solid $IF_6^+AsF_6^-$ on a different instrument (Beckman IR-7 with CsI interchange). Figure 1 shows a typical spectrum of $IF_6^+AsF_6^-$ obtained under experimental conditions similar to those used with the Beckman IR-11 spectrophotometer.[1] This figure demonstrates that the band observed at about 340 $cm^{-1}$ is real. Hence, this band is assigned to $\nu_4(F_{1u})$ of $IF_6^+$ resulting in a more satisfactory value for this mode. This new assignment causes the following changes in our original paper:[1] (i) Table II, infrared, 343 mw, $\delta_{asym}$, $\nu_4(F_{1u})$ of $IF_6^+$; (ii) Table III, the symmetry force constants calculated for the $F_{1u}$ block of $IF_6^+$ based on the new assignment are $F_{33} = 5.335$, $F_{34} = 0.023$, and $F_{44} = 0.459$ mdyn/A. The new value for $F_{44}$ fits very well the series $SbF_6^-$, $TeF_6$, $IF_6^+$. The value of $F_{34}$ decreased slightly, but the change is not significant as was stated in the original paper.[1] The value of $F_{33}$ and, hence, the valence force constant remained unaltered owing to the very weak coupling between $\nu_3$ and $\nu_4$. Consequently, our conclusions concerning the bonding in $IF_6^+$ remain valid.

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## Comment on the Choice of an Eight-Coordinate Polyhedron

*Sir:*

For each of the most commonly occurring coordination numbers (CN), four, five, six, and eight, there are two idealized coordination polyhedra (CP) of importance. These CP are the square and tetrahedron for CN four, the square pyramid and trigonal bipyramid for CN five, the octahedron and trigonal prism for CN six, and the square antiprism and triangular dodecahedron for CN eight. With increasing CN, it becomes increasingly difficult to distinguish the geometries of these polyhedron pairs. For CN eight the choice can be particularly subtle, especially when there is no distinctive crystallographically required symmetry for the metal atom complex. It is the intention of the present correspondence to point out the problems which arise and to provide useful criteria for deciding which idealized CP, if either, is more suitable for describing a particular eight-coordinate complex.

One possible way to distinguish the square antiprism from the triangular dodecahedron might be to examine a good three-dimensional model. Such an approach can lead to difficulties, however, not only because it lacks rigor, but because of the inherent similarity between the molecular frameworks of these two CP. A demonstration of this point is set forth in Figure 1, where stereoviews of the idealized CP and a structure which is halfway between the two are presented. From the drawings the reader can appreciate the necessity for the reference axes and the lines identifying the polyhedron edges. These can only be provided *after* the choice of CP has been made.

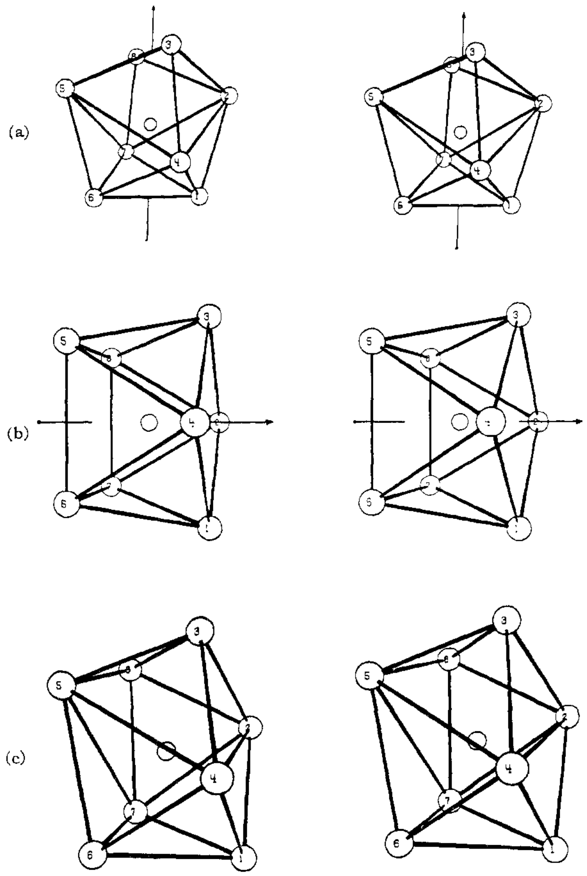

Figure 1.—(a) the idealized $D_{2d}$ triangular dodecahedron; (b) the idealized $D_{4d}$ square antiprism; (c) the idealized intermediate configuration. The views constitute stereoscopic pairs and can be viewed with a small hand stereoscope.

Previously,[1] attention has been focused on the polyhedron-shape parameters,[2-4] as defined originally by Hoard and Silverton[2] (see Figure 2). Although these parameters are without question the most useful set for describing the two CP, they are not necessarily the most convenient for distinguishing between CP. To illustrate, let us consider the angular-shape parameter, $\theta$, which refers to the angle between a metal–ligand bond axis and the principal axis of the CP. There are some immediate difficulties since two such parameters ($\theta_a$ and $\theta_b$) are generally defined for the dodecahedron as opposed to one for the antiprism[2] and since the principal axis, $\bar{8}$, of the square antiprism is orthogonal to the principal axis, $\bar{4}$, of the corresponding dodecahedron. By "corresponding dodecahedron," we mean the one

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(1) For references see S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).
(2) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
(3) D. L. Kepert, *J. Chem. Soc.*, 4736 (1966).
(4) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

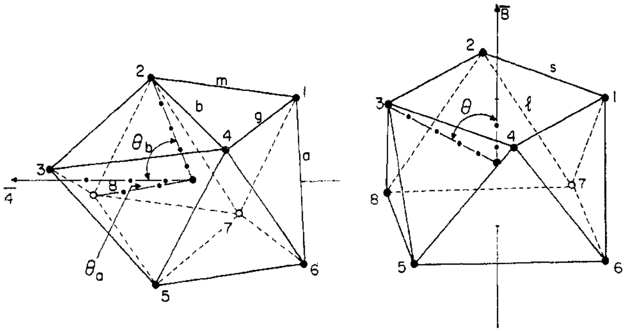

Figure 2.—The idealized dodecahedral configuration (left) and the corresponding square antiprism (right) showing the orthogonal relationship of the two principal axes of the polyhedra and the usual[2] angle- and edge-labeling scheme.

formed by a suitable distortion[5] of the square antiprism, as shown in Figure 2. Clearly, a comparison of angular-shape parameters will offer little basis for choice between the two CP. It is of course possible to define new angular-shape parameters for the dodecahedron which would be directly comparable to the $\theta$ parameter of the corresponding antiprism, but this is generally not the most convenient course nor does it provide a definitive basis for choosing a CP (*vide infra*).

Problems can also arise when the various other shape parameters (edge lengths and angles within the polyhedron faces) are considered. These parameters are usually normalized by the metal–ligand bond distance[2] which, although it is a single value for the idealized antiprism, can have two values for the corresponding dodecahedron. Additional ambiguities occur in mixed-ligand and unsymmetrical chelate complexes, where variations in metal–ligand bond lengths and nonbonded ligand–ligand distances might be expected. Furthermore, whereas only two edge lengths are required to describe the idealized square antiprism, four are needed for the corresponding dodecahedron (Figure 2), a situation which can also cause problems. For example, let us suppose that a complex is dodecahedral but that the investigator has chosen to describe it as the related square antiprism (Figure 2). In order to calculate the length of the *s* edges, he averages the values for edge lengths 1–2, 2–3, 3–4, 4–1, 5–6, 6–7, 7–8, and 8–5. This process naturally obscures the nonequivalence of the *m* and *g* edge lengths of the corresponding dodecahedron and is therefore of questionable value.

As a possible approach which appears to avoid most of the above limitations and complications, we suggest that use can be made of the original suggestion of Hoard and Silverton[2] that the dodecahedron may be considered as consisting of two mutually perpendicular trapezoids, whose line of intersection contains the central metal atom and coincides with the $\bar{4}$ axis. Accordingly, for any given molecule which is thought to be dodecahedral, the best planes through the atoms comprising the two trapezoids may be calculated, and, from the direction cosines, the angle between these planes may be computed and compared to the ideal value of 90°. In Figure 2, the appropriate planes for the dodecahedron contain the metal atom and either (1) the set of ligand atoms 2, 1, 6, 5 or (2) the set of ligand atoms 4, 3, 8, 7 for the orthogonal plane. For comparison, we have computed[6] the angle between the corresponding best planes for the idealized square antiprism (Figure 2) which has a value of 77.4°. In the idealized antiprism, these planes are of course not planes at all, but it is still possible to compute the "best plane" through the appropriate atoms. This angle thus appears to be both a useful and valid criterion for choosing an eight-coordinate CP.

To summarize, we suggest that a given eight-coordinate complex can best be identified with one of the idealized CP in the following manner: (1) compute the trapezoidal best planes for a supposed dodecahedron; (2) calculate the value for the angle of intersection between these assumed planes; (3) compare the angle so obtained with the values of 90° for the idealized dodecahedron and 77.4° for the idealized square antiprism (4) if a choice of CP is not obvious at this point, additional criteria (see examples below) may be employed.

In order to test the utility of this approach, we have applied it to a number of complexes containing bidentate chelating ligands with oxygen as the donor atom, for which three-dimensional X-ray crystallographic information was available. In each case, trapezoidal best planes were computed, the direction cosines of which were used to calculate the angle of intersection between planes for a supposed dodecahedron. In addition, best planes through the square faces of a supposed square antiprism were computed for each complex. The results are summarized in Table I[7-12] where, for the sake of comparison, we also tabulate the idealized CP originally chosen by the authors to describe their results. Also listed in Table I are the crystallographically required symmetries (if any) for the various complexes and the relevant geometric values for the two idealized CP.

None of the examples listed in Table I has crystallographic symmetry higher than a simple twofold axis, which is insufficient to distinguish between the two possible CP. On the basis of the angle between calculated trapezoidal best planes, it can be seen that dodecahedral $Y(hfa)_4^-$, $Pr(tta)_4^-$, and $Zr(ox)_4^{4-}$, as well as antiprismatic $Eu(tta)_3(H_2O)_2$, were correctly formulated by the original authors. In the case of the $Zr(ox)_4^{4-}$ ion, it is noteworthy that the mean displacement of the ligand atoms from the best trapezoidal planes, $d_T$, while not negligible, is still not nearly so

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[5] J. C. Bailar in "Helvetica Chemica Acta Fasciculus Extraordinarius Alfred Werner," Basel, 1967, p 90.

[6] All molecular geometry calculations reported here were carried out on the IBM 7094 computer using MGEOM, a molecular geometry program by J. S. Wood, MIT, 1964.

[7] S. J. Lippard, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **88**, 5930 (1966); M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, submitted for publication.

[8] R. A. Lalancette, M. Cefola, W. C. Hamilton, and S. J. LaPlaca, *Inorg. Chem.*, **6**, 2127 (1967); Dr. S. J. LaPlaca, private communication.

[9] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

[10] J. V. Silverton and J. F. Hoard, *ibid.*, **2**, 243 (1963).

[11] J. G. White, private communication.

[12] J. A. Cunningham, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **6**, 499 (1967).

TABLE I

RESULTS OF GEOMETRY CALCULATIONS ON EIGHT-COORDINATE CHELATE COMPLEXES

| Complex[a] | Required symmetry[b] | $d_T$, Å[c] | $d_S$, Å[d] | Angle, deg[e] | Reported CP[f] | Ref |
|---|---|---|---|---|---|---|
| $Y(hfa)_4^-$ | 2 | 0.07, 0.07 | 0.19, 0.19 | 88.3 | D | 7 |
| $Pr(tta)_4^-$ | ... | 0.06, 0.07 | 0.17, 0.16 | 86.8 | D | 8 |
| $Zr(ox)_4^{4-}$ | 2 | 0.11, 0.12 | 0.20, 0.20 | 88.7 | D | 9 |
| $Zr(acac)_4$ | 2 | 0.30, 0.31 | 0.03, 0.03 | 83.3 | A | 10 |
| $Eu(tta)_3(H_2O)_2$ | ... | 0.43, 0.28 | 0.00, 0.02 | 78.0 | A | 11 |
| $Y(acac)_3(H_2O)_2$ | ... | 0.14, 0.20 | 0.07, 0.21 | 86.1 | A | 12 |
| Perfect antiprism | $\bar{4}2m$ | 0.37, 0.37[g] | 0.0 | 77.4 | A | ... |
| Perfect dodecahedron | $\bar{8}2m$ | 0.0 | 0.31, 0.31[g] | 90.0 | D | ... |

[a] Ligand abbreviations: hfa, hexafluoroacetylacetonate; tta, thenoyltrifluoroacetonate; ox, oxalate; acac, acetylacetonate. [b] From space group symmetry. [c] $d_T$ is the average distance of ligand atoms from best plane through two intersecting trapezoids of dodecahedron. [d] $d_S$ is the average distance of ligand atoms from best plane through two square faces of antiprism. [e] Angle between two intersecting trapezoidal best planes. [f] A = square antiprism; D = dodecahedron; polyhedron chosen by the original authors to describe their results. [g] Assuming a metal–ligand bond distance of ~2.6 Å; it should be noted that the entries reported in the table will decrease with decreasing metal–ligand bond distances.

great as the deviations of the atoms from the best square planes, $d_S$. Even better results were obtained for the other three complexes mentioned above. Thus both the angle and the mean displacement of ligand atoms from the appropriate best planes lead to an unambiguous choice of CP for these four complexes.

For $Zr(acac)_4$, the angle is midway between the ideal values, demonstrating that whichever idealized polyhedron is adopted, it will have to be recognized as significantly distorted. The original authors chose to describe the complex as an antiprism and, from a comparison of $d_T$ and $d_S$ (Table I), their choice appears to have been a sensible one. Of interest is the authors' comment[10] that the deviations from their idealized choice of geometry (square antiprism) were such that the molecule tended toward dodecahedral symmetry. It appears to be generally true that the observed distortions of either polyhedron are toward the other.

In the case of $Y(acac)_3(H_2O)_2$, the angle of 86.1° clearly points to the dodecahedron as the most suitable CP, whereas no distinction seems possible on the basis of $d_T$ and $d_S$ values. Using the dodecahedral model, the three chelating ligands are found to span *m* edges with two water molecules occupying the remaining A and B sites (see ref 2 and Figure 2 for nomenclature adopted here). This ligand-wrapping pattern is quite reasonable, since bidentate chelates have been found to span dodecahedral *m* edges in a variety of other complexes.[1] The original authors, on the other hand, discuss their results using the square antiprism as the idealized CP.[12] In particular, they compare the observed average polyhedron-shape parameters with those calculated by Hoard and Silverton[2] for minimization of ligand repulsive energy and imply good agreement. We have made an analogous comparison for the dodecahedral model, the results of which are shown in Table II along with the treatment of the original authors. In some cases the values reported in the table obscure wide variations in the individual shape parameters being averaged. This occurs for both idealized models and is not unexpected for a mixed-ligand complex. It is evident, however, that since the agreement for the dodecahedron is about as good as that for the antiprism, no choice can be made on this basis.

TABLE II

AVERAGE POLYHEDRON-SHAPE PARAMETERS FOR $Y(acac)_3(H_2O)_2 \cdot H_2O$[a,b]

| Dodecahedral model | | | Antiprismatic model | | |
|---|---|---|---|---|---|
| Parameter | Complex | MFP[c] | Parameter | Complex | MFP[c] |
| *a* | 1.22 | 1.17 (1.20) | *l* | 1.27 | 1.26 (1.26) |
| *m* | 1.17 | 1.17 (1.20) | *s* | 1.20 | 1.19 (1.26) |
| *g* | 1.22 | 1.24 (1.20) | *l/s* | 1.06 | 1.06 (1.0) |
| *b* | 1.47 | 1.49 (1.50) | $\theta$, deg | 57.1 | 57.3 (59.3) |
| $\theta_a$, deg | 37.1 | 35.2 (36.9) | | | |
| $\theta_b$, deg | 71.2 | 73.5 (69.5) | | | |

[a] All parameters refer to those defined by Hoard and Silverton[2] and are normalized by the average Y–O bond length, 2.39 Å.[12] [b] Data for the complex taken from ref 12; average values only are reported. Intersecting dodecahedral trapezoids have been taken as $O_1$, $O_9$, $O_3$, $O_6$ and $O_4$, $O_5$, $O_7$, $O_8$ of the original reference. [c] Most favorable polyhedron, calculated to minimize ligand repulsive energies; numbers in parentheses refer to the hard-sphere model (HSM) values.[2]

In conclusion, we wish to emphasize that the criteria proposed here are intended as an aid to identifying a particular eight-coordinate complex with either idealized polyhedron. They are not meant to provide a means of assigning a CP to a complex which is clearly intermediate between the two configurations (Figure 1). For such cases it is not really important whether one describes the molecule as a distorted square antiprism or distorted dodecahedron, so long as the choice is recognized as ambiguous. Finally, it should be pointed out that the foregoing analysis could be applied to nontransition metal compounds of analogous geometry, *e.g.*, the polyhedral boranes. For such cases it would be sufficient to consider an arrangement of atoms in precisely the same manner as the eight ligand atoms in the above discussion for coordination compounds.

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## Thermal Reactions in the Mass Spectrometry of Organometallic Compounds[1]

*Sir:*

Thermal reactions in the inlet system and/or the ion source of mass spectrometers cause data interpreta-

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2257.