a maximum of triangular faces and one or two square faces and can be easily generated from the reference, fully triangulated form through small bending-stretching motions which are intrinsically low frequency and large amplitude vibrational modes.[2-4] These alternative forms are often very close in energy to the reference forms with relative ordering sensitive to ligand features, core atom electronic states, and stereospecific interactions in condensed states. Interrelationship of the forms appears to be an important feature for stereochemically nonrigid molecules wherein one form may serve as a reaction intermediate or transition state in an intramolecular transposition of ligands.[2] A classic model is the 5-atom system in which D_{3h}-trigonal bipyramids and C_{4v}-square pyramids are found in ML_5 coordination complexes.[2] All ML_5 molecules and ions are stereochemically nonrigid and the rearrangement path is generally presumed to follow a C_{2v} reaction path (Berry Mechanism[7]) at which symmetry limits are the D_{3h}-trigonal bipyramid and the C_{4v}-square pyramid. The collec-

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†If L is a group of atoms, the reference atom is the one bonded to the central atom. In some molecules, the metal atom is a peripheral atom, e.g. pyramidal ML_3.

‡This term is used in a general context that includes all molecules or ions in which there is a "central" atom bonded to x atoms or groups. In this context methane is a coordination compound. Ethane may be similarly perceived with focus on a single C atom. Attention may however shift in for example a long chain hydrocarbon to the subject of conformation.

§The convention is to refer to the cluster atoms M rather than the ligand atoms because x may not be equal to y.

tive evidence for this reaction course is rather compelling but it is not rigorous.[2,4,9,10] It is the objective of this article to outline another approach, developed in a collaborative effort with Dr. L. J. Guggenberger,[8] to definition of intramolecular rearrangements through a reaction coordinate analysis of solid state structural data. This analysis appears generally applicable to dynamic stereochemistry of molecules in the solution state[8] although the *relative* energies of idealized forms may be significantly altered in the solution state as is illustrated for a specific cluster molecule in the 8-atom family.

Definition of intramolecular reaction paths through analysis of solid state structural data

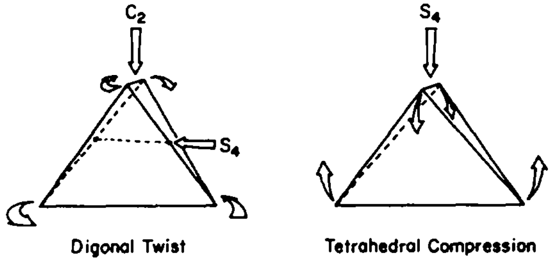
For molecules of any complexity, the most accurate structural information is obtained for the solid state by analysis of X-ray diffraction data. In this condensed state, energy may be gained through more effective packing if the molecular structure departs from an idealized model. This excursion from idealized form should follow closely the path of least resistance, a path that is likely followed in intramolecular rearrangements of the isolated molecule—unless there are significant intermolecular interactions in the condensed state. Thus, we may examine structural data for a group of ML_x coordination compounds in which two or more idealized forms are found to see if a single reaction path (two forms) or single reaction cycle (more than two forms) can be discerned from the data. To do this, a quantitative measure of polyhedral shape is required so that a molecular structure of nonideal form can be quantitatively related to the limiting idealized forms. Here *the concept of shape is presented in terms of a dihedral angle relationship between adjacent polytopal faces.*[8] This procedure was first employed by Porai-Koshits and Aslanov[11] to map out structural form in the relatively complicated 8-atom family.

First, the idealized model with all faces triangular is defined in terms of dihedral angles formed by *normals* to the adjacent faces in the polygon or polyhedron. Each dihedral angle is referenced to the polyhedral edge enclosed by the angle.[8] A maximum of faces or dihedral angles is directly found in the idealized, fully triangulated form. An alternative form with one, two, or three square faces will have respectively a total of one, two or three less faces than the reference (fully triangulated form). Each such square face has a diagonal that may be related to an edge common to two adjacent faces ("diamond" face) in the reference polyhedron.[3] Hence the dihedral angle defined by the "diamond" face becomes zero in the square face of the alternative form. A simple example should suffice to clarify these points.

In the 4-atom family, there are two limiting ML_4 forms, the regular tetrahedron and the square which have four and two faces respectively. For the regular tetrahedron, the six dihedral angles (δ) generated by the *normals* to faces are obviously 109·5°. For the square, two dihedral angles referenced to the face diagonals are zero and four associated with square edges are 180°. Most ML_4 molecules or ions have limiting T_d or D_{4h} forms. An exceptional case is d^9 $CuCl_4^{2-}$ which has Cl–Cu–Cl interbond angles that range from 100 to 131°. The dihedral angles for three $CuCl_4^{2-}$ solid state structures[12] have been calculated[8] and are as follows:

Salt	*δ Angles*
Cs_2CuCl_4	86·4, 87·9, 121·3, 121·3, 122·0, 122·0
$(CH_3NC_5H_4)_2CuCl_4$	87·1, 87·1, 121·3, 121·7, 121·7, 122·2
$[C_6H_5CH_2N(CH_3)_3]_2CuCl_4$	82·8, 83·5, 123·6, 123·9, 124·3, 123·3

Several features of these data are noteworthy. The dihedral angle criterion shows that there is a substantial departure from regular tetrahedral form. The three $CuCl_4^{2-}$ polyhedra are very similar in shape; the first two are identical almost within experimental error. In each structure, the angles are in sets of two and four with the former set decreasing and the latter increasing in magnitude from tetrahedral values; these intermediate forms have essentially D_{2d} symmetry. A reaction path interconnecting T_d and D_{4h} forms is the digonal twist or tetrahedral compression mechanism (Fig 1) which path has D_{2d} constraints. Although the $CuCl_4^{2-}$ structures lie on this reaction coordinate, the data for $CuCl_4^{2-}$ structures are too limited and the spread (geometric) too small to incisively document an



Digonal Twist Perspective

Tetrahedral Compression Perspective

Fig 1. Representation of the diagonal twist or tetrahedron compression mechanism which interconvert the tetrahedron and the square. The reaction path has D_{2d} constraints. These mechanisms are equivalent, i.e. they are physically indistinguishable provided that in the digonal twist *all* interbond angles are allowed to vary from 109·5° to 90°. A strict diagonal twist can achieve only D_{2h} symmetry at the planar form.

explicit reaction coordinate. Nevertheless, the 4-atom problem serves as a simple example of the dihedral angle-shape concept.

Let us now apply the dihedral angle shape criterion to a more substantive structural issue—the nature of polyhedra in the family of five coordination. To limit and simplify discussion, the purview is constrained to ML_5 species in which all ligand atoms are equivalent. First we define the reference form, the trigonal bipyramid of D_{3h}-symmetry. For D_{3h}-symmetry, there remains one degree of freedom in shape, namely the ratio of the two types of polyhedral edge lengths. Since the experimentally observed ratio for axial to equatorial bond lengths ranges only from 0·96 to 1·07,[13,14] a unitary bond ratio is assumed for the idealized model (the dihedral angle criterion is relatively insensitive to small changes in such shape parameters).[8] The nine dihedral angles accordingly generated by the adjacent face *normals* in this model are then 53·1° for the three associated with equatorial polyhedral edges and 101·5° for those associated with the six edges joining equatorial and apical vertices (Figs 2 and 3).[8] The alternative polyhedral form, the C_{4v}-square pyramid, also has only one degree of freedom with regard to shape, namely the ratio of edge or alternatively bond lengths, but because in coordination compounds the position of the central atom is not fully defined by the C_{4v} point group symmetry another shape parameter, the L_{apical}–M–L_{basal} bond angle, must be specified.[8] Bond length ratio is set at unity since observed ratios range only from 0·97 to 1·17 and the LML angle is set at 102° with "theory" and experiment yielding an average value of ~ 102°.[8,13,14] The eight dihedral angles computed for this idealized C_{4v} form are 75·7° for those (4) generated by *normals* to adjacent apical–apical faces and 119·8° for those from apical–basal faces.[8] The ninth angle is 0°; this is for the face diagonal in the square face (Fig 3).[8]

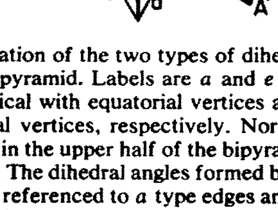
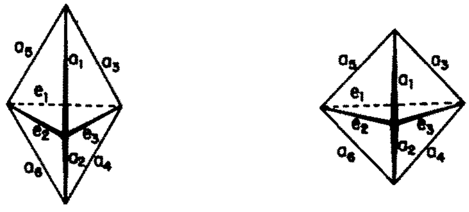


Fig 2. Illustration of the two types of dihedral angles in the trigonal bipyramid. Labels are *a* and *e* for the edges connecting apical with equatorial vertices and equatorial with equatorial vertices, respectively. Normals to faces are labelled A in the upper half of the bipyramid and A' in the lower half. The dihedral angles formed by A and A (or A' and A') are referenced to *a* type edges and are labelled δ_a. There are six of these which have a value of 101·5° in the idealized (see text) trigonal bipyramid. The dihedral angle formed by A and A' are referenced to *e* type edges and are labelled δ_e. There are three of these which have a value of 53·1° in the idealized form.



D_{3h} - Trigonal Bipyramid C_{4v} - Square Pyramid

Fig 3. Labelled reference edges for the dihedral angles generated by normals to adjacent faces in the trigonal bipyramid and the square pyramid. Correspondence of edge labelling in the two forms follows the relationship of the two forms as dictated by the Berry rearrangement (Fig 4).

Observed dihedral angles compared with those for the idealized forms are listed in Table 1. Note that the two entries for $Ni(CN)_5^{3-}$ and for $Nb(NC_5H_{10})_5$ refer to crystallographically distinct polyhedra in the unit cells (*tris*-(ethylenediamine)-chromium (III) salt for the anionic nickelate). For purposes of later discussion of the Berry[7] rearrangement mechanism, the labelling of dihedral angles is consistently referenced to the edges of the trigonal bipyramid with the same labels applied to related (in the Berry mechanism) edges in the square pyramid (Fig 3). Ordering of entries in the Table for actual molecules has been purposely structured so that descending entires more closely approach the C_{4v} limiting form.

Table 1 is basically ordered with respect to column entries by increasing dihedral angles from left to right. The notable feature immediately evident on inspection is that all experimental *intermediate* structures have the following common features.

A. There is one small dihedral angle (δe_1).
B. The larger δe angles (δe_2 and δe_3) are equivalent or nearly so.
C. In the δa group, there is one set of two small angles and one of four larger angles with near angle equivalence within each set.

From this observation we can immediately generalize with reasonable accuracy for all observed ML_5 structures that those intermediate between D_{3h} and C_{4v} limits have C_{2v} or near C_{2v} symmetry. The only 5-coordinate rearrangement mechanism with physical plausibility and with proper permutational character that has a C_{2v} constraint is the Berry mechanism.

The Berry rearrangement mechanism comprises a relative bending of the two apical and of two equatorial bonds (e_2 and e_3) of the trigonal bipyramid as shown in Fig 4. This process transforms the trigonal bipyramid into a C_{4v} square pyramid thereby effectively permuting two axial

Table 1. Dihedral angles in discrete ML_5 complexes*

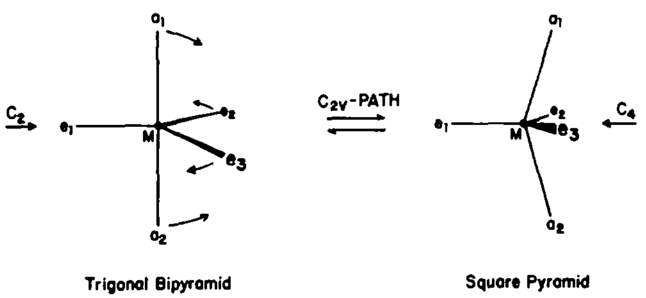
Complex	Crystal structure-reference	Angles° δe_1	δe_2	δe_3	δa_1	δa_2	δa_3	δa_4	δa_5	δa_6
D_{3h}-IDEAL. MODEL	8	53·1	53·1	53·1	101·5	101·5	101·5	101·5	101·5	101·5
$CdCl_5^{3-}$	15	53·8	53·8	53·8	101·1	101·1	101·1	101·1	101·1	101·1
$Ni[P(OC_2H_5)_3]_5^{2+}$	16	50·8	57·3	54·2	98·9	98·0	103·3	102·9	100·9	101·8
$P(C_6H_5)_5$	17	45·7	51·8	52·3	101·4	101·3	104·0	106·2	105·4	102·5
$Co(C_6H_7NO)_5^{2+}$	18	37·8	54·5	58·5	93·4	98·6	106·7	105·9	105·9	110·0
$Ni(CN)_5^{3-}$ (I)	19	32·2	68·6	62·7	88·2	87·4	108·3	110·3	106·3	106·4
$Nb(NC_5H_{10})_5$ (II)	20	23·2	67·0	65·4	85·7	87·0	112·0	112·5	111·7	109·3
$Nb(NC_5H_{10})_5$ (I)	20	15·8	70·6	68·6	82·6	82·8	115·2	114·3	112·8	113·2
$Nb[N(CH_3)_2]_5$	20	15·6	70·2	70·2	83·0	83·0	113·2	113·7	113·7	113·2
$Sb(C_6H_5)_5$	21	14·4	69·2	68·5	82·0	79·7	115·5	116·9	114·8	115·9
$Ni(CN)_5^{3-}$ (II)	19	0·3	75·0	79·4	78·5	78·2	115·6	115·7	118·4	119·6
C_{4v}-IDEAL. MODEL	8	0	75·7	75·7	75·7	75·7	119·8	119·8	119·8	119·8

with two equatorial positions. In one step, one equatorial bond (e_1) correlates with the unique, apical bond of the square pyramid and thereby is permutationally unaffected. For this reaction, it should be evident (Fig 4) that there is a C_{2v} constraint with the e_1 bond (vertex) representing the twofold axis (four fold in the C_{4v} limit) and with the a_1 and a_2 pair and e_2 and e_3 in conjunction with e_1 representing the mirror planes. For correlation of these vertices with edges that serve as references for dihedral angles simply refer to Fig 3. Note that the rate of movement of the a_1–a_2 pair and the e_2–e_3 pair (vertices—Fig 4 or edges—Fig 3) cannot be the same if from the trigonal bipyramid is to be formed a square pyramid with an L_{apical}–M–L_{basal} angle of ~ 102°.

These solid state data provide rather convincing support for the Berry rearrangement. The range of "intermediate" structures is sufficiently large to justify this probing for an explicit reaction path connecting the two forms. This is evident from Table 1 data and is further documented by the illustration in Fig 5 where two near limiting and five intermediate experimental structures shown in the same perspective blend together in a smooth transition from left to right. The perspective has the e_1 vertex (Fig 4) of all structures vertical or nearly so; this vertex is unique in C_{4v} and in intermediate forms.[8]

A final incisive illustration of the C_{2v} constraints in these experimental structures and of the relative rates of vertex or edge motion (apical vs equatorial) is generated by plotting the smallest dihedral angle (δe_1) of the observed polyhedron versus the *departure* of two angles θ_{12} *and* θ_{23} from the idealized values of 156° for the square pyramid.[8] The latter angles may be identified from Fig 4 where θ_{12} is the a_1Ma_2 angle and θ_{23} is the e_2Me_3 angle. In D_{3h} θ_{12} and θ_{23} are 180 and 120°, respectively.

In Fig 6 is the plot of δe_1 vs θ_{12} and of δe_1 versus θ_{23} for structurally defined ML_5 complexes.[8] For each there is a near straight line relationship. It is also evident that the relative rates of changes in these two angles, θ_{12} and θ_{23}, are not the same, as they should not be if the square pyramid with an L_{apical}–M–L_{basal} angle of ~ 102° is to be achieved. All ML_5 ions or molecules whose structures are established for the crystalline state fall on a narrow reaction coordinate with C_{2v} contraints which is the



BERRY REARRANGEMENT

Fig 4. Representation of the Berry Mechanism that comprises a bending mode interrelating or interconverting the D_{3h} and C_{4v} forms.

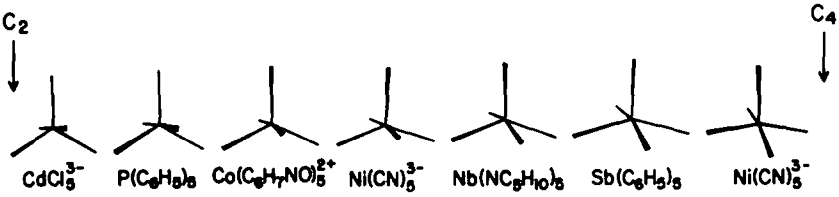


Fig 5. Models of experimental ML_5 structures in a fixed (C_{2v}) perspective with the C_{4v} limiting form on the right. Orientation is such that the apical vertex in C_{4v} and one equatorial vertex in D_{3h} are vertical; intermediate structure follow this orientation. Note the smooth transition of D_{3h} to C_{4v} in going from left to right.

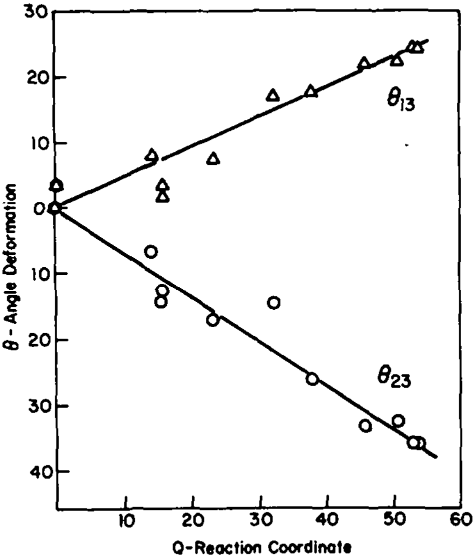
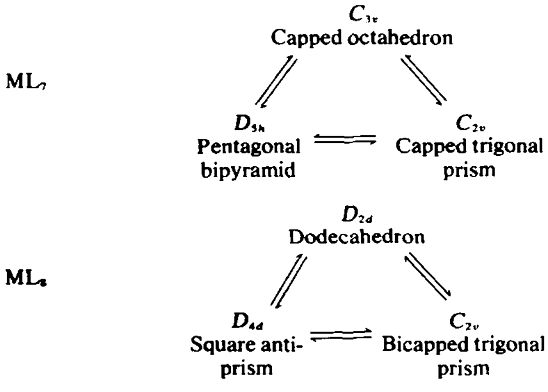


Fig 6. Plot of δe_1 (Fig 3) versus the departure of angles θ_{12} and θ_{23} (Fig 4) from the 156° idealized angle in C_{4v}. This relationship provides the final comprehensive measure of geometry for the ML_5 coordination compound through the interrelationship of the position of the M atom with respect to the dihedral angle-defined coordination polyhedron. Near straight line relationships establish the C_{2v} constraint in intermediate structures (intermediate between C_{4v} and D_{3h}).

Berry reaction coordinate between D_{3h} and C_{4v}. At least for ML_5 coordination compounds, there then seems to be little basis to seriously consider alternative reaction or rearrangement paths that have lower symmetry constraints, e.g. the C_s path in the turnstile mechanism.[22] A similar analysis could and should be done for C_{2v} or C_{4v} ML_4L' complexes although normalization of the observed dihedral angles will be required for those cases where the M-ligating atom distances are significantly different for ML and ML′. All mixed ligand 5-coordinate complexes whose limiting forms are not of D_{3h}, C_{2v} or C_{4v} symmetry cannot strictly (symmetry grounds) undergo the Berry rearrangement; rather reaction paths are then so diffuse and potential energy surfaces so relatively complex that mechanistic distinctions cannot be easily made on symmetry or permutational grounds.[9]*

Analysis of accurate structural data for other x-atom systems can be and have been made[8] although the available structural data are now too limited to allow definitive identification of reaction paths or cycles. For example in some 6-coordinate metal trischelates, a rearrangement reaction path of D_3 symmetry connecting the idealized D_{3h} trigonal prism and D_3 trigonal antiprism is reasonably well documented by NMR studies.[23-25] This path is consonant with the trigonal twist mechanism shown in Fig 7. Reaction path is not as fully defined as in the 5-atom case because essentially all known structures are either at or close to the limiting idealized forms or lie in that half of the reaction path close to the D_{3d}-trigonal antiprismatic form.[8] Reaction cycles for the 7- and 8-atom families have been proposed[8] and analysis[8] through the dihedral angle criterion of the limited structural data for ML_7 and ML_8 complexes show the experimental points to fall on or close to the explicit reaction cycles:



but the data are too limited to say that such reaction cycles are defined. I feel confident that with an increasing number of ML_7 and ML_8 compounds being

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*In the NMR experiments, the Berry mechanism, the turnstile mechanism and other physical modes are permutationally indistinguishable.[9]

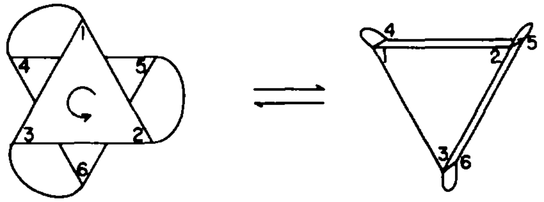

Fig 7. The trigonal twist mechanism that converts the D_3 trigonal antiprism (*tris* chelate complex) to theD_{3h} trigonal prism.

synthesized and analyzed by X-ray analysis, that these reaction cycles will soon be delineated in a convincing fashion through the dihedral angle shape criterion. A similar analysis of the 9-atom family is in progress with initial presumption that there will be a reaction path with D_{3h} symmetrically tricapped trigonal prismatic and C_{4v}-monocapped (square face) square antiprismatic limiting forms.[2,4,26]

Major problems in structure and stereochemistry for the 7- and 8-atom families are a definition of solution state structure and dynamic stereochemistry. These problems are discussed below in some depth for the relatively complicated 8-atom system.

The eight-atom problem

The potential energy surface for an ML_8 complex as a function of shape must be exceedingly complex with *possible* minima at points representative of a cube (O_h), square antiprism (D_{4d}), dodecahedron (D_{2d}), and bicapped trigonal prism (C_{2v}), with relatively small energy separations between points representative of these idealized forms, and with small barriers for interconversion between idealized forms. Structural definition has been realized, with but one exception, *only* for complexes in the solid state. ML_8 complexes with cubic, square antiprismatic, and dodecahedral arrays of ligating atoms have been established rigorously by X-ray diffraction studies.[27-33] The cube is not an especially favorable coordination polyhedron because nonbonding interactions (Born repulsion) of ligand atoms are larger than for alternative forms. However if the polyhedral radius (M–L) to polyhedral edge length (L–L) ratio approaches 0·85 or is larger, then the cube becomes a plausible entity. For smaller ratios, the dodecahedron and the square antiprism are preferred forms with small energy distinctions between them (see the classic analysis by Hoard and Silverton[28]). Cubic coordination is in fact found only for relatively large actinide metal ions with fluoride ion ligands and observed ratios of polyhedral radius to polyhedral edge lengths are 0·85 to 0·89.[34] With transition metal ions such as Ta (V) and Mo (IV), the only coordination polyhedra observed to date are the square antiprism and the dodecahedron.[29,30] Application[8] of the dihedral angle criterion to an observed set of $Mo(CN)_8$ and $W(CN)_8$ anionic structures has yielded the results shown below.

If we add to these structural results the high probability that the potassium salts of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ are isostructural,* then we see that at least for the $W(CN)_8^{4-}$ ion set that structural form is significantly affected by packing effects and perhaps most importantly by anion–cation interactions in the solid state with either the D_{2d} or D_{4d} form being present. The dodecahedral form of the $M(CN)_8^{4-}$ ion in $K_4Mo(CN)_8 \cdot 2H_2O$ and in $K_4W(CN)_8 \cdot 2H_2O$ is retained on dissolution in water as established by very careful Raman studies.[41a]

Focus here on the octacyanomolybdate ions is predicated on two important considerations. Accurate structural data are available for a variety of salts which allows an assessment of the cation–anion interactions in crystals with different $M(CN)_8^{4-}$ polyhedral form. Secondly, the octacyanometallates are the only known discrete ML_8 complexes that retain their constitutional integrity in aqueous, as well as nonaqueous media. These complexes are robust; substitution reactions require relatively high energy inputs and specifically the anions do not exchange their ligands with free cyanide ion at a significant rate.[41b] Exchange for $Mo(CN)_8^{4-}$ and C^*N^- in water is less than 2% in 7 days in the dark although the exchange is photocatalyzed. This stability feature makes the octacyanomolybdates excellent candidates for sol-

Salt	*Crystal structure reference*	*Structure*
$K_4Mo(CN)_8 \cdot 2H_2O$	35,36	D_{2d}—Dodecahedron
$[(n\text{-}C_4H_9)_4N]_3Mo(CN)_8$	37	on $D_{2d} \rightleftharpoons D_{4d}$ reaction path, slightly removed from D_{2d}
$H_4W(CN)_8 \cdot 6H_2O$	38	on $D_{4d} \rightleftharpoons C_{2v}$ reaction path, very slightly removed from D_{4d}
$H_4W(CN)_8 \cdot 4HCl \cdot 12H_2O$	39	on $D_{4d} \rightleftharpoons D_{2d}$ reaction path, slightly removed from D_{4d}
$Na_3W(CN)_8 \cdot 4H_2O$	40	on $D_{4d} \rightleftharpoons C_{2v}$ reaction path, at mid point

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*We find that $K_4W(CN)_8 \cdot 2H_2O$ has an orthorhombic lattice with the same space group and cell dimensions as reported[35,36] for the molybdenum analog.

ution structural studies in sharp contrast to the much more labile octafluorometallate complexes.

Since $\mathrm{Mo(CN)_8^{4-}}$ and $\mathrm{W(CN)_8^{4-}}$ have dodecahedral form for the potassium salts in water, their ^{13}C NMR spectra should consist of two resonances representative of the two types of coordination sites in the dodecahedron (Fig 8). In fact, only a single ^{13}C resonance has been observed[42,43] for

(a) $\mathrm{K_4M(CN)_8 \cdot 2H_2O}$ in water and in water–methanol to 0°
(b) $\mathrm{[(\mathit{n}\text{-}C_3H_7)_4N]_4M(CN)_8}$ in water–ethanol–hexafluoroacetone to −50°
(c) $\mathrm{[(\mathit{n}\text{-}C_3H_7)_4N]_4M(CN)_8}$ in dichloromethane–chloro–difluoromethane down to −160°.

Cyanide ion is relatively nonlabile; therefore, the single line resonance cannot be due to a fast exchange process (1)

$$\mathrm{Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_7^{3-} + CN^-} \qquad (1)$$

For case (a), dodecahedral form is well established; hence the explanation can only be either that there is an accidental degeneracy in ^{13}C resonances or that the complex is stereochemically nonrigid. The former is a relatively unlikely situation so let us presume that the latter is the correct explanation.

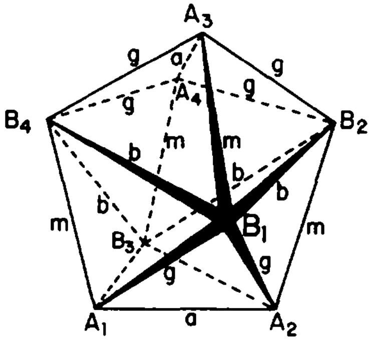

Fig 8. The D_{2d} dodecahedron labelled according to the Hoard–Silverton[28] convention. There are two types of vertices (A and B) in this polyhedron.

Structural form for the $\mathrm{[(\mathit{n}\text{-}C_3H_7)_4N]_4M(CN)_8}$ complexes is unknown for the crystalline state and for the solution states noted in (b) and (c) above. Since the electronic spectra and the infrared CN stretch for $\mathrm{K_4Mo(CN)_8 \cdot 2H_2O}$ in water and for $\mathrm{[(\mathit{n}\text{-}C_3H_7)_4N]_4Mo(CN)_8}$ in water and dichloromethane are very similar it seems reasonable to conclude that dodecahedral form also prevails for solution states (b) and (c). Hence it appears that dodecahedral $\mathrm{M(CN)_8^{4-}}$ is stereochemically nonrigid on the NMR time scale to temperatures as low as −160° and that the barriers to intramolecular rearrangements in $\mathrm{ML_8}$ complexes are very low.[43]

The previously mentioned reaction cycle of

$$\begin{tikzcd} & D_{2d} \arrow[dl, shift left] \arrow[dr, shift left] & \\ D_{4d} \arrow[ur, shift left] \arrow[rr, shift left] & & C_{2v} \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

for 8-coordinate complexes is physically outlined in Fig 9. This reaction cycle with traverse of three idealized forms may be very fast in $\mathrm{M(CN)_8^{4-}}$ or alternatively a single reaction path between D_{2d} and either D_{4d} or C_{2v} could be a uniquely low energy pathway. Especially notable here is the $D_{2d} \rightarrow D_{4d}$ path, the Hoard–Silverton[28] mechanism, in which the process $D_{2d} \rightarrow [D_{4d}] \rightarrow D'_{2d}$ permutes the A and B ligand sites (Figs 8, 9 and 10) in one step. Previously cited structural data (X-ray) could be used to argue[8] for this specific mechanism but more data for other salts of $\mathrm{M(CN)_8}$ ions are required to document such a proposal. It is neverthe-

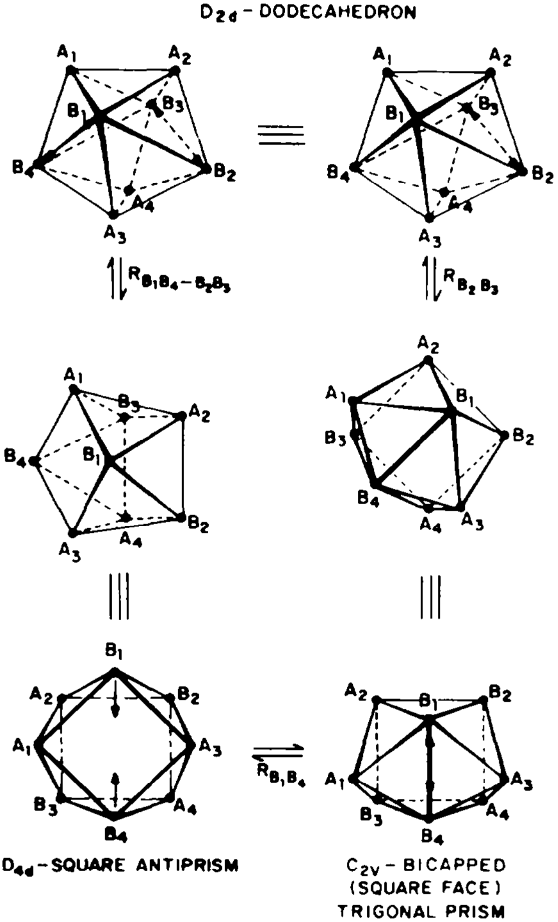

Fig 9. Interrelationships of the D_{2d}, D_{4d} and C_{2v} polyhedra. Elongation of one b edge in D_{2d} generates the C_{2v} form while elongation of two opposed b edges generates the D_{4d} form (See Fig 10).

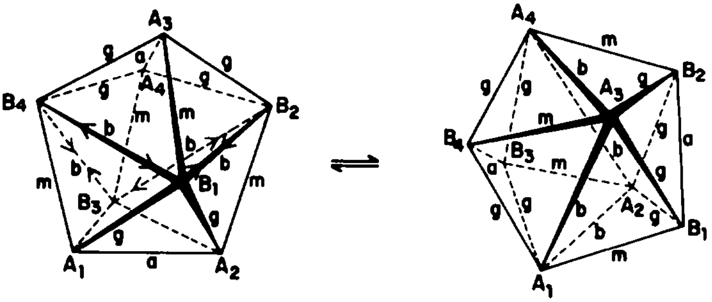

Fig 10. The concerted Hoard–Silverton[28] rearrangement mechanism which consists of elongation of two b edges in D_{2d} (passing through D_{4d}) and formation of two new b edges. This effects permutation of A vertices with B vertices.

less notable that the idealized C_{2v}-bicapped trigonal prism has not been observed in the crystalline state for any ML_8 complex where the complex is discrete or part of an extended lattice.[8]

Resolution of the dynamic stereochemistry for ML_8 complexes will require synthesis of new types where electronic and steric factors may enhance the rearrangement barrier to allow NMR monitoring of the slow-, intermediate- and fast-exchange regions and concomitant permutational analysis to delimit rearrangement mechanisms ($D_{2d} \rightleftharpoons D_{4d}$ and $D_{2d} \rightleftharpoons C_{2v}$ are permutationally distinct mechanisms). However it is not clear, other than trying to build up ligand bulk, what synthetic tack to take. Fortunately we have recently discovered a very unusual behavior in an anionic cluster and the initial findings clearly point the way to a resolution of solution state structure and dynamic stereochemistry in the 8-atom family.[44]

Some years ago, we examined the ^{11}B NMR spectrum of $B_8H_8^{2-}$, a cluster that has dodecahedral geometry in the crystalline $Zn(NH_3)_4^{2+}$ salt.[45] A single ^{11}B doublet (doublet due to B–H spin–spin coupling) was observed for the cesium salt in water.[45] I casually assumed that this result was due to a degeneracy in chemical shift because up to that point all polyhedral borane clusters (and all carborane analogs) exhibited large barriers to rearrangement.[4,45] Frustrated in attempts to assay stereochemistry in most 8-atom coordination compounds, I began to reexamine my "position" on 8-atom clusters. My first thought was to examine the low temperature ^{11}B spectrum of $B_8H_8^{2-}$ and in this the help of Professor M. F. Hawthorne and Dr. R. J. Wiersema was solicited for collection of the NMR data.

To pursue the low temperature NMR behavior of $B_8H_8^{2-}$, a salt soluble in nonpolar solvents was prepared. This salt, $[(n\text{-}C_4H_9)_4N]_2B_8H_8$, dissolved in 1,2-dimethoxyethane, yielded a quite unexpected result: there were three ^{11}B doublets of relative intensities 2:4:2.[44] Only the C_{2v}-bicapped trigonal prismatic form could yield such spectral detail. Furthermore, this form is fluxional; the three doublets merge into a single doublet at +46°. Next the sodium salt was prepared and the spectrum of this salt in dimethoxyethane comprised the 2:4:2 set of doublets of the C_{2v} form in addition to one doublet characteristic of the doublet for $Cs_2B_8H_8$ in water. Clearly, there are two polytopal forms coexisting in this solution. The two forms rapidly interconvert but at a rate that is not fast on the NMR time scale. This conclusion is based on the observation that the intensity of the 2:4:2 set of doublets relative to that of the single doublet increased on temperature decrease.

What polytopal form is represented by the single doublet ^{11}B resonance? This cannot be decisively answered today but the most plausible answer is the D_{4d} square antiprismatic form which can give rise only to a doublet ^{11}B resonance. The dodecahedral form should yield a ^{11}B spectrum comprised of two doublets with equal intensity. A postulate that the doublet represents a fluxional (NMR time scale) dodecahedral molecule is not consistent with the experimental data if it is assumed that the reaction cycle presented in Fig 9 fully represents dynamic stereochemistry for $B_8H_8^{2-}$ within the experimental (NMR) temperature range. The NMR data clearly establish that the C_{2v} form and the second coexisting form do not rapidly interconvert *on the NMR time* scale. The C_{2v} form is fluxional and is in fast equilibrium (NMR time scale) with either D_{4d} or D_{2d}. If we assume the other polytopal form, representing the single doublet, is a fluxional D_{2d} form then D_{2d} must be in fast equilibrium with D_{4d} hence with C_{2v} which contradicts experimental observation.

We may represent the interpretation of the NMR data for the ^{11}B NMR data by the two dimensional potential energy diagram shown in Fig 11 with the energy levels for D_{4d} and C_{2v} arbitrarily set at the same level. The barrier for the $C_{2v} \rightleftharpoons D_{2d}$ interconversion, to account for the fluxionality of C_{2v}, is ~12 kcal/mole. Since C_{2v} and D_{4d} do interconvert but not rapidly on the NMR time scale, the barrier to $D_{4d} \rightleftharpoons C_{2v}$ interconversion must be less than ~20 kcal/mole; in fact, the barrier to this intercon-

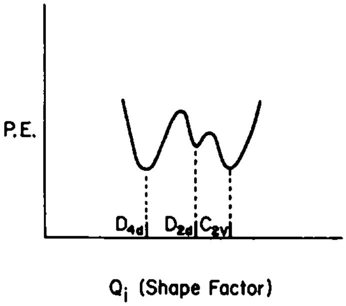

Fig 11. Conceptual two dimensional slice of the potential energy surface in the 8-atom problem. Alternative forms such as O_h are not included for simplicity. The diagram follows the reaction cycle that connects D_{2d}, D_{4d} and C_{2v}.

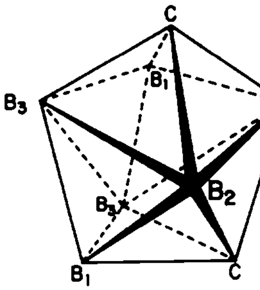

Fig 12. The stereochemistry of 1,6-B_6H_6 $(CCH_3)_2$. In the ^{11}B NMR spectrum only B_1 boron atoms are distinguished from the remaining boron atoms. A rapid Hoard–Silverton rearrangement (Fig 10) would effect equivalence of the B_2 and B_3 sets.

version need only be something like 2–4 kcal/mole greater than for the $C_{2v} \rightleftharpoons D_{2d}$ interconversion. Note the arbitrary aspect of this representation in Fig 11 in that one, or two, of the paths of the reaction cycle, $D_{4d} \rightleftharpoons D_{2d}$ or $D_{4d} \rightleftharpoons C_{2v}$, or both, may have a relatively large barrier. Also D_{2d} may or may not be a relative minimum in the potential energy diagram.

Low barriers to polyhedral rearrangement in this boron cluster are quite unexpected because the boron atoms are in a strong bonding interaction mode as contrasted to a nonbonding relationship of ligand atoms in a coordination compound. Do these data simply underscore the relative flatness of the potential energy surface around D_{2d}, D_{4d} and C_{2v} forms in the 8-atom case? Perhaps so, since even in the neutral carborane $1,6B_6H_6(CCH_3)_2$ (Fig 12) there are detectable in the ^{11}B NMR spectrum only two of the three boron atom environments,[46] a result that can be rationalized in terms of a rapid Hoard–Silverton[28] rearrangement. We may then tentatively conclude that rearrangement barriers in the ML_8 (all ligand atoms equivalent) coordination complexes will be uniformly very low—less than 5 or possibly 3 kcal/mole—because rearrangement barriers in clusters are generally 3 to 5 times larger than those in analogous x-atom coordination compounds.[2,4] Manipulation of flexible structural models suggests, on a purely comparative motional analysis, that other boron clusters, specifically $B_7H_7^{2-}$, and $B_{11}H_{11}^{2-}$, should be comparably nonrigid with $B_8H_8^{2-}$. In fact, $B_9H_9^{2-}$ exhibits no fast fluxional behavior to 200°,[47] $B_7H_7^{2-}$ is nonfluxional in H_2O at 25°,[45] and $B_{11}H_{11}^{2-}$ appears to be a nonrigid cluster *par excellence.*[48] Clearly, these areas of boron cluster chemistry require more detailed study.[49] Resolution of the dynamic stereochemical behavior of these clusters is a substantive issue since the clusters are relatively faithful models for the analogous but intrinsically more fluxional x-atom coordination compounds (ML_x).

The striking dependence of polytopal form in $B_8H_8^{2-}$ on solvent medium is a discovery that should prove to have far reaching general consequences on future studies of solution state structure and dynamic stereochemistry of coordination compounds and of clusters.[4] Wherever the energy separation between alternative idealized polytopal forms is small, there is the possibility of shifting the population of structural forms by altering the nature of the solvent molecules.* Such a shift should be especially feasible if the complex or cluster has a formal charge because then stereospecific cation–anion interactions should be most effective in manipulating structure. Particularly appropriate for studies of this type are the 5, 7, 8, 9 and 11-atom families. This approach also may be effective in modifying the rates of intramolecular rearrangements so that they then may be susceptible to study by the powerful NMR method; the *general* strategy required is to lower rearrangement rates in coordination compounds and raise rates in clusters. These solvent effects should not alter the idealized, *geometric* reaction path or cycle representation which was discussed in the first part of this article; only the energetics associated with the path or cycle will be perturbed.

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*As yet the factors that stabilize C_{2v} or D_{4d} forms in $B_8H_8^{2-}$ (sln.) cannot be identified. Aqueous media favor D_{4d} and nonpolar media favor C_{2v}. Further studies of $B_8H_8^{2-}$ with systematic variation of solvent characteristics and of the associated cation are in progress.[49] Principles established in the cluster system may be applicable to the $Mo(CN)_8^{4-}$ systems, e.g. a shift of polytopal form in solution of these octacyanometallates should be feasible with proper selection of solvent system.

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