consistent with a formal oxidation state of 4+ as proposed from Mössbauer spectra.[1,9,10] The platinum $4f_{7/2}$ binding energies for both Pt_3Sn_2 cluster compounds fall well within the range of 72.4–73.9 eV reported by Riggs[8] for 18 Pt compounds of oxidation state 2+. (This range does not overlap those of Pt complexes with oxidation states of 0 and 4+.) Thus, the platinum atoms in these clusters should be regarded as divalent rather than zerovalent if an assignment of oxidation state must be made. The assignment is quite arbitrary; a molecular orbital treatment of the cluster provides a better representation.[11]

The platinum $4f_{7/2}$ binding energy of 73.2 eV for the $[Pt(SnCl_3)_5]^{3-}$ anion[12] likewise indicates an oxidation state of 2+ for the platinum and suggests that there is little accumulation of negative charge on the central metal atom. The similarity of Pt environments in this complex and in the cyclooctadiene complex is consistent with the postulate[13] that the $SnCl_3$ ligand is like an olefin in being able to accept electron density from a metal through π-bonds.

Acknowledgment.—The author is deeply indebted to Dr. W. M. Riggs for determination of the spectra and for permission to quote his results prior to publication.

(9) As pointed out by a reviewer, a correlation between Mössbauer chemical shifts and 4d binding energies has previously been noted.[10] It is quite reasonable that a similar correlation with the 3d energies should exist.

(10) M. Barber, P. Swift, D. Cunningham, and M. J. Frazer, *Chem. Commun.*, 1338 (1970).

(11) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, **91**, 1574 (1969).

(12) R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

(13) G. W. Parshall, *ibid.*, **88**, 704 (1966).

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On the Detailed Nature of the Six-Coordinate Polyhedra in Tris(bidentate ligand) Complexes

Sir:

Recently there have been a significant number of reports of six-coordinate geometries other than the classical octahedron. Starting in 1965 there have been seven reports of full X-ray crystallographic investigations of molecular complexes wherein a nearly perfect trigonal-prismatic coordination obtains. In three[1-3] the trigonal-prismatic coordination is clearly enforced by overwhelming ligand structural and steric effects. However, the remaining four structures are of tris(1,2-dithiolate)[4-6] or tris(1,2-diselenate)[7] complexes where overriding steric requirements are not apparent and at least a partial electronic structural explanation for the stabilization of the trigonal prism must be sought.[8-10] Additionally, recent reports described geometries presumably between octahedral and prismatic limits.[11-13] In many cases the detailed nature of the coordination polyhedron was not adequately described. For example, the term "trigonally distorted octahedron" is often used to describe a tris(bidentate ligand) complex without specifying the nature of this distortion. Thus, twisted, compressed, and elongated structures (*vide infra*) have each been referred to as trigonally distorted octahedra. It is the purpose of this correspondence to (a) compare in detail the octahedral and trigonal-prismatic coordination geometries, (b) clearly describe the nature of the distortions which occur in trichelated six-coordinate complexes, and (c) assess the constraint placed on the coordination geometry by rigid bidentate ligands whose bite is more or less fixed by the organic part of the chelate. In this respect we show that many of the known structures can be looked upon as minimally distorted from a regular octahedron with the distortion attributable solely to the short bite of the ligand.

An octahedron can be viewed as a special case of the D_{3d} trigonal antiprism, which occurs when two perfectly staggered equilateral triangles of side s are exactly $\sqrt{2/3}\,s$ apart. Distortions (which maintain at least D_3 symmetry) can be broken down into two components: (1) a component which twists the triangles with respect to each other and (2) a component which changes the ratio of the side of the triangle to the distance between the triangles. The angle ϕ as defined in Figure 1a is a measure of the amount of twisting which has occurred and by precedent is set equal to 60° for the undistorted octahedron. The second type of distortion can be described by the ratio s/h where, as shown in Figure 1b, h is the distance between the parallel equilateral triangles. This ratio is a measure of the extent to which the distorted figure is compressed or elongated with respect to the regular octahedron where $s/h = \sqrt{3/2} = 1.22$. A ratio larger than 1.22 indicates a compressed structure while a

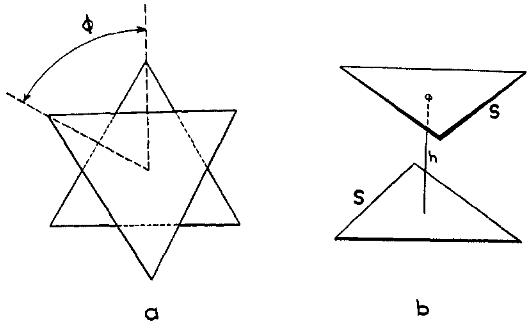

Figure 1.—(a) View of the polyhedron down the C_3 axis illustrating the angle ϕ. (b) View of the polyhedron illustrating the intertriangle distance h and the triangle side s.

(1) J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, **91**, 2395 (1969).

(2) W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969).

(3) M. R. Churchill and A. H. Reis, Jr., *ibid.*, 879 (1970); J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970).

(4) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).

(5) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. S. Heinrich, *J. Amer. Chem. Soc.*, **87**, 5798 (1965).

(6) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966); R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967).

(7) C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971).

(8) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(9) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

(10) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).

(11) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 511 (1968).

(12) G. F. Brown and E. I. Stiefel, *ibid.*, 729 (1970).

(13) A. Aveef, J. P. Fackler, Jr., and R. G. Fischer, Jr., *J. Amer. Chem. Soc.*, **92**, 6964 (1970).

smaller ratio indicates an elongated structure. [We note here that the compression ratio (s/h) carries with it the same information as does the polar angle θ occasionally used by other authors.[14,15] The polar angle is defined as the angle between the z (C_3) axis and the M–L direction. This angle is directly related to the compression ratio s/h by the formula $\theta = \arctan((s/h)2/\sqrt{3})$ and is 54° 44′ for the perfect octahedron. We prefer to use the compression ratio in our discussion since it is more closely related to normally reported geometric parameters.] Most (D_3) distorted octahedral structures and in particular those with three bidentate chelating ligands are distorted in *both* of the above ways; *i.e.*, they are both twisted and either compressed or elongated.

A trigonal prism, as a geometric figure of D_{3h} symmetry has no definite proportions; *i.e.*, its rectangular faces may assume any dimensions. However, the trigonal prism found in structural studies does have a specific shape. In the three tris(dithiolate) and one tris(diselenate) structures and in many of the extended lattices[16-18] in which trigonal-prismatic coordination is present, the sides of the prism are nearly perfect squares. Applying the parameters introduced above, the prism has $\phi = 0°$ and a compression ratio (s/h) uniformly close to 1.00 (range 0.96–1.04). It is intriguing to note that valence-bond theory[19] leads to the conclusion that bonding in a trigonal prism should be strongest when the prism has square sides. Thus, in known chemical systems the trigonal prism is also a precisely defined polyhedron.

In view of the above considerations we suggest that the two limiting six-coordinate polyhedra and all intermediate polyhedra be defined with respect to their common D_3 symmetry by the two parameters ϕ and s/h. These give a concise but accurate description of the shape of the coordination geometry. Utilizing this efficient way of describing six-coordinate (D_3) polyhedra it is instructive to inspect the literature for trends in the details of molecular geometry. In particular we look at the structures of tris(bidentate ligand) complexes where the ligand is rigid, *i.e.*, of approximately constant bite.[20] In such complexes the compression ratio s/h and the twist angle ϕ are not independent quantities. They are in fact related (but not individually determined) by the ligand bite and the metal–ligand bond length. The appropriate equations derived by geometric considerations are $(4/3)s^2 \sin^2(\phi/2) + h^2 = b^2$ and $s^2/3 + h^2/4 = a^2$, where b and a are the bite and metal–ligand distances, respectively. [Alternatively, these relations can be expressed using the angular parameters ϕ, θ, and β (the bite angle). Using spherical trigonometry we derive the appropriate equation: $\cos\beta = \sin^2\theta\cos\phi - \cos^2\theta$.] These equations are very useful when all the pertinent parameters are not reported in the literature.[21] We have determined these shape parameters for a large number of tris complexes which otherwise had little common basis for comparison. Calculations from selected complexes are shown in Table I.

TABLE I

SHAPE PARAMETERS FOR TRIS COMPLEXES

Complex[h]	a = M–L, Å	b, Å	b/a	s, Å	h, Å	s/h	ϕ, deg	Ref
Octahedron			1.41			1.22	60	
Trigonal prism			1.31			1.00	0	
$Re(S_2C_2Ph_2)_3$	2.33	3.03	1.30	3.05	3.03	1.01	3	4
$Mo(S_2C_2H_2)_3$	2.33	3.10	1.33	3.11	3.10	1.00	0	5
$V(S_2C_2Ph_2)_3$	2.34	3.06	1.31	3.07	3.05	1.01	3	6
$Mo(Se_2C_2Ph_2)_3$	2.49	3.32	1.33	3.22	3.32	0.97	0	7
$Mo(mnt)_3^{2-}$	2.39	3.14	1.31	3.24	3.02	1.09	28	12
$Fe(Etxan)_3$	2.32	2.80	1.21	3.54	2.48	1.43	41	*a*
$Co(Etxan)_3$	2.28	2.81	1.23	3.34	2.42	1.38	43	*b*
$Ni(Budtc)_3^{+}$	2.26	2.79	1.24	3.33	2.45	1.36	45	13
$Cr(ox)_3^{3-}$	1.96	2.59	1.32	2.83	2.18	1.30	50	*c*
$Fe(acac)_3$	1.99	2.75	1.38	2.80	2.32	1.21	54	*d*
$V(acac)_3$	1.98	2.75	1.39	2.79	2.30	1.21	56	*e*
$Si(opd)_3^{2-}$	1.79	2.49	1.39	2.54	2.02	1.26	59	*f*
$Y(bzac)_3 \cdot H_2O$	2.28	2.76	1.21	3.39	2.09	1.62	53	*g*

[a] B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970). [b] S. Merlino, *Acta Crystallogr.*, *Sect. B*, **25**, 2270 (1969). [c] J. N. van Niekerk and F. R. L. Schoening, *ibid.*, **5**, 499 (1952). [d] J. I. Ball and C. H. Morgan, *ibid.*, *Sect. B*, **23**, 239 (1967). [e] B. Morosin and H. Montgomery, *ibid.*, *Sect. B*, **25**, 1354 (1969). [f] J. J. Flynn and F. P. Boer, *J. Amer. Chem. Soc.*, **91**, 5756 (1969). [g] F. A. Cotton and P. Legzdins, *Inorg. Chem.*, **7**, 1777 (1968). [h] Abbreviations used: mnt = maleonitriledithiolate = $S_2C_2(CN)_2^{2-}$; Budtc = di-*n*-butyldithiocarbamate = $(C_4H_9)_2NCS_2^-$; Etxan = ethyl xanthate = $C_2H_5OCS_2^-$; ox = oxalate = $C_2O_4^{2-}$; acac = acetylacetonate = $C_5H_7O_2^-$; opd = *o*-phenylenedioxy = $C_6H_4O_2^{2-}$; bzac = benzoylacetonate = $(C_6H_5)(CH_3)C_3HO_2^-$.

We note first that the neutral dithiolate and diselenate complexes are very close to or exactly at the trigonal-prismatic limits of $\phi = 0°$ and $s/h = 1.00$. On the other hand the Fe and V complexes of acac and the complex $Si(opd)_3^{2-}$ are quite close to the octahedral limits of $\phi = 60°$ and $s/h = 1.22$. In the latter cases it is clear that the ratio of the bite to the M–L distance (b/a) is compatible with the chelate being able to approach spanning the edge of the octahedron (b/a = 1.41 for the perfect octahedron). Additional complexes in this table have ϕ values between 0° and 60° and thus must be regarded as "distorted" from the limiting cases. The distorted complexes lie in two distinct groups. The first group is exemplified by $Mo(mnt)_3^{2-}$ where the s/h ratio at 1.09 is also roughly between octahedral and trigonal prismatic values. In this case with $\phi = 27°$ and $s/h = 1.09$, both shape criteria show the structure to be roughly midway between octahedral and trigonal-prismatic limits. The second group contains all those complexes where the bite is too short (b/a is substantially less than 1.41) to span an octahedron. This group includes tris complexes of oxalate, dialkyldithiocarbamate, and alkyl xanthate. For these complexes, although the twist angle is indeed between the two limiting structures, the compression

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(14) A. G. Karipedes and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

(15) P. H. Davis and J. S. Wood, *Chem. Phys. Lett.*, **4**, 466 (1969).

(16) R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, **45**, 1466 (1923).

(17) L. Bragg, G. F. Claringbull, and W. H. Taylor, "Crystal Structures of Minerals," Cornell University Press, Ithaca, N. Y., 1965.

(18) H. F. Franzen, *J. Inorg. Nucl. Chem.*, **28**, 1575 (1966).

(19) R. Hultgren, *Phys. Rev.* **40**, 891 (1932).

(20) The extent of rigidity of the ligand system is an unknown quantity. That is, when does it become favorable energetically to distort the intraligand bond angles and distances as opposed (or in addition) to the metal-ligand bond angles? It appears from the large amount of data available that the ligand bite in a given sized chelate ring is much closer to being constant than any other structural parameter. We note that in cases where different ring sizes are involved this argument is no longer valid. See for example D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970), or ref 10.

(21) We have in this process also discovered some errors in the literature. For example, in ref 11 the intertriangle distance (h) is reported as 2.87 Å, with a twist angle (ϕ) of 32°. From the data reported the bite (b) is also calculated to be 2.87 Å. This is clearly incompatible and in this structure it appears that the h distance must be considerably smaller. Thus, these equations can be particularly useful as an internal check on molecular geometry reportage.

ratios lie in the range 1.3–1.5; *i.e.*, they are much larger than the regular octahedral value. Thus, while the octahedron is compressed with respect to the trigonal prism, these structures are even more compressed than the regular octahedron. We further note that within this group, those complexes having the largest twist from the octahedron are significantly those having the largest compressions and most significantly also those with the smallest b/a ratios. Thus, the distortion in this group of complexes is not truly in the direction of the trigonal prism. In fact, if the trends in twist angle and compression ratios are extrapolated to angles close to $\phi = 0°$, they lead to severely compressed structures which are chemically unreasonable. Such complexes are no longer viable in six-coordination and in fact in cases where the b/a ratio is quite low, seven- or eight-coordination occurs through either dimerization or solvent (or ligand) addition. Such situations occur for β-keto enolates of rare earths,[22–24] for dithiocarbamate complexes of larger second transition elements,[25] and in many of the complexes of the early transition metals.[26–28] Thus it seems clear that six-coordinate complexes of ligands with small bites are not truly twisted toward trigonal-prismatic coordination but can be simply viewed as minimally distorted from an octahedron. We are currently doing overlap calculations to determine if the actual direction of distortion is such that loss of metal–ligand overlap is minimized.

We hope these considerations may have impact on various aspects of tris(chelate) chemistry other than the purely structural one discussed above. For example our results have interesting consequences in considering the mechanism of racemization of various D_3 octahedral complexes.[29] One of the mechanisms often considered is the trigonal or Bailer twist. For tris complexes with rigid ligands a trigonal twist from the octahedron must be accompanied by a trigonal elongation (assuming a and b remain constant). In this respect we note that complexes already partially twisted from the octahedral limit are not necessarily better candidates for a trigonal-twist mechanism. As we have pointed out, many of these which contain short-bite ligands would necessarily produce quite flat (compressed) trigonal prisms which may be energetically unfavorable. For example, Holm and coworkers[29] suggested a twist mechanism for Fe(MePhdtc)$_2$-($S_2C_2CF_3$) on the basis of nmr studies and lent physical support to this conclusion by looking at the static structure of the distorted complex. Although this complex has lower symmetry than we have considered thus far, an approximate evaluation of shape parameters leads to its placement in the twisted and highly compressed class. The ease with which this complex can be further twisted is not at all clear from any previous or present thinking.[30]

As another example, a large series of tris(1,10-phenanthroline) complexes has been studied with respect to spin-delocalization mechanisms,[31] molecular orbital energy levels,[32] and sources of optical activity in absorption bands.[33] In most cases a single, nearly octahedral structure has been assumed for all M(phen)$_3^{2+,3+}$ complexes. However the phen ligand has a very rigid bite and it seems that the M–L distance should vary sufficiently in these complexes (*e.g.*, from Cr(II) to Ni(II) or from Fe(III) to Os(III)) to cause the structures to be significantly different. Thus, in computations involving geometrical parameters a common structure cannot be assumed for all complexes in this class. We hope our considerations may be of aid to those studying these problems.

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[22] This effect is most clearly seen in Y(bzac)$_3$·H_2O[23] (bzac = benzoylacetonate) where the seventh coordination position is occupied by a water molecule. Here, the "octahedron" formed by the other six donor atoms is severely compressed to accommodate the H_2O molecule in its trigonal face. In this case the b/a ratio at 1.21 is smaller than that encountered in most six-coordinate complexes (and especially smaller than any with oxygen donor atoms). Recently, Erasmus and Boeyens[24] have used similar considerations in discussing the structure of Pr_2(thd)$_6$ (thd = 2,2,6,6-tetramethylheptane-3,5 dione) where Pr achieves a coordination number of 7 by dimerization.

(23) F. A. Cotton and P. Legzdins, *Inorg. Chem.*, **7**, 1777 (1968).

(24) C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970).

(25) T. Brennan and I. Bernal, *Chem. Commun.*, 138 (1970).

(26) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

(27) E. L. Meutterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(28) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970).

(29) See, for example, L. H. Pignolet, R. A. Lewis, and R. H. Holm, *ibid.*, **93**, 360 (1971), and references therein.

(30) In fact, in highly compressed complexes of short-bite ligands, consideration should perhaps be given to a planar pathway in which a distorted hexagonal planar structure obtains. This mechanism would be topologically similar to the trigonal twist for tris(bidentate ligand) complexes.

(31) See for example G. N. LaMar and G. R. Van Hecke, *Inorg. Chem.*, **9**, 1546 (1970); R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 2343 (1970), and references therein.

(32) I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 648 (1969), and references therein.

(33) B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969); A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1428 (1969), and references therein.

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