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REPRESENTATION OF CONFIGURATION IN COORDINATION POLYHEDRA AND THE EXTENSION OF CURRENT METHODOLOGY TO COORDINATION NUMBERS GREATER THAN SIX

(IUPAC Technical Report)

Prepared for publication by

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Representation of configuration in coordination polyhedra and the extension of current methodology to coordination numbers greater than six

(IUPAC Technical Report)

Abstract: Established IUPAC recommendations for the representation of configuration are reviewed briefly, and then methodologies are examined for dealing with regular polyhedra that are typically used when working with coordination numbers greater than 6. More than one method is available and can be used for many such geometries, but the deviations from regular polyhedral geometries that are typically found in such molecules can make it difficult to arrive reproducibly at the same description for a complex using purely objective criteria. Recommendations are made for some geometries of coordination numbers 7, 8, and 9, but not for higher coordination numbers.

Keywords: coordination polyhedra; configuration; nomenclature; inorganic; higher coordination numbers; IUPAC Chemical Nomenclature and Structure Representation Division.

INTRODUCTION

The concept of coordination compounds is at least a century old. Initially, attention was devoted principally to coordination numbers 4 and 6, and the basic principles of coordination theory were developed using these. However, as the subject has developed, so has the list of coordination numbers, so that now coordination compounds with coordination numbers between 1 and perhaps 14 have been cited in the literature.

Once the idea of four- and six-fold coordination had been established, it was evident that different geometrical arrangements of ligands around the acceptor metal ion were possible and needed to be defined, along with the relative positions of the ligands, if these were of different kinds. Organic chemists had already used the concept of the tetrahedron to rationalize aspects of carbon chemistry, and inorganic chemists adopted readily the tetrahedron, the square plane, and the octahedron for similar purposes in simple coordination compounds. These are now referred to as coordination polyhedra, and the list of such polyhedra can be extended to include the complete range of compounds defined as coordination compounds. Not all such polyhedra are regular in the mathematical sense, and some, those with coordination numbers 1, 2, 3, and sometimes 4, are not polyhedra at all. Nevertheless, the general term “coordination polyhedron” is well understood and widely employed, whatever the coordination number.

In order to define the relative positions of different ligands within a coordination sphere (the coordination sphere is a more generalized term for any coordination polyhedron), inorganic chemists have traditionally used terms such as *cis*, *trans*, *meridional*, and *facial*. Although these are useful, only in relatively few cases can they be used to define fully the configuration about a coordination center, which may be, in formal terms, an ion or an atom, usually of a metal. To do this in the general case, a more powerful methodology needed to be developed, and at least two of these are available, one of which (see below) has been adopted by IUPAC in the *Nomenclature of Inorganic Chemistry, Recommendations 1990* (the “Red Book”) [1] and its subsequent revision, the *Recommendations 2005* [2].

In general terms, this methodology involves identifying an appropriate coordination polyhedron to describe the geometry of the complex. Once the coordination polyhedron has been identified, the locations of ligands are specified using the Cahn–Ingold–Prelog (CIP) priority numbers [3] for the ligand set in a defined sequence that depends on the coordination polyhedron. This article reviews briefly the application of this methodology to coordination geometries that are covered by the *Recommendations 2005* and then discusses the extension of this methodology to other, less common geometries, with higher coordination numbers.

COORDINATION POLYHEDRA AND THE POLYHEDRAL SYMBOLS

Coordination polyhedra are generally idealized when being used to describe metal complexes. This means that when choosing the polyhedron, the angles between the metal–ligand bonds of the same type and the lengths of metal–ligand bonds of the same type are treated as if they were all equal. The deviations from ideality are often indicated by qualifying the choice of coordination polyhedra with adjectives such as “distorted”. Whereas this causes little problem with the lower coordination numbers, even with coordination number 6 the choice can become arbitrary (e.g., distorted octahedron vs. distorted trigonal prism), with higher coordination numbers the definition of the appropriate idealized polyhedron can become problematic.

The polyhedra defined as “regular” in mathematical terms (the Platonic solids) in the range of coordination numbers 4 to 20 are only five in number. They are the tetrahedron, octahedron, cube, icosahedron, and dodecahedron. There are no regular polyhedra with an odd number of vertices, but mathematicians have recognized further polyhedra, including some with an odd number of vertices. The most complete treatment is due to Johnson [4], who listed all the polyhedra with regular polygonal faces. His list includes the five Platonic solids with equivalent faces and the Archimedean solids with regular polygonal faces, but of more than one kind (e.g., truncated cube, cuboctahedron, truncated octahedron, great rhombicuboctahedron, lesser rhombicuboctahedron, truncated dodecahedron, icosidodecahedron, truncated icosahedron, great rhombicosidodecahedron, lesser rhombicosidodecahedron, snub cube, snub dodecahedron, and truncated tetrahedron). In addition, it is possible to create polyhedra by amalgamating appropriate pieces of two or more different polyhedra. The International Union of Crystallography (IUCr) [5] has published a list of recommendations for all the coordination numbers generally recognized by crystallographers.

All these polyhedra are potentially available to coordination compounds, but the problem is even more complex because a coordination polyhedron is not required to have regular polygonal faces. In fact, they rarely do so. The larger the coordination number, the more difficult it often becomes to assign a regular polyhedron to the shape exhibited by any given compound. Confusion also arises because different authorities sometimes use different names for any given polyhedron.

The polyhedra recognized by both IUCr and IUPAC are listed in Table 1. The designations given in the table are all of the type *ABC-X*, where *ABC* defines the idealized polyhedron and *X* defines the coordination number. This designation is referred to as the polyhedral symbol. Those currently recognized by coordination chemists are: CN (coordination number) 2 (linear), *L-2*; CN 2 (angular or non-linear), *A-2*; CN 3 (triangle coplanar or trigonal planar), *TP-3*; CN 3 (triangle non-coplanar or trigonal pyramidal) *TPY-3*; CN 4 (tetrahedron), *T-4*; CN 4 (square coplanar or square planar), *SP-4*; CN 4 (square non-coplanar or square pyramidal), *SPY-4*; CN 5 (tetragonal pyramid, central acceptor in basal plane), *SPY-5*; CN 5 (trigonal bipyramid), *TBPY-5*; CN 6 (octahedron), *OC-6*; CN 6 (trigonal prism), *TPR-6*; CN 7 (pentagonal bipyramid), *PBPY-7*; CN 7 (square face monocapped trigonal prism), *TPRS-7*; CN 8 (square face bicapped trigonal prism), *TPRT-8*; CN 8 (cube, otherwise square or tetragonal prism), *CU-8*; CN 8 (anticube, otherwise square antiprism), *SAPR-8*. Additional polyhedra recognized by crystallographers, but not normally cited by coordination chemists are: CN 6 (trigonal antiprism); CN 8 (tetragonal prism); CN 8 (tetragonal antiprism); CN 12 (cuboctahedron); CN 12 (icosahedron); CN 12 (anticuboctahedron); CN 12 (truncated tetrahedron); and CN 12 (hexagonal

prism). It is noticeable that the greater the CN the more coordination polyhedra are available, but that for CN 10 and 11 the IUCr designates no polyhedra whatsoever.

Table 1 Crystallographic- and coordination-related polyhedra.

Coordination shape defining the chemical coordination polyhedron [1,2]	Alternative names [1,2,4,5]	Number of vertices	Quoted by IUCr [5]	Polyhedral symbol cited by IUPAC [2] or here*
Single neighbor	–	1	Yes	
Linear	–	2	Yes	<i>L-2</i>
Angular	–	2	Yes	<i>A-2</i>
Trigonal plane	Triangular planar	3	Yes	<i>TP-3</i>
Triangular non-coplanar		3	Yes	<i>TPY-3</i>
T-shaped		3	No	<i>TS-3</i>
Tetrahedron	Triangular/trigonal pyramid	4	Yes	<i>T-4</i>
Square plane	–	4	Yes	<i>SP-4</i>
Square non-coplanar	–	4	Yes	<i>SPY-4</i>
See-saw	–	4	No	<i>SS-4</i>
Pentagonal plane	Pentagon	5	Yes	<i>PP-5</i>
Square pyramid	–	5	Yes	<i>SPY-5</i>
Trigonal bipyramid	Trigonal/triangular dipyramid	5	Yes	<i>TBPY-5</i>
Octahedron	Square di/bi-pyramid, triangular/trigonal antiprism	6	Yes	<i>OC-6</i>
Trigonal prism	Triangular prism	6	Yes	<i>TPR-6</i>
Pentagonal pyramid	–	6	No	<i>PPY-6</i>
Pentagonal bipyramid	Pentagonal dipyramid	7	Yes	<i>PBPY-7</i>
Square-face capped trigonal prism	Augmented triangular prism	7	Yes	<i>TPRS-7</i>
End-/trigonal-face capped trigonal prism	Augmented triangular prism	7	No	<i>TPRT-7</i>
Face-capped octahedron	Monocapped octahedron	7	No	<i>OCF-7</i>
Cube	Square prism, tetragonal prism	8	Yes	<i>CU-8</i>
Square antiprism	Tetragonal antiprism, anticube	8	Yes	<i>SAPR-8</i>
Square-face bicapped trigonal prism	–	8	Yes	<i>TPRS-8</i>

(continues on next page)

Table 1 (Continued).

Coordination shape defining the chemical coordination polyhedron [1,2]	Alternative names [1,2,4,5]	Number of vertices	Quoted by IUCr [5]	Polyhedral symbol cited by IUPAC [2] or here*
Triangular-face bicapped trigonal prism	–	8	No	<i>TPRT-8</i>
Dodecahedron with triangular faces	Snub disphenoid or siamese dodecahedron	8	Yes	<i>DD-8</i>
Hexagonal bipyramid	Hexagonal dipyramid	8	Yes	<i>HBPY-8</i>
Bicapped octahedron	–	8	No	<i>OCT-8</i> (3 isomers in all)
Triangular cupola	–	9	No	<i>TCA-9</i>
Tricapped triangular prism	Triaugmented trigonal prism	9	Yes	<i>TPRS-9</i> (3 isomers in all)
Heptagonal dipyramid	Heptagonal bipyramid	9	No	<i>HBPY-9</i>
Tridiminished icosahedron	–	9	No	
Square-face monocapped antiprism	Gyroelongated square pyramid	9	No	<i>SAPRS-9</i> (2 isomers)
Square-face capped square prism	Monocapped cube	9	No	<i>CUS-9</i>
Tricapped octahedron	–	9	No	<i>TOCT-9</i> (2 isomers)
Pentagonal prism	–	10	No	<i>PPR-10</i>
Pentagonal antiprism	Paradiminished icosahedron	10	No	<i>PAPR-10</i>
Square-face bicapped square antiprism/cube	Bicapped anticube, gyroelongated square dipyramid	10	No	<i>SAPRS-10</i>
Metabidiminished icosahedron	–	10	No	
Sphenocorona	–	10	No	
Hexadecahedron	–	10	No	<i>HDN-10</i>
Bicapped square prism	Bicapped cube	10	No	<i>CUS-10</i> (2 isomers)
Trigonal-face bicapped square antiprism	–	10	No	<i>SAPRT-10</i> (3 isomers)

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Table 1 (Continued).

Coordination shape defining the chemical coordination polyhedron [1,2]	Alternative names [1,2,4,5]	Number of vertices	Quoted by IUCr [5]	Polyhedral symbol cited by IUPAC [2] or here*
Pentagonal-face capped pentagonal antiprism	Gyroelongated pentagonal pyramid, diminished/truncated icosahedron	11	No	PPRP-11
Hendecahedron	Bisymmetric hendecahedron	11	No	
Sphenoid hendecahedron	–	11	No	
C _s -octahedron	–	11	No	
Diminished icosahedron	–	11	No	
Icosahedron	–	12	Yes	IC-12
Pentagonal-face bicapped pentagonal prism	–	12	No	PPRP-12
Truncated tetrahedron	–	12	Yes	
Cuboctahedron	–	12	Yes	
Anticuboctahedron	Triangular bicupola	12	Yes	
Square cupola	–	12	No	
Sphenomegacorona	–	12	No	
Hexagonal prism	–	12	Yes	HPR-12
Hexagonal antiprism	–	12	No	HAPR-12
Dodecahedron	–	20	No	DD-20

*The polyhedral symbols in bold type are suggestions of the authors and developed from existing IUPAC usage, but have not been officially approved by the IUPAC Chemical Nomenclature and Structure Representation Division.

Whereas the idealized geometries of coordination polyhedra corresponding to coordination numbers 4, 5, and 6 are relatively easy to define, for higher coordinations the number of possibilities increases and the difficulty of selecting a unique geometry becomes greater. Whether this is important as long as the selected geometry leads to a unique descriptor of the geometry is not clear. This issue will not be pursued in this document, which recommends procedures for dealing with coordination numbers 7, 8, and 9, based upon established principles as well as the established methodology for coordination numbers 1 to 6. For higher coordination numbers (>9), the extended use of coordination polyhedra to define stereochemistries seems currently not worthwhile.

Although we shall not consider generally coordination numbers 11 and higher, some chemists have also recognized further polyhedra, such as the 11-vertex bisymmetric hendecahedron and its distorted variant, the sphenoid hendecahedron. The terms dodecahedron, decahexahedron, C_{2d}-dodecahedron, and C_s-dodecahedron have been mentioned in the literature, but it is not always clear to which polyhedron they refer. We have surveyed the literature describing coordination compounds of coordination numbers 9, 10, 11, and 12, and find that, much more often than not, the authors discussing such structures have contented themselves with stating a coordination number and have tended not to define the more complex polyhedral geometries.

STEREOCHEMICAL DESCRIPTORS AND CONFIGURATION INDICES

The general methodology for designating configurations of coordination compounds was developed by Brown, Cook, and Sloan [6], adopted by IUPAC in the *Nomenclature of Inorganic Chemistry, Recommendations 1990* [1], and has been retained, in slightly modified form, in the *Recommendations 2005* [2]. The individual coordination positions about a coordination center, with a coordination indicated by a polyhedral symbol as defined above, are designated by a configuration index. This index allows diastereoisomers to be distinguished from one another. The CIP rules [3] are used to establish a priority sequence of coordination sites that are numbered according to the CIP sequence of the ligating atoms. The method was exemplified in detail for coordination numbers 4, 5, and 6, and to some degree for bipyramidal structures of coordination numbers 7, 8, and 9. Essentially, the method relies upon defining a reference axis, which is related to the basic coordination polyhedron and using priority numbers to assign ligating atoms to specific coordination positions.

These configuration indices are a simple number for *SP-4*, a two-digit number for *SPY-5*, *TPBY-5*, and *OC-6*, and a more complex index in two parts, the first defining the principal axis and the second defining the arrangement of ligands in the pentagonal plane for *PBPY-7*. These rules have been elaborated for complexes with monodentate ligands, but more complicated procedures are required to define completely complexes with chelating ligands. In any case, it is generally only for coordination numbers 4, 5, and 6, plus bipyramidal complexes of higher coordination number that the methodology has been completely worked out and adopted by IUPAC. The reader is referred to [2] for more details.

Brown, Cook, and Sloan [7] also considered in more detail the question of coordination numbers 7, 8, and 9, using essentially the same approach that they had elaborated for lower coordination numbers. The method is even more complex, but it also relies upon the definition of a principal axis and the use of CIP priorities. Chirality labels are also invoked, and precise stereochemistries are defined, but only for selected geometries: 3 of coordination number 7, 7 of coordination number 8, and only 2 of coordination number 9 (many more geometries are shown in Table 1).

Although ref. [7] suggests that extensions to these procedures may eventually be desirable or even necessary, we are not aware of any further extensions having been discussed in the literature. This document attempts to define such extensions and the limitations that arise as higher coordination numbers are treated.

Coordination number 7

There are established polyhedral symbols, *PBPY-7*, *OCF-7*, and *TPRS-7*, for this coordination number. In principle, a further structure exists in which a trigonal prism is capped on a triangular face. Using established patterns, this might be labeled *TPRT-7*.

There would appear to be no problem with using the existing treatment to develop a configuration index for the pentagonal bipyramid, *PBPY-7*, as recommended in [2]. The principal axis is easily defined, and the assignment of the stereodescriptor follows the normal route that is applied to related bipyramidal geometries of lower coordination number. The generality of the approach is appealing, and we consider this approach to be the best one to adopt.

However, for *OCF-7*, *TPRS-7*, and *TPRT-7* we examine both the approach presented in [2,7] and an alternative approach which regards each of the geometries as being derived from a 6-coordinate species by a process of face-capping, and then developing an index that describes the base structure and then the nature of the face-capping (which face is capped and which ligand is capping).

Conventional approach [2,7]

This kind of approach is presented by Brown et al. [7] and used by *Chemical Abstracts*. Each polyhedron possesses a unique axis that runs through the capping ligand and the central atom in the structure. In the case of *OCF-7*, this axis would pass through the opposite face, and the index defines this face by listing the CIP priorities for the non-capping ligands in the order they are reached on moving

around the principal axis. The CIP priorities for the three ligands in the plane closest the capping ligand are first, third, and fifth in the configuration index, while those for the remote plane will be second, fourth, and sixth.

In the case of *TPRS-7*, the principal axis would intersect the remote edge of the prism, and the index would have to define both the capping ligand and the ligands on this edge by listing the CIP priorities for ligands at sites in the trigonal prism in a predetermined order (the capping ligand CIP priority is given first, separated by a hyphen, and the priorities of the ligands on the remote edge will be second and fifth in the sequence of the six remaining numbers).

TPRT-7 is not treated in [7], but it is a straightforward extension to propose that the configuration index should be made up of the CIP priority number of the capping ligand, separated by a hyphen from the CIP priorities of the three ligands in the remote plane. The order of the sequence of three numbers would be determined by the lower sequence in the nearer plane (in the same way as it is done for the trigonal prismatic system [2,6]).

Capping approach

This has been presented by Hey-Hawkins and Sommer [8,9], and is a logical extension of the established procedures for coordination number 6. Once one has identified the capping ligand and defined the “original” trigonal prism or octahedron, then the only additional requirement is to define the position of the capping ligand. It is suggested that the three or four CIP priority numbers of the ligands on the face could define the capped face, and that these and the priority number of the capping atom should be separated from the configuration index for the “original” polyhedron. We do not ultimately recommend this approach due to its limited applicability, but others may find it useful in other contexts, and may be able to extend its application using further devices. A detailed consideration of a capping procedure for coordination number 7 may be found in Appendix 1.

Coordination number 8

Table 1 lists the polyhedra of coordination number 8 that are treated by Brown et al. [7] and several more. For example, the two caps on a bicapped octahedron need not necessarily be located *trans* to one another (they could be on faces that share either an edge or a vertex), and a trigonal prism could, in principle at least, be capped on one square face and one triangular face.

Conventional approach

As illustrated earlier, this method relies on assigning a principal axis and often requires a principal face to be selected (usually based on CIP priorities or geometrical proximity to a capping ligand). In their paper, Brown et al. [7] often deal with relatively symmetrical examples, which can simplify the choice of polyhedron and preferred axis. For *CU-8*, they discuss a uranium complex with four identical bidentate nitrogen donors and for *SAPR-8* a europium complex with four identical bidentate oxygen donors. In both cases, identification of the C_4 axis of the polyhedron is a critical first step in the process of producing the configuration index. The CIP priority numbers of the eight ligands are then listed in a defined sequence (based on their positions on the polyhedron, and beginning with the highest priority ligand). *HPBY-8*, like other bipyramids, is straightforward.

For *OCT-8*, an extension of the approach used for *OCF-7* is employed, again using the C_3 axis as a basis of defining the configuration number. Finally, *TPRT-8* and *TPRS-8* rely on C_3 and C_2 axes, respectively, also using procedures that are closely related to those used for the related 7-coordinate structures.

DD-8 structures are treated by orienting the molecule in a defined manner (based on identifying the edge which has the ligands of the highest CIP priority) and then listing the CIP priorities in a defined sequence.

The less symmetrical bi-capped structures mentioned above are not treated by Brown et al., and additional rules would need to be developed before this kind of principal axis-principal face methodol-

ogy could be used (particularly in the case of the octahedral structures). A capping approach to these structures is presented in Appendix 1. For specific polyhedra, particular methods may be adopted, but since these are not general, we do not feel it wise to recommend any one at this stage. A specific example is presented in Appendix 2.

Coordination numbers 9, 10, and greater

Neither IUPAC nor Brown et al. [7] have made general recommendations for higher coordination numbers, though the latter have published a general treatment of the heptagonal bipyramid, *HBPY-9*, and the square-face tricapped trigonal prism, *TPRS-9*. However, there are now many more examples in the literature of higher coordination numbers and shapes established by X-ray crystallography than there were 20 years ago. Unfortunately, in many of these the geometry seems to be determined as much by a polydentate ligand as by the inherent electronic properties of the coordination center, and it is clearly often difficult to establish any kind of idealized geometry. This difficulty only increases with higher coordination numbers, so that the chances of finding a general procedure to treat all such examples appear slight.

It may be possible to simplify certain cases. In the few examples where there are only monodentate ligands present, an idealized geometry may be evident. Where all the ligands are bidentate, it may be possible to treat, say, a 12-coordinate species as a kind of octahedral derivative, and a 10-coordinate species as effectively 5-coordinate. In general, these cases remain to be explored. For the purposes of this document, we have added a few examples of idealized geometries that may become significant as more data are gathered, but we feel that there is little value in pursuing conventional approaches beyond coordination number 10.

For regular structures, identifying an ideal polyhedron may be relatively easy and such an approach provides few problems, as shown below. However, it can be very difficult to identify an appropriate ideal polyhedron on which to base the configurational description of the molecule or ion. Since the choice of polyhedron leads to different polyhedral symbols and to different methods for constructing configuration indices, the likelihood of different configuration indices being produced for the same molecule increases. This problem is also broached below.

The two regular geometries that are used most often to describe 9-coordinate structures are the square-face tricapped trigonal prism and the square-face capped square antiprism. The former is the most common and is adopted by the $[M(H_2O)_9]^{3+}$ ions of the lanthanides. The established polyhedral symbol for the square-face tricapped trigonal prism or trigonal prism, square-face tricapped is *TPRS-9*. We propose *SAPRS-9* here for the square-face capped square antiprism (or square antiprism, square-face capped). In a similar way, the 10-coordinate square-face bicapped square antiprism (or square antiprism, square-face bicapped) could be assigned the polyhedral symbol *SAPRS-10*, and the pentagonal antiprism the symbol *PAP-10*.

In the proposal of Brown et al. [7], the configuration index for a *TPRS-9* structure is produced by listing the CIP priority numbers for all nine ligands in a defined sequence, beginning with the preferred donor in the preferred end plane of the structure (the end plane with more of the most preferred donor), and is followed by the priority number for the eclipsed donor in the other end plane, the preferred adjacent capping donor, and then succeeding end donors and capping donors, while moving in the same direction around the structure. The absolute configuration derived in this way is assigned for the arrangement shown in Fig. 1, and is *TPRS-9-147368259-C*. A capping approach is outlined in Appendix 1.

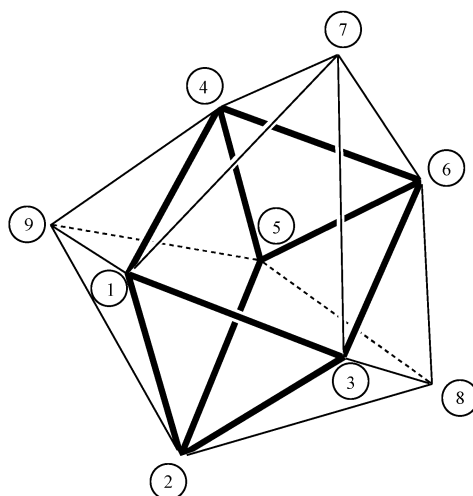


Fig. 1 Derivation of the descriptor for a polyhedron *TPRS-9*, after [7].

The square-face capped square antiprism, *SAPRS-9*, can be assigned a configuration number based on a method very similar to that proposed by Brown et al. [7] for the square antiprism. The capped square antiprism should be viewed from the capping donor, and the CIP priority of this ligand is first in the configuration index, and separated from the rest by a hyphen. The second number in the configuration index is given by the priority number of the highest ranked ligand in the square plane of donors closer to the capping donor, and the third by the higher-ranking adjacent donor in the plane further away from the capping donor (if they are the same then the next donor in the sequence is used to determine the direction of the progression). Succeeding priority numbers are found for the configuration index by alternating between the two square planes while moving in the same direction around the structure. Thus, the example in Fig. 2 has the configuration index 5-12834697, and the absolute configuration is *A*, because of the anticlockwise direction that is taken around the structure when constructing the index. The full descriptor is therefore *SAPRS-9-5-12834697-A*. Figure 3 shows the assignment for a real structure.

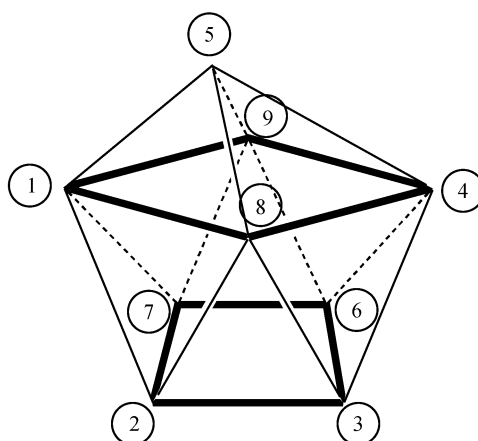
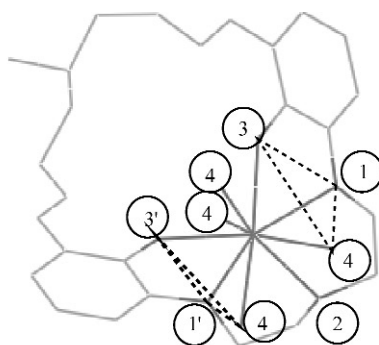


Fig. 2 Priority assignment for a 9-coordinate polyhedral structure, *SAPRS-9*.



TPRS-9-11'244433'4

Fig. 3 Example of a real *TPRS-9* lutetium complex. The dotted lines indicate the triangular faces of the trigonal prism.

Ten-coordinate square face bicapped square antiprismatic structures, *SAPRS-10*, are named in a similar way, except that the priority numbers of both capping groups are placed at the beginning and the plane closer to the higher-ranked capping group is preferred and is used as the starting point for describing the configuration of the resulting structure. If both capping groups are the same, then the preferred plane is that with the greater number of donors with the highest CIP priority. The example in Fig. 4 would be given the descriptor *SAPS-10-49-135827106-A*. Note that the 10 has been underlined in order to avoid any ambiguity with two separate designators, 1 and 0.

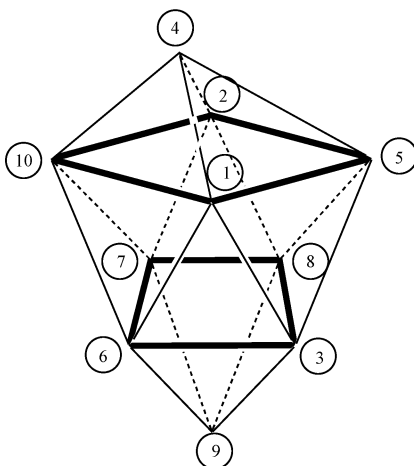


Fig. 4 Assignment of priorities for *SAPRS-10*.

REAL STRUCTURES

Actual molecules deviate from ideality, and this produces difficulties in elucidating a unique and unambiguous description of the configuration using the methods outlined above. For example, when attempts were made to classify 9-coordinate structures in the Cambridge Crystal Database as square-face tricapped trigonal prisms (*TPRS-9*), square-face capped square antiprisms (*SAPRS-9*), or neither, often

no consistent assignment could be made. Different initial assignments of coordination polyhedra would lead to different descriptors. Figure 5 illustrates this. In these structures, the donor atoms are in identical places, and so the complexes of the (omitted) metal atom are identical. The only differences are in the ways the donor atoms are linked to form the (notional) polyhedron. The bold lines illustrate how the same complex may be categorized as either a square-face tricapped trigonal prism (*TPRS-9*), or a square-face capped square antiprism (*SAPRS-9*). Which is chosen to describe a real molecule will depend on the bond lengths and angles in the molecule, and upon which donors are regarded as capping groups (which is likely to be a subjective matter).

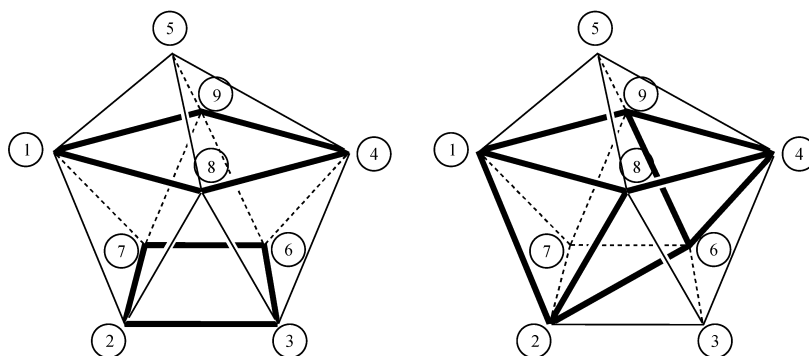


Fig. 5 Two permissible assignments for a 9-coordinate polyhedral structure, designated *SAPRS-9* and *TPRS-9* (see also Fig. 8 for the corresponding configuration indices).

Even small deviations from ideality will cause problems. Consider the two structures shown in Fig. 6. The slightly distorted square antiprism on the left becomes the distorted cube (square prism) on the right if the upper square plane is twisted slightly clockwise. In this case, the plane of the cube with the lowest sequence just happens to correspond with the upper plane of the square antiprism, but the number sequences in the coordination indices of the two structural interpretations of the complex are quite different.

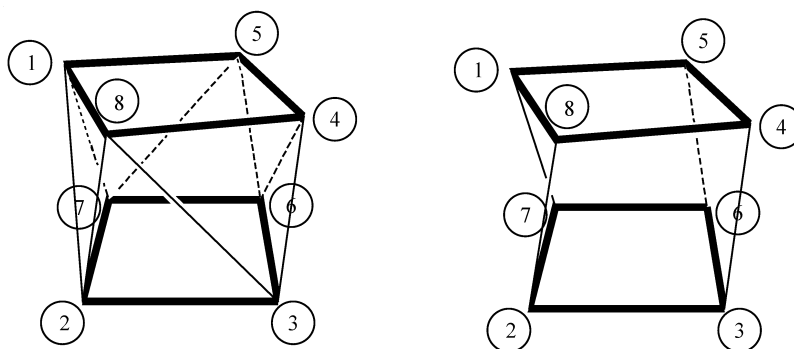


Fig. 6 Single 8-coordinate structure giving completely different coordination indices, although both represent one and the same structure.

As the coordination number increases, the differences in angles and donor positions between the various polyhedra become smaller, and choosing reproducibly and unequivocally a polyhedral symbol becomes impossible. Different configuration indices will inevitably be used for the same molecule.

Although this may not prevent the development of an unambiguous index, it will not be evident that two structures with different indices are essentially similar. Clearly, this is unsatisfactory.

ALTERNATIVE APPROACHES

The capping method described in the Appendices is useful but limited in application, and we do not recommend its wider use. We have briefly considered other approaches which do not involve assigning polyhedra in an attempt to solve this problem.

The first we have called the disking method. Just as in Fig. 5, we have used Chemical Abstract Services (CAS) methods to derive “conventional” indices for the two 8-coordinate structures in Fig. 7, for which IUPAC currently offers no recommendation. The two polyhedra are a square-face bicapped trigonal prism, *TPRS*-8, and a square antiprism, *SAPR*-8. The corresponding polyhedral symbols and configuration indices are shown. The differences between the polyhedra are rather subtle. Just which would be chosen to describe a real molecule will probably depend on the relative bond lengths and angles and a subjective choice as to which donors should be designated as capping. In this particular case, which is not general, it is fortunate that the CAS methodology yields the same configuration indices.

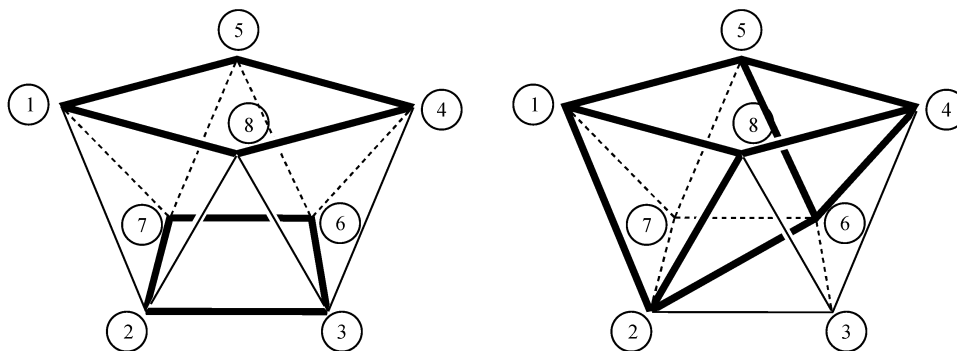


Fig. 7 Two different polyhedral assignments for the same 8-coordinate structure.

The problem extends to the 9-coordinate structures (Fig. 8) that would arise from further capping of the two polyhedra shown in Fig. 7, the square-face capped square antiprism and the square-face tricapped trigonal prism. The complete configurational descriptor for the trigonal prism-based structure is *TPRS*-9-195843267-C, but the CAS/Brown [7] procedure does not cover the capped square antiprismatic structure, although extending the standard procedures would result in the configuration index 5-12834697, where the separated number defines the capping group and the rest of the index is produced in essentially the same way as that for a square antiprismatic structure. Clearly, these are very different.

The “disking” approach is an attempt to treat non-ideal structures. It relies on the idea of identifying parallel planes, or disks, within which the donor atoms may be assumed to lie, even if not exactly. Many of the 9- and 10-coordinate structures in the Cambridge Crystallographic Database can be described as if their donor atoms lie in disks or planes perpendicular to a particular metal–ligand axis. For example, it is possible to choose arbitrarily one ligand in the 9-coordinate structures shown above (Fig. 8) and then to examine the relative locations of the remaining ligands. They will be in two planes that contain either 5 and 3, or 4 and 4 ligands, depending on the choice of the initial ligand.

The problem is to ensure that there is only one configuration index that can be adduced for a given structure. Such a configuration index must be readable to produce one, and only one, structure. This means the development of unequivocal rules for the choice of the senior ligand. The same problem has

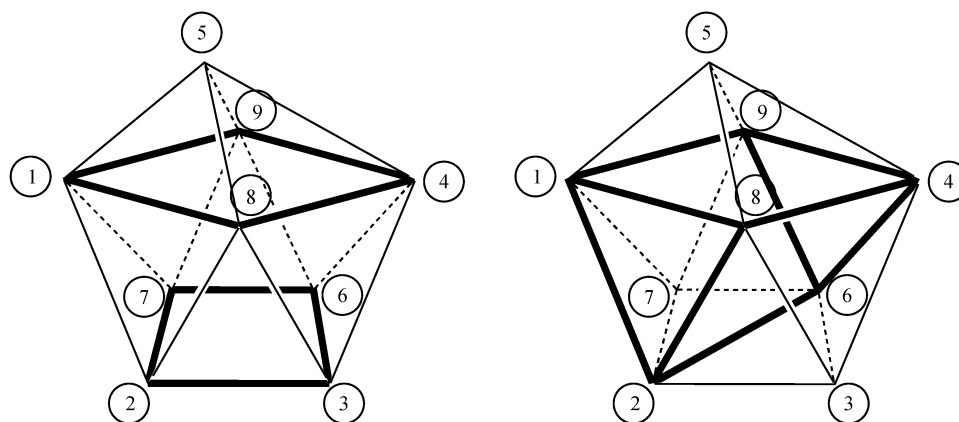


Fig. 8 The similar 9-coordinate arrangements giving completely different configuration indices, yet both representing one and the same structure.

arisen in producing configuration indices for the lower coordination numbers, but these have rules for identifying the principal axis for a structure, based on the relative CIP priorities of the donor atoms. An analogous approach might be applied here by, for example, requiring the selected ligand to be that with the highest CIP priority. If there were a choice of more than one highest-priority ligand then presumably the principle of “trans maximum difference” could be applied in some way.

Unfortunately, in real structures not all choices of initial ligand leave the other ligands occupying clearly defined disks. Indeed, in some structures the nature of distortions from the ideal polyhedron is such that it was essentially impossible to identify disks perpendicular to the bond from the central metal to the highest priority ligand. There were often other initial ligand selections that did seem suitable for “disking”, but it is a matter of subjective judgment whether any particular choice is satisfactory. It does not seem possible to identify a systematic, objective procedure for making this choice that can survive application to real systems.

We conclude that the “disking” approach is a nice idea in principle, but like more conventional attempts to assign unique configuration indices to real structures, it does not solve the problems that are created by the deviations from ideal polyhedra.

A further approach has been suggested but is yet to be worked out in detail on real examples. This consists in regarding a mononuclear complex as consisting of a central metal atom at the center of a sphere, and then imagining that the ligating atoms are projected onto the surface of that sphere. Selecting a “north pole” (ligand of highest CIP priority) can then indicate the positions of the projections, and reading the positions and identities of the projections as a series of CIP priorities coupled with appropriate “latitudes” and “longitudes” would give the relative positions of all the ligating atoms. Rules to govern this method need to be developed. Undoubtedly real examples, with the wide range of angles observed between metal–ligand bonds, even in closely related coordination compounds, will raise difficulties, and may also make this method unusable. Further, it is not clear what criteria might be employed to determine whether two sets of latitudes and longitudes are sufficiently similar to be regarded as referring to the same structure.

CONCLUSION

Procedures exist for the description of the coordination geometry and positions of ligands for complexes with coordination numbers 6 to 9, at least for some geometries. However, we find that there is no unequivocal way to extend the Brown et al. [7] or Hey-Hawkins and Sommer [8,9] systems to all con-

ceivable structures of coordination numbers 7 and 8, though each of them clearly work with particular kinds of structure.

A more serious problem exists as a result of the distortions from ideal polyhedra that are typically found in these compounds of higher coordination number. As the coordination number increases, the number of possible polyhedra becomes larger, and the differences between them become much less significant—of the order of the distortions from ideality that are seen in real molecules. This means that different polyhedral symbols may be chosen and different procedures for the determination of configuration indices used, so that different chemists might describe the same molecule differently. This would defeat the purpose of using a configuration index in the first place.

We have investigated other methods that might produce the same configuration index regardless of the choice of polyhedral symbol. However, it does not seem possible to apply them in a general way that can be applied to all molecules. We feel that any method that tries to impose ideal shapes on real molecules is almost certain to fail sooner or later. The current methodology is satisfactory for small coordination numbers because the chemist can appreciate that distortions in such cases still do not often undermine the choice of polyhedron. However, even with coordination number 6 there are often problems (octahedron or trigonal prism?). Furthermore, we do not wish to introduce a new but not general methodology, particularly when current methods for low coordination numbers are well understood, and sometimes used to the full extent of IUPAC recommendations. We recommend that IUPAC endorse the methods of Brown et al. [6,8] for all coordination numbers up to 7, and extend them to include specific examples that are reliable for use for coordination numbers 8 and 9.

It is evident from the literature that authors tend not to define coordination polyhedra for large coordination numbers, perhaps because, in real structures, it is often not evident what those polyhedra might be. While this is not a problem for the interested reader, it does make easy comparisons of structures in databases impossible. We feel that efforts should be made to develop a comprehensive system for all coordination numbers. It may be that this will only arise from direct comparison of bond lengths and angles, but such a solution will only be generally acceptable if it is reasonably transparent, and if the resulting designations can be constructed and read easily. A solution that is usable primarily for searching databases will be of value, but only to a limited degree.

REFERENCES

1. IUPAC. *Nomenclature of Inorganic Chemistry, Recommendations 1990*. G. J. Leigh (Ed.), Blackwell Science, Oxford (1990).
2. IUPAC. *Nomenclature of Inorganic Chemistry, Recommendations 2005*. Prepared for publication by N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton, RSC Publishing, Cambridge (2005).
3. (a) R. S. Cahn, C. Ingold, V. Prelog. *Angew. Chem., Int. Ed. Engl.* **5**, 385 (1966); (b) R. S. Cahn, C. Ingold, V. Prelog. *J. Org. Chem.* **14**, 2849 (1970).
4. N. W. Johnson. *Can. J. Math.* **18**, 169 (1966).
5. See IUCr. *Nomenclature for Crystal-chemical Formulae. II, Coordination of Atoms*. <<http://journals.iucr.org/iucr-top/comm/cnom/inorg/node4.html>>.
6. M. F. Brown, B. R. Cook, T. E. Sloan. *Inorg. Chem.* **14**, 1273 (1975).
7. M. F. Brown, B. R. Cook, T. E. Sloan. *Inorg. Chem.* **17**, 1563 (1978).
8. R. Sommer. Dissertation, Universität Leipzig (2002).
9. R. Sommer, P. Lönnecke, J. Reinhold, P. K. Baker, E. Hey-Hawkins. *Organometallics* **24**, 5256 (2005).

APPENDIX 1: CAPPING APPROACHES FOR COORDINATION NUMBERS 7, 8, AND 9**Capping approach for coordination number 7 [8]**

This stereodescriptive nomenclature approach has primarily been developed to describe monocapped octahedral structures (*OCF-7*). However, in principle, it can be extended to describe other mono- or bi-capped polyhedra (see other appendices).

The first two numbers of the coordination index of the octahedral core structure follow the polyhedral symbol *OCF-7*. These are the priority number of the atom *trans* to the atom of the highest priority, and the priority number of the atom *trans* to the atom of the highest priority on one of the remaining two perpendicular axes of the octahedron. The two consecutive numbers are connected to the polyhedral symbol by a hyphen, according to the IUPAC rules developed for octahedral (*OC-6*) structures.

Then the seventh ligand, capping a triangular face of the octahedral core, is identified using the same CIP priority system that is used for the other ligands, for example, a capping CO ligand will receive the same priority number as a CO ligand in any of the octahedral positions. The capping ligand in the *OCF-7* system is designated by its priority number, which is placed after the polyhedral symbol and the configuration index that describes the octahedral core, separated from them by a hyphen. The priority numbers of the three ligands that form the capped face complete the sequence, again separated from the other portions of the descriptor by a hyphen. These three numbers are listed in ascending order.

The chirality of the complex is determined as follows: if the three-fold reference axis which runs through the position of the capping ligand, the central atom, and the center of the triangular face *trans* to the capped position, is directed with the capped position pointing toward the observer, the direction of rotation (*A* for anticlockwise, *C* for clockwise) is given by direction of travel around ascending sequence of priorities for the capped face. If at this point no decision about the direction of rotation can be made (e.g., the sequence 244 can be achieved by counting three ligands in either direction), the priority numbers of the ligands in the far plane must be examined, bearing in mind the principle of *trans* maximum difference. That is, if two ligands have the same priority among two or more equal ligands, the one that is located *trans* to the ligand of lowest priority is preferred. Sequences of priority numbers that do not exhibit any preferential orientation at this point are not indicated. The chirality symbols *A* and *C* are written in italics and are separated from the previous elements of the descriptor by a hyphen. The procedure is described in the caption to Fig. 9.

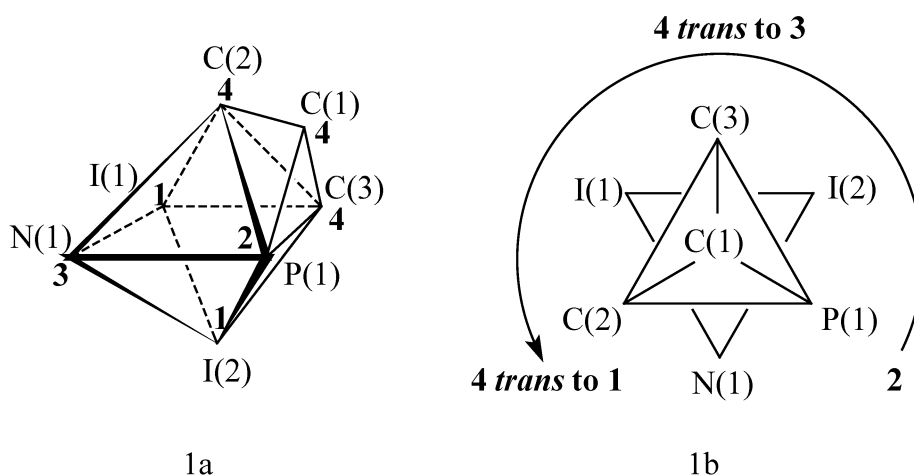


Fig. 9 Schematic representation of the capped octahedral structure of $[\text{Wl}_2(\text{CO})_3(\text{NCCH}_3)\{\text{PH}(\text{CH}_2\text{Fc})_2\}]$ as determined by X-ray crystal structure analysis (1a) [9]. The priority numbers are set in boldface, and the descriptor derived by the approach described here, which differs from the standard descriptor [6,7], is *OCF-7-42-4-244-A*. The chirality of the complex can be seen when the C atom C(1) of the capping carbonyl is turned toward the observer (1b). The C atom C(3) of the CO ligand *trans* to the lower-ranking nitrogen atom N(1) of the acetonitrile ligand is preferred over the C atom C(2) of the CO ligand, which is *trans* to the iodo ligand I(2). Thus, the sequence of the coordinating atoms of the ligands in the capped face is P(1)-C(3)-C(2), which is reflected in the anticlockwise (A) direction of rotation.

Capping approach for coordination number 8 [8]

The same capping approach that was described for coordination number 7 can be applied to the capped structures with coordination number 8. In such cases, a second numerical capping sequence can be used to identify the additional capping ligand and the face of the “original” polyhedron to which it is attached. The advantage of this approach is that it is readily adapted for the description of the less symmetrical bicapped structures.

Most easily the described procedure can be adapted to describe *trans*-bicapped octahedral structures (*OCT-8*). The two capping ligands are named in the second element of the configuration index according to their priority. The structure is then treated according to the rules described for *OCF-7*, counting only priority numbers of the capped trigonal face with the capping ligand of higher priority, or, in case of equal priority numbers of both capping ligands, counting the capped face that itself gives the smaller priority number sequence.

An 8-coordinate bicapped octahedral complex with eight different ligands is shown in Fig. 10.

If there is more than one capped face, for example, in bicapped octahedral structures where the capped faces are not *trans* to each other, capping ligands do not necessarily need to be cited together as in the example of Fig. 10. In such a case, the count of the capping positions should start with the capping ligand of higher priority.

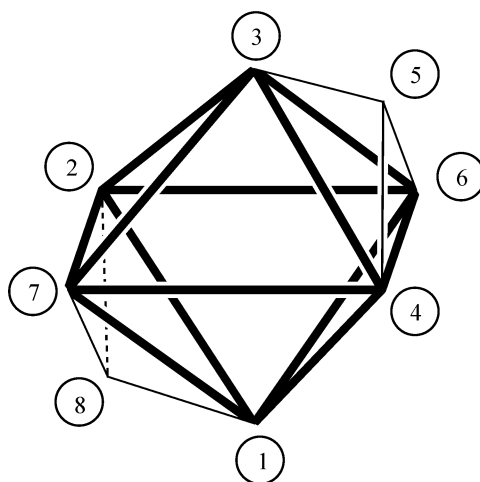


Fig. 10 Schematic representation of a *trans*-bicapped octahedron with eight different ligands. According to the ligand count described here, the stereodescriptor for this ligand arrangement would be *OCT*-8-34-58-346-*A*.

Capping approach for coordination number 9

It is necessary first to identify the trigonal prismatic portion of the structure (to assign its configuration index) and then to add the capping information. The configuration index for a 6-coordinate trigonal prismatic structure is determined by first identifying the triangular face with the greater number of ligating atoms of highest CIP rank. The CIP priority numbers of the three ligating atoms on the *other* triangular face are then used in the configuration index. These three priority numbers are placed in order based on being adjacent to the higher-ranked ligands in the higher-ranking face. If there are two ligands of identical priority in either face, they can be distinguished, if required, by considering the priorities of the ligands that are adjacent to them on the other triangular face. The higher-ranked adjacent ligand leads to a prime being added, and a primed ligand is treated as if it had lower priority than an unprimed ligand of the same CIP rank.

The chirality of the structure is then determined by noting the direction of progression of the priority numbers on the less-preferred triangular face. Thus, for the left-hand case in Fig. 11, the configuration index 564 indicates that the ligand with priority number 5 lies below that labeled 1, priority number 6 below 2, and 4 below 3. The clockwise movement from ligand 4 to ligand 5 gives the absolute configuration *C*. If the absolute configuration cannot be assigned in this way because the ligands in the less-preferred face are the same, the absolute configuration can be assigned in a similar way using the ligands on the more-preferred face. A priming convention may be needed to distinguish between ligands of the same priority.

Consideration of the ligands in the higher-ranked triangular face of the trigonal prism leads to the capping portion of the *TPRS*-9 configuration index. The square faces of the trigonal prism can be ranked by the priorities of the ligands on that triangular face that also mark the top edges of the square faces. In Fig. 11, the face that points away from the reader is ranked highest in both structures. In Fig. 1, the priority number of the ligand that caps the preferred square face is 9, giving the full stereodescriptor of this example as *TPRS*-9-456-978-*A*. The real example shown in Fig. 3 would have the following descriptor if the capping method were used: *TPRS*-9-1'3'4-424.

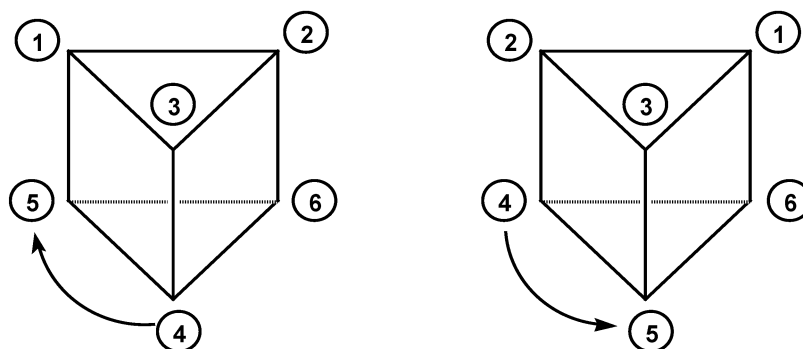


Fig. 11 Chirality determination in a polyhedral structure, *TPRS-9*.

APPENDIX 2: ALTERNATIVE APPROACH TO *DD-8* STRUCTURES

The *DD-8* structure can also be treated in a different manner to that described by Brown et al. [7]. An 8-vertex dodecahedron has 12 trigonal faces and 8 vertices. The vertices are of two kinds, those connected to four other vertices (first-class sites), and those connected to five other vertices (second-class sites) (Fig. 12). The C_2 axis of the dodecahedron passes through the midpoints of the lines connecting each pair of first-class vertices. These four sites form a tetrahedron, and the highest priority atom is selected to lie on a C_3 axis of this tetrahedron, which will normally be distorted (see Fig. 13). The numbering of these first-class sites and the site sequence are discussed below and shown in Fig. 14.

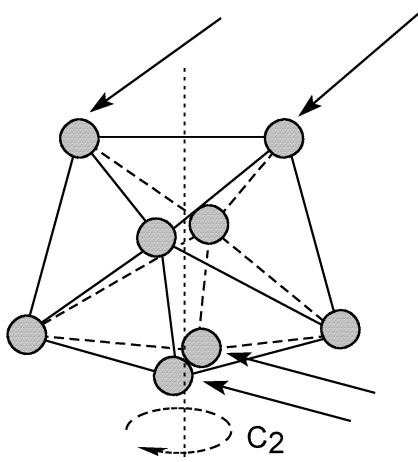


Fig. 12 First-class dodecahedral vertices, which are connected only to four other ligands, are indicated by arrows. The remaining four vertices are of the second class.

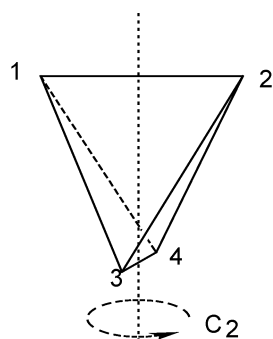


Fig. 13 Orientation of the “internal” tetrahedron of the dodecahedron.

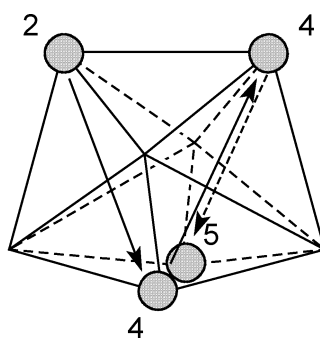


Fig. 14 Counting sequence for the first-class ligands of the tetrahedron.

The ligand count starts around one of the C_2 axes of the tetrahedron, the one orientated vertically with the line between the two most-preferred ligands uppermost (Fig. 12). This ignores the highest-order (C_3) reference axis, but it is useful in the description of the monoaxially distorted tetrahedral shapes usually encountered in dodecahedral complexes. The ligand count starts with the ligand of highest priority among the first-class ligands, and continues around the C_2 axis to give the lowest lexicographic order (Fig. 14).

This sequence 2-4-4-5 gives the first part of the descriptor, 2445. The remaining four ligands are then considered, starting with the ligand which lies closest to the first-class site of highest priority, and in the plane which is defined by the ligand with the highest priority at a first-class site, its immediate neighbor of the same class, and the central atom. The ligands of the second class are counted around the C_2 axis of the dodecahedron in the same direction as the ligands on the first-class sites (Fig. 13).

In Fig. 15, the sequence of the second-class ligands is 3-3-5-1, so the partial index is 3351. The absolute configuration (*C/A*) is established by viewing down the C_2 axis from the side of the most preferred ligand, which in the current example gives an anticlockwise sense of direction, rendering the complete stereodescriptor as *DD*-8-2445-3351-*A*. If the absolute configuration cannot be derived from the ligands of the first class, the ligands of the second class are considered in terms of their sense of direction around the C_2 axis. In Fig. 16, such an ambiguous case is shown. The count of the first-class ligands is 1-1-2-2 starting from either ligand of the priority number 1, whatever the direction taken, but since the sequence 1-1-1-2 is lower than 1-1-2-1, the ligand count of the second-class ligands will be E-F-G-H (and hence the first-class ligand count has to be A-B-C-D). The full descriptor in this case would be *DD*-8-1122-1112-*A*.

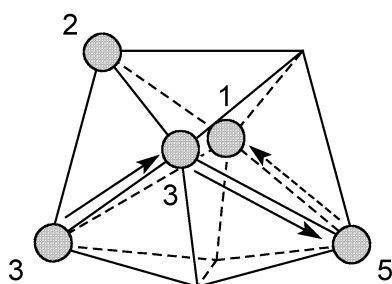


Fig. 15 Assignment of the index to denote ligands at the second-class sites.

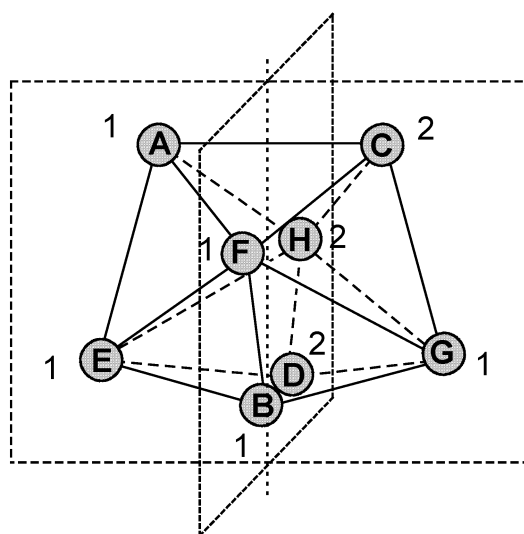


Fig. 16 Dodecahedral structure *DD-8-1122-1112-A*. The ligands lie in two perpendicular planes, giving two possible sequences. The priority numbers are given with each ligand; the letters A to H in alphabetical order symbolize the correct sequence of the ligand count. The incorrect sequence would be B-A-D-C – F-E-H-G.