Pergamon

0277–5387(95)00213–8

Polyhedron Vol. 14, No. 20–21, pp. 2871–2878, 1995

0277-5387/95 \$9.50+0.00

A NEW SIMPLE CRITERION FOR DISTINGUISHING THE TYPES OF STRUCTURES IN EIGHT-COORDINATE COMPLEXES: THE PATTERN OF BOND ANGLES

C. W. HAIGH

Department of Chemistry, University College, Swansea, Singleton Park,
Swansea SA2 8PP, U.K.

(*Received* 28 *February* 1995; *accepted* 3 *May* 1995)

Abstract—Square antiprismatic, triangular dodecahedral and (rectangularly) bicapped trigonal prismatic (or hendecahedral) eight-coordinate structures are shown to manifest distinct patterns of LML′ bond angles, which are validated by many straightforward examples from the literature. Our criterion was used to re-classify seven published structures: in one of these, a completely new type of eight-coordination, christened the C_s decahedron, has been discovered. The same type of analysis has been applied to the rarer types of eight-coordination: the cube, the hexagonal bipyramid, the axially bicapped trigonal antiprism and the trigonally bicapped octahedron, and the axially bicapped trigonal prism: useful insights have thus been obtained concerning several published structures.

Eight-coordinate complexes are now far from uncommon; frequent in lanthanide chemistry, they have now been found with central atoms from most Groups of the Periodic Table, including most Main Groups, and all the first-row transition metals except apparently nickel.[1] The two most frequent geometries are the square antiprism (henceforth A) and the triangular dodecahedron (D); less common is the bicapped trigonal prism or hendecahedron (H); our representations of these are given in Fig. 1. The energy differences between these structures are small, as are the energy barriers between them.[1] It is not always easy to distinguish between these structures: several criteria have been proposed.[2] We present here a new simple criterion for making this distinction.

Viewed as a solid figure in space (or, equivalently, as a graph) A has 16 edges, H 17 edges and D 18 edges (Fig. 1). Hence of the 28 LML′ angles subtended at the central atom, either 16 or 17 or 18, respectively, will be small. We derive the following criteria:

(a) if the gap between the 16th and 17th lowest LML′ angles is more than about 20°, the structure is A;*
(b) if the gap between the 17th and 18th lowest LML′ angles is substantial, the structure is H;†
(c) if the 16th, 17th and 18th lowest LML′ angles are close together, the structure is D.‡

Having obtained (from the identity of the 16, 17 or 18 edges), the connectivity of the relevant graph, one needs to check that it is indeed the A, H or D graph, as the case may be. Thirty-three cases from the literature (15 A, 18 D) were straightforwardly classified in accordance with this criterion and in

---

*In the ideal A, obtained by twisting a cube about a tetrad by 45°, this gap is from $\cos^{-1}[(\sqrt{2}-1)/3] = 82°4'$ to $2\ \mathrm{s}^{-1}\sqrt{3} = 109°28'$, namely 27° 24′. We have derived our critical value of about 20° empirically, from published crystallographic data.

†Too few data are available for a quantitative estimate.

‡For a very brief treatment, somewhat analogous to this, see Ref. 3.

agreement with the published conclusions.* We proceed to comment on some further interesting examples.

We firstly present two hitherto unclassified cases. The complex (THF)$_5$La{OCMo(CO)$_2$Cp}$_3$[6] is eight-coordinate, with 16 OLaO angles less than or equal to 84°, with the 17th angle 137°: it has clearly the A structure. The eight-coordinate complex In(O$_2$CPh)$_3$(4Mepy)$_2$[7] was recently stated to be a "pseudo square pyramid", a description ascribing one coordination site to each bidentate benzoate ligand. In order to obtain a more standard description, we examined the LInL′ angles: the 16th, 17th and 18th lowest were 92, 93 and 93°: the structure is thus D.

We next present seven cases where the present criterion has resulted in a re-classification. The structure of calcium picrate pentahydrate[8] was reported to be A, but the angle O(5)CaO(6) of 80° is not acceptable for two ligands forming the diagonal of a square face; the angle O(7)CaO(7′) was omitted from Table 2 in Ref. 8: its value is 68.8°. When this is included, the 16th, 17th and 18th lowest OCaO angles are 86°, 99° and 123° respectively. We therefore re-classify the structure as the comparatively rare H (see Fig. 2). The crystal structure of [Mn(NO$_3$)$_2$(dppn)$_2$] has been reported,[9] where dppn is 3,4-di-2-pyridylpyrazine, a molecule containing four nitrogen atoms, which here acts as an unsymmetrical bidentate ligand. These authors commented that the structure could be viewed as distorted A or distorted D, though "not particularly close to either"; in citing this structure, Donohue *et al.*[10] assumed it to be D. However, the 16th and 17th lowest LMnL′ angles are both 89.1°, and the 18th is 114.7°: this also we re-classify as H (see Fig. 3). The crystal structure of V(S$_2$CMe)$_4$[11] contains two independent molecules in the unit cell, which were found, most unusually, to be isomeric. Of these two, complex 1 is by our criterion indubitably D, in agreement with Ref. 11. Complex 2 was there classified as also D, but with a different arrangement of ligands: however, the 16th lowest SVS angle is 89°, but the 17th and 18th, equal by symmetry, are 108°: instead of D with a major distortion, we here re-classify it as A, with a slight distortion towards D—an even more striking exam-

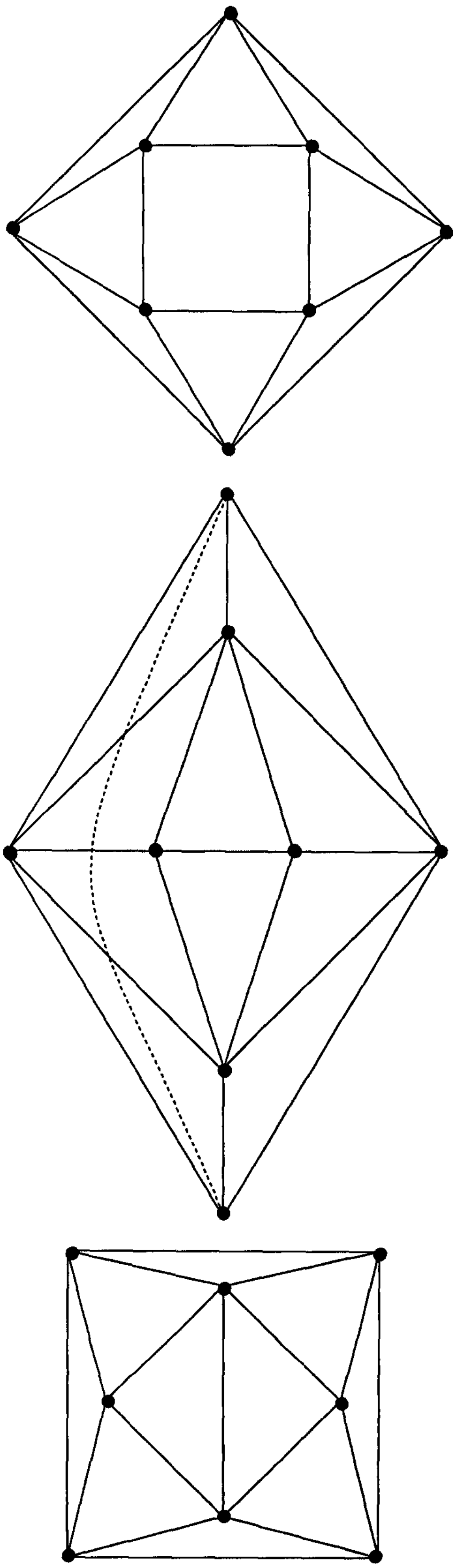


Fig. 1. Representations of eight-coordinate structures: (a) square antiprism (A); (b) triangular dodecahedron (D); (c) bicapped trigonal prism or hendecahedron (H).

---

*Sometimes after correction of errors in Tables, e.g. for U(NCS)$_4$(OPMe$_3$)$_4$,[4] the value of the angle N(2) U O(2′) is 74.7° and not 137°: our criterion *then* gives a clear A structure. Also, in Table VII of Ref. 5, concerning M(NCS)$_4$(bpy)$_2$, M = Nb, Zr, the angle N(2a) M N(2d) is misprinted as N(2c) M N(2d); when this is corrected, a consistent set of 16 angles for an A structure results.

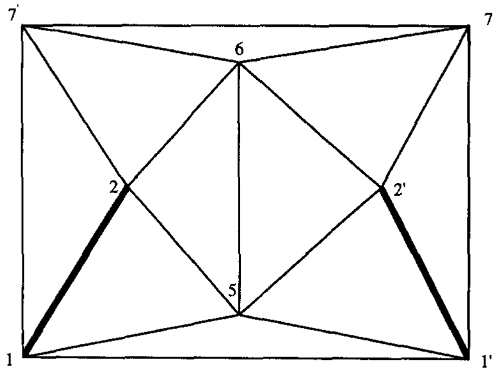


Fig. 2. Schematic representation of the re-classified structure of $[Ca\{OC_6H_2(NO_2)_3\}_2(H_2O)_4]$ (Ref. 8). The thick lines, here *and henceforth*, indicate edges spanned by bidentate or multidentate ligands.

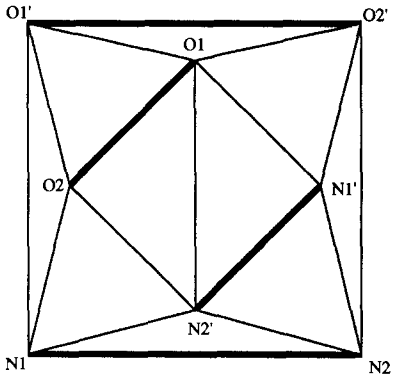


Fig. 3. Schematic representation of the re-classified structure of $[Mn(NO_3)_2(dppn)_2]$, (dppn = 3,4-di-2-pyridylpyrazine).[9]

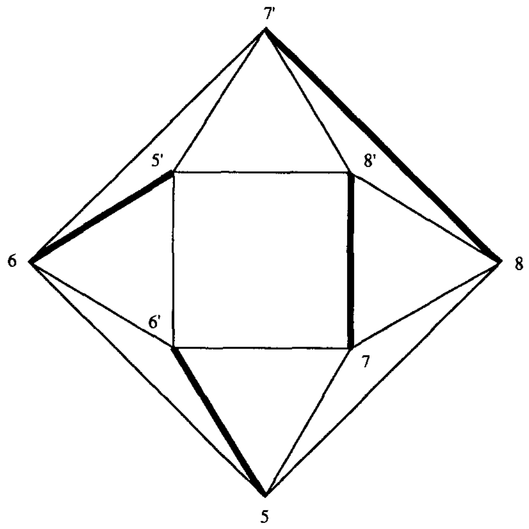


Fig. 4. Schematic representation of the re-classified $V(S_2CMe_2)_4$ complex 2 (Ref. 11). The dodecahedral edges we have deleted are 68 and 6′8′.

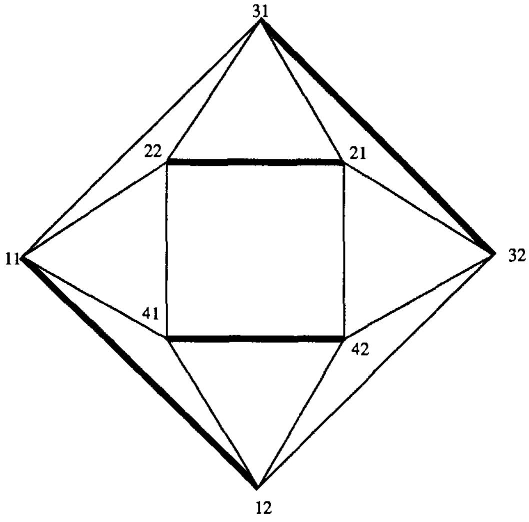


Fig. 5. Re-classified isomer of $Sn(O_2CMe)_4$, molecule 4 (Ref. 12). The dodecahedral edges we have deleted are 12—31 and 41—21.

ple of isomerism (see Fig. 4). The crystal structure of $Sn(O_2CMe)_4$[12] contains four independent molecules per unit cell, and turns out now to exhibit the same remarkable type of isomerism. Omitting the four OSnO angles in four-membered rings from single bidentate ligands, molecules 1, 2 and 3 each have 14 OSnO angles ranging from 74 to 95°, and were correctly classified as D. However, in the case of molecule 4, the 16th, 17th and 18th lowest OSnO angles are 85, 101 and 105°: we therefore re-classify it also as A, slightly distorted towards D (see Fig. 5). Bertazzi *et al.*[13] stated that the coordination around Bi in the dimer $Bi_2(NCS)_6(bpy)_4$ could not be described in terms of a regular polyhedron. However, there are 16 smallest LBiL′ angles, the largest being 83.8°, and the 17th smallest is 108.1°. With such a gap, we are justified in calling the structure distorted A (see Fig. 6). Preut and Huber[14] described the structure for $In(O_2CMe)_3$(1,10-phenanthridine) as a distorted D, but the 16th smallest LInL′ angle is 91.1°, and the 17th is 108.1°. A better description then would be a distorted H (see Fig. 7). In the remarkable structure of $Er_8O(Me_3CCOCHCOCMe_3)_{10}(OH)_{12}$[15] the coordination of the inner four Er atoms was there described as H *or* D, but, e.g. for Er(1), the 16th, 17th and 18th smallest OErO angles are 88.4, 105.9 and 109.6°: thus one cannot satisfactorily classify it as H or as D but rather as a somewhat distorted structure with 16 edges. This structure, though it does have two quadrangular and eight triangular faces, is not A, but *a completely new structure for*

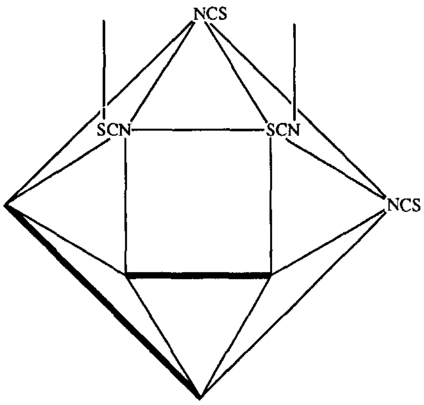


Fig. 6. The revised coordination about a Bi atom in the dimer $Bi_2(NCS)_6(bpy)_4$ (Ref. 13). Two of the thiocyanates are bridging.

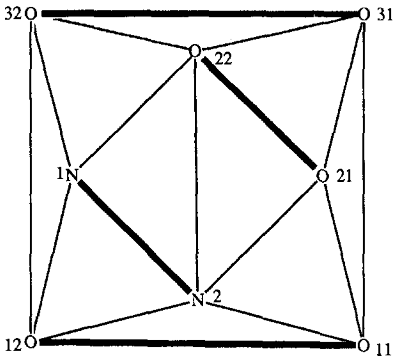


Fig. 7. Re-classified structure of $In(O_2CMe)_3$(1,10-phenanthridine) (Ref. 14). The dodecahedral edge O(12)—O(31) has been deleted.

eight-coordination (see Fig. 8); we dub it the *C_s decahedron*.

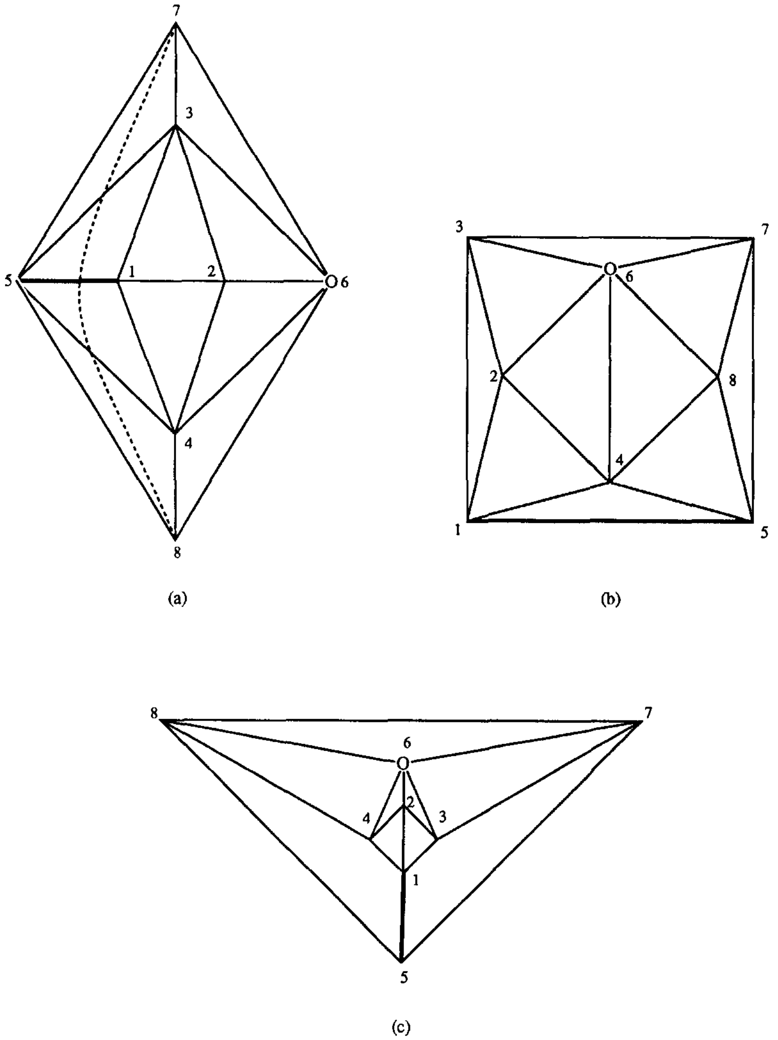
We next examine by our criterion some borderline cases from the literature. The dimer {Sc(tropolone)(tropolonate)$_3$}$_2$* was described in Ref. 17(a) as H distorted towards D, but in the adjacent paper, Ref. 17(b), as D. The 16th, 17th and 18th lowest OScO angles are respectively 87, 91 and 110°, clearly agreeing with the description of Ref. 17(a). The structure of $WMe_4\{ON(Me)NO\}_2$[18] is described as intermediate between A and D. The 16th, 17th and 18th lowest LWL′ angles are 86.1, 99.4 and 111.6°: this allows us to classify it as A, distorted towards H. In $La\{S_2P(OEt)_2\}_3(Ph_3PO)_2$,[19] the 16th, 17th and 18th lowest LLaL′ angles are 88, 96 and 102°: with two gaps (between angles) which are of intermediate magnitude, it is safest to classify this as A distorted towards H and D. In $Mo(CN)_4(CH_3NC)_4$,[20] the 16th lowest LMoL′ angle is 88°; the 17th and 18th, equal by symmetry, are 99°. With a gap of such intermediate magnitude, we cannot disagree with the authors of Ref. 20(b) that the structure is D, but distorted (with C_2 crystallographic symmetry) towards A. Similarly, in the classic case of $[Zr(C_2O_4)_4]^{4-}$,[21] the 16th lowest OZrO angle is 87.5°, the 17th and 18th lowest, equal by symmetry, are 101.3° (these angles are tabulated in Ref. 3): thus again D is distorted towards A. In the case of $[Ca(H_2O)_4$(tetraoxocyclododecane)$]^{2+}$,[22] the structure is described as distorted A. The gap from the 16th to the 17th lowest OCaO angle is $99.3-85.3 = 13.7°$, again an intermediate value. The distortion is towards D, with C_2 symmetry, and obviously derives from constraints imposed by the tetradentate macrocyclic ligand.

Aslanov has pointed out[23] that the present type of criterion, considering the pattern of LML′ angles, can also usefully be applied to the other rarer structures found in eight-coordination. *The cube* is less uncommon than sometimes thought. In the ideal geometry, the 12 smallest angles are $2\ \text{cosec}^{-1}\sqrt{3} = 70°\ 32'$, and the next 12, corresponding to face-diagonals, have the supplementary value of 109° 28′. In structures with small deviations from this ideal, we expect a similar pattern, with a comparatively large gap between the 12th and 13th smallest angles, and this is indeed found. In $[PaF_8]^{3-}$,[24] the anion has crystallographic D_{4h} symmetry, and is described as an almost perfect cube: the gap between the 12th and 13th smallest angles is $108.2-71.8 = 36.4°$. In [La(2,2′-bipyridyl bis N-oxide)$_4]^{3+}$,[25] the coordination symmetry is described as being nearly perfect D_4 and only slightly deformed from the ideal cube: the corresponding gap has been reduced only slightly to $112.0-72.8 = 29.2°$. There appear to be similarly small distortions in the cases of $[U(bpy)_4]$[26] and the NEt_4^+ salt of $[U(NCS)_8]^{2-}$.[27]

Elongation or compression of a cube to give a tetragonal prism will not greatly affect the gap under consideration; but the commonest further type of distortion is a twist about the tetrad, resulting eventually in A. Eight of the smallest angles, corresponding to the two remaining square faces, will be unaltered, but four will be increased. Of the 12 angles of 109° 28′, similarly four will be unaffected, four will increase, but four will decrease, thus decreasing the gap. In the ion $[MnL]^{2+}$, where L is the octadentate macrocyclic ligand $\{\text{-}CH_2CH_2N(CH_2.N\text{-pyrazolyl})\text{-}\}_4$,[28] although the angle of twist is stated to be as high as 24°, the above pattern is retained to a surprising extent, the gap between the 12th and 13th smallest angles being

---

*For a discussion of the formulation and hydrogen-bonding in this structure, see Ref. 16.



(a) (b)

(c)

Fig. 8. The coordination of Er(1) in $Er_8O(Me_3CCOCHCOCMe_3)_{10}(OH)_{12}$:[15] (a) as D; (b) as H; (c) (preferred) as a C_s decahedron. The thick line represents the only bidentate ligand coordinated to this Er; the unique O atom is indicated; the five other ligands are hydroxyl. The D or H edges deleted to obtain (c) are 3–5 and 4–5, which are adjacent in the D structure.

110.6 − 76.3 = 34.3°: doubtless the considerable constraints arising from such an unusual ligand mitigate the substantial changes which otherwise would arise. An interesting point arises in connection with the unusual chain compound 3/4Pb $(O_2CH)_2\{SC(NH_2)_2\}_4$.[29] The tetragonal prisms are stated to be twisted by about 18°; but there are two distinct Pb positions in the unit tetragonal cell, both being surrounded by eight S atoms. For Pb(1), the gap between the 12th and 13th smallest angles is 101 − 77 = 24°, but for Pb(2), the 12 smallest angles range from 59 to 73°, the next 12 from 89 to 129°; thus the gap has been reduced to 16°, considerably smaller than the latter range. We deduce that the coordinate polyhedron around Pb(2) is more distorted than that around Pb(1). Now, in the chain-structure, the central Pb(1) is adjacent to two Pb(2) atoms; but the Pb(2) atom has on one side a vacant site (note the 3/4 stoichiometry). Although the authors actually comment that "the distances separating planes of S atoms are virtually constant, irrespective of whether a prism is occupied or not", our consideration of SPbS angles has shown that the presence of a vacant site does result in more distortion. We turn finally to an extreme case of twisting. In $[La(pyridine\text{-}N\text{-}oxide)_8]^{3+}$,[30] the angle of twist is stated to be 27°, and the authors describe the structure as a square antiprism distorted towards a cube. In confirmation of this assignment, we find the gap between the 12th and 13th smallest angles is as small as 86.2 − 78.4 = 7.8°, while the gap between the 16th and 17th is around 20°.

Hexagonal bipyramidal geometry is favoured by many eight-coordinate uranyl complexes, the UO_2 oxygens always being found in the axial positions. In the ideal case, there are six LML′ angles of 60°, 12 equatorial-axial angles of 90°, followed by six 120° angles. For small distortions, we expect substantial gaps between the 6th and 7th, and between the 18th and 19th smallest angles. The latter gap occurs at the same position as that for the D polyhedron discussed earlier (indeed, topologically, both are eight-vertex triangulations of the sphere), but if the graphs corresponding to the 18 edges formed are drawn, they will be different. A good example with small distortion is furnished by the ion $[UO_2(NO_3)_3]^-$ (Ref. 31, neutron diffraction). The ion has crystallographic D_{3d} symmetry, and the gap between the 18th and 19th smallest angles has only been reduced to 117.5 − 92.2 = 25.5°. Similar situations appear to arise in $UO_2(NO_3)_2 \cdot 6H_2O$ (Ref. 32, neutron diffraction), $[UO_2(CO_3)_3]^{4-}$,[33] $[UO_2(O_2CMe)_3]^-$,[34] together with the comparatively rare non-uranyl examples $[MCl_2(18\text{-crown-}6)]$, M = Hg and Cd[35] and $[PbPh_2(O_2CMe)_3]^-$.[36]

The commonest type of distortion of the hexagonal bipyramid is puckering, alternate equatorial ligands being above and below the mean plane. Its effect is to increase the 60° angles, decrease half of the equatorial–axial angles and increase half of them, but also to decrease the 120° angles, thus reducing both gaps. The result is that, when a certain degree of pucker has been reached, there will no longer be any clear gaps among the 24 smallest angles, particularly when the crystallographically imposed symmetry is low. Such a case arises for the ion $[CdL(MeOH)_{1/2}(H_2O)_{1/2}(NO_3)]^+$, where L is a hexadentate macrocycle, and the monodentate nitrate and half-molecules of methanol and water are axial.[37] The distortions resulting from the constraints imposed by the macrocycle have reduced the two "gaps" to 4 and 2° respectively. A similar situation may well result in $[UO_2(S_2CNEt_2)_3]^-$,[38] but Ref. 38 is only a preliminary communication.

When the degree of puckering is still larger, half the equatorial–axial angles have become so large as to no longer qualify as edges of the coordination polyhedron; but this is compensated by the fact that the six angles whose values in the ideal hexagonal bipyramid were 120° have now been so reduced as to become edges. The new polyhedron thus created is an *axially bicapped trigonal antiprism.* It too has 18 edges (being topologically a third eight-vertex triangulation of the sphere),* and will show a gap between the 18th and 19th smallest LML′ angles. The structure of the *trans* isomer of $SmI_2(MeOCH_2CH_2OCH_2CH_2OMe)_2$, with axial iodines, is most instructive in this context, being described initially in Ref. 41(a) as a distorted hexagonal bipyramid, but subsequently in Ref. 41(b) as an axially bicapped trigonal antiprism. The coordination shell is centrosymmetric. There are small gaps of 82.0 − 66.7 = 15.3° and 113.3 − 98.0 = 15.3° between the 6th and 7th and between the 18th and 19th smallest angles respectively: taken in isolation, such gaps could be consistent with either description, allowing for appreciable distortion, but the 13th to 18th smallest angles (see Fig. 9) are ∠I Sm O(1a) = 95.6°, ∠I Sm O(3a) = 96.7° and ∠I Sm O(2) = 98.0°, all enlarged equatorial–axial angles, and not e.g. ∠O(2) Sm O(3a) = 121.5°, which would be an edge in the description as an axially bicapped trigonal antiprism. This analysis shows clearly that the original description as a distorted hexagonal bipyramid was correct.

A special case of the axially bicapped trigonal antiprism is the *trigonally bicapped octahedron*: here the 7th to 18th smallest angles are all right angles in the ideal case.

Lastly, we consider the *axially bicapped trigonal*

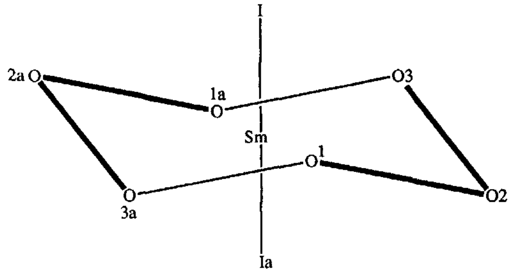


Fig. 9. Schematic representation of the *trans* isomer of $SmI_2(MeOCH_2CH_2OCH_2CH_2OMe)_2$,[41] illustrating a puckered hexagonal bipyramid.

---

*Since the Euler relation must be fulfilled, all three are technically dodecahedra; but in practice only the D polyhedron of Fig. 1(b) is so called. Actually, there are no less than 14 topologically distinct eight-vertex triangulations of the sphere! Their planar duals are 12-vertex cubic graphs of connectivity 3 (Refs 39, 40). Of the additional ones, the example perhaps least unlikely to have chemical relevance can be described as a cube, in which half the face-diagonals have been shortened to become edges, thus leading to T_d symmetry; alternatively, and more succinctly, it is the quadruply capped tetrahedron.

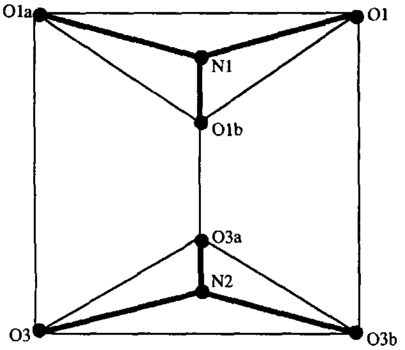


Fig. 10. The axially bicapped trigonal prism. Schematic representation of $[Bi\{N(CH_2CO_2)_3\}_2]^-$.[42]

prism (Fig. 10): this is not to be confused with polyhedron H above, the *rectangularly* bicapped trigonal prism. The present polyhedron has 15 edges; we would therefore expect a gap in the values of the LML′ angles between the 15th and 16th smallest. We are only aware of one example, the ion $[Bi\{N(CH_2CO_2)_3\}_2]^{-42}$ (see our Fig. 10).* The gap in this case turns out to be rather small, $113.7-104.1 = 9.4°$, because the structure, constrained by crystallographic trigonal symmetry, is twisted from the ideal D_{3h} symmetry—a twist which would eventually lead to an axially bicapped trigonal antiprism, just considered. The extent of twist is indicated by the fact that, whereas in D_{3h} symmetry all six LML′ angles corresponding to the diagonals of rectangular faces would be equal, here we have (see Fig. 10) $\angle$O(1b) Bi O(3b) = 113.7°, but $\angle$O(1) Bi O(3a) = 138.2°.†

Our new simple criterion is thus presented as a useful addition to those of Ref. 2. In the present paper, we have already used it to re-classify seven published structures and to uncover a completely new type of eight-coordination. Furthermore, when applied also to the rarer forms of eight-coordination, it has provided useful insights.

Acknowledgement—The author is grateful to Professor L. A. Aslanov for several useful ideas in expanding this work.

REFERENCES

1. M. G. B. Drew, *Coord. Chem. Rev.* 1977, **24**, 179; D. L. Kepert, *Prog. Inorg. Chem.* 1978, **24**, 179; D. L. Kepert, *Inorganic Chemistry Concepts*, Vol. 6, *Inorganic Stereochemistry*, Ch. 12–13. Springer, Berlin (1982); D. L. Kepert, in *Comprehensive Coordination Chemistry* (Edited by Sir G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 1, pp. 83–95. Pergamon Press, Oxford (1987).
2. J. L. Hoard and J. V. Silverton, *Inorg. Chem.* 1963, **2**, 235; S. J. Lippard and B. J. Russ, *Inorg. Chem.* 1968, **7**, 1686; M. A. Porai-Koshits and L. A. Aslanov, *J. Struct. Chem.* (*Eng. Trans.*) 1972, **13**, 244; E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.* 1974, **96**, 1748.
3. F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chem.* 1987, **26**, 2889.
4. C. E. F. Rickard and D. C. Woollard, *Aust. J. Chem.* 1979, **32**, 2181.
5. E. J. Peterson, R. B. Von Dreele and T. M. Brown, *Inorg. Chem.* 1976, **15**, 309.
6. A. A. Pasynskii, I. L. Eremenko, G. Z. Suleimanov, Yu. A. Navier, I. P. Beletskaya, V. E. Shklover and Yu. T. Struchkov, *J. Organomet. Chem.* 1984, **266**, 45.
7. M. T. Andras, A. F. Hepp, S. A. Duraj, E. B. Clark, D. A. Scheiman, D. G. Hehemann and P. E. Fanwick, *Inorg. Chem.* 1993, **32**, 4150.
8. V. Diakiw, T. W. Hambly, D. L. Kepert, C. L. Raston and A. H. White, *Aust. J. Chem.* 1979, **32**, 301.
9. J. E. Andrew, A. B. Blake and L. R. Fraser, *J. Chem. Soc., Dalton Trans.* 1975, 800.
10. C. J. Donohue, E. C. Kosinski and V. A. Martin, *Inorg. Chem.* 1985, **24**, 1997.
11. L. Fanfani, A. Nunzi, P. F. Zanazzi and A. R. Zanzari, *Acta Cryst., Sect. B* 1972, **28**, 1298.
12. N. W. Alcock and Valerie L. Tracy, *Acta Cryst., Sect. B* 1979, **35**, 80.
13. N. Bertazzi, G. Alonzo, L. P. Battaglia, A. Bonamartini Corradi and G. Pelosi, *J. Chem. Soc., Dalton Trans.* 1990, 2403.
14. H. Preut and F. Huber, *Z. Anorg. Allg. Chem.* 1979, **450**, 120.
15. J. C. A. Boeyens and J. P. R. de Villiers, *J. Cryst. Mol. Struct.* 1972, **2**, 197.
16. C. W. Haigh, *Polyhedron*, in press.
17. (a) A. R. Davis and F. W. B. Einstein, *Inorg. Chem.* 1974, **13**, 1880; (b) T. J. Anderson, M. A. Neuman and G. A. Melson, *Inorg. Chem.* 1974, **13**, 1884.
18. S. R. Fletcher and A. C. Skapski, *J. Organomet. Chem.* 1973, **59**, 299.
19. A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.* 1976, 2466.
20. (a) F. H. Cano and D. W. J. Cruikshank, *Chem. Commun.* 1971, 1617; (b) M. Novotny, D. F. Lewis and S. J. Lippard, *J. Am. Chem. Soc.* 1972, **94**, 6961.
21. G. L. Glen, J. V. Silverton and J. L. Hoard, *Inorg. Chem.* 1963, **2**, 249.
22. P. P. North, E. C. Steiner, F. P. van Remoortere and F. P. Boer, *Acta Cryst. Sect. B* 1976, **32**, 370.

---

*In Table 2 of Ref. 42, "$\angle$ $O_3BiO_3{}^{b}$" is a misprint for "$\angle O_3BiN_2$".

†For a further discussion of some of the transformations discussed in the second half of this paper, see Ref. 43.

23. Professor L. A. Aslanov, Moscow, personal communication.
24. D. Brown, J. F. Easey and C. E. F. Rickard, *J. Chem. Soc. (A)* 1969, 1161.
25. A. R. Al-Karraghouli, R. O. Day and J. S. Wood, *Inorg. Chem.* 1978, **17**, 3702.
26. G. del Piero, G. Perego, A. Zazzetta and G. Brandi, *Cryst. Struct. Commun.* 1975, **4**, 121.
27. R. Countryman and W. S. McDonald, *J. Inorg. Nucl. Chem.* 1971, **33**, 2213.
28. M. Di Vaira, F. Mani and P. Stoppioni, *J. Chem. Soc., Dalton Trans.* 1992, 1127.
29. I. Goldberg and F. M. Herbstein, *Acta Cryst., Sect. B* 1972, **28**, 410.
30. A. R. Al-Karraghouli and J. S. Wood, *Inorg. Chem.* 1979, **18**, 1177.
31. G. A. Barclay, T. M. Sabine and J. C. Taylor, *Acta Cryst.* 1965, **19**, 205.
32. J. C. Taylor and M. H. Mueller, *Acta Cryst.* 1965, **19**, 536.
33. R. Graziani, G. Bombieri and E. Forselloni, *J. Chem. Soc., Dalton Trans.* 1972, 2059.
34. W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.* 1959, **12**, 526.
35. C. R. Paige and M. F. Richardson, *Can. J. Chem.* 1984, **62**, 332.
36. N. W. Alcock, *J. Chem. Soc., Dalton Trans.* 1972, 1189.
37. K. R. Adam, S. Donnelly, A. J. Leong, L. F. Lindoy, B. J. McCool, A. Bashall, M. R. Dent, B. P. Murphy, M. McPartlin, D. E. Fenton and P. A. Tasker, *J. Chem. Soc., Dalton Trans.* 1990, 1635.
38. K. Bowman and Z. Dori, *Chem. Commun.* 1968, 636.
39. F. C. Bussemaker, S. Cobeljic, D. M. Cvetkovic and J. J. Seidel, Computer investigation of cubic graphs, Table on p. 9; pp. 16–19; pp. 59–62, T. H. Report 76-WSK-01, Technological University, Eindhoven (1976).
40. F. Harary, *Graph Theory*, Theorem 11.6, p. 106, Ch. 5 and 11. Addison-Wesley, Reading, MA (1969).
41. (a) V. Chebolu, R. R. Whittle and A. Sen, *Inorg. Chem.* 1985, **24**, 3082; (b) A. Sen, V. Chebolu and A. L. Rheingold, *Inorg. Chem.* 1987, **26**, 1821.
42. K. D. Suyarov, L. M. Shkol'nikova, M. A. Porai-Koshits and V. S. Fundamenskii, *Dokl. Akad. Nauk S.S.S.R.* (*Eng. Transl.*) 1990, **311**, 93 (Russian original p. 1397).
43. I. G. Shterev, G. S. T. Nikolov, N. Trendafilova and R. Kirov, *Polyhedron* 1991, **10**, 393, and refs therein.