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Exhaustive Examination of Chiral Configurations of Edges on a Regular Octahedron: Analysis of the Possibilities of Assigning Chirality Descriptors within a Generalized Δ/Λ System

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The 144 configurations of edges on a regular octahedron, relevant as models for octahedral chelate complexes, have been systematically examined. By using the unoriented-skew-lines chiral reference system, it is easy to obtain chirality descriptors for 72 of the 74 chiral configurations. For the 2 remaining ones the use of a new chiral reference system based upon skew pairs of oriented lines is demonstrated. The concept of mutually complementary configurations is found to be useful. The conclusion is that it is possible to formulate quite simple conventions for obtaining chirality descriptors in all cases. However, the present paper is *not* meant to be a set of nomenclature proposals; rather, its fundamental results may serve as a useful background for the eventual development of nomenclature in this area. All the configurations mentioned, achiral as well as chiral, are presented as drawings and may serve as an inspiration to the preparative chemist.

Since the appearance of "the Red Book" on inorganic nomenclature¹ some 10 years ago, the descriptors Δ and Λ have become universally adopted for labeling chiral configurations of chelate-spanned octahedron edges in *cis*-bis(bidentate) and tris(bidentate) octahedral complexes with the purpose of distinguishing configurations from their mirror images. Correspondingly, the descriptors δ and λ have been used in the specification of chiral conformations of five- and six-membered chelate rings. As described in detail in Section 7.8 of ref 1, the basic geometry of this descriptor system lies in the fact that a chiral pair of lines in three-dimensional space corresponds unambiguously to a screw (a helix) and is thus in an obvious way either a "right" (Δ) pair or a "left" (Λ) pair. Further discussion of the geometry of line pairs may be found in ref 2.

In chiral configurations of lines in space such as the ones defined by the octahedron edges in the above examples, one may examine all pairs of lines and, if they are chiral, note whether they are Δ or Λ . Let n_{Δ} be the number of Δ pairs encountered and n_{Λ} the number of Λ pairs, and let us for the purposes of the present discussion define the chiral pair index (or, for short, the "index") of a line configuration to be the ordered number pair $(n_{\Delta}, n_{\Lambda})$. We shall often alternatively

denote an index (m, n) by the symbol $\Delta_m\Lambda_n$, dropping subindices which are equal to 1 and leaving out altogether a Δ or Λ with subindex 0. Then the edge configuration defined by the *cis*-bis(bidentate) octahedral complex of Figure 1a has the chiral pair index $(1, 0)$, and its mirror image the index $(0, 1)$; i.e., the sole chiral pair of edges is a Δ pair and a Λ pair, respectively. Similarly, the tris(bidentate) complex of Figure 1b has the index $(3, 0)$ and its mirror image has the index $(0, 3)$. In the IUPAC publication,¹ it was recommended to attribute to both configurations of Figure 1 the simple descriptor Δ and to their mirror images the descriptor Λ . Figure 2 shows a less trivial example for which the chiral pair index is $(1, 2)$; the mirror image then obtains the index $(2, 1)$.

In all these cases, the chiral pair index distinguishes one enantiomer (catoptromer,⁶ mirror image form) from the other and may thus be used as a chirality descriptor. It is of course always true that, if a given configuration has an index (m, n) , then its mirror image has the index (n, m) , and thus if $(n, m) \neq (m, n)$, i.e., $m \neq n$, the configuration is chiral and the index may serve as a chirality descriptor. However, it was exemplified already in ref 1 that the converse does not necessarily hold; i.e., a chiral configuration of edges on an octahedron may have $n_{\Delta} = n_{\Lambda}$. Consider Figure 3. In this case the index of either enantiomer is $(1, 1)$, so the index cannot serve as a chirality descriptor. A solution to this particular problem was suggested in ref 1, namely, that one should consider only the subconfiguration consisting of the terminal edges spanned by the chelate ligand; in that way the pair indices attributed to the two enantiomers become $(1, 0)$ and $(0, 1)$, respectively, and these may be used as chirality descriptors.

One or two questions now arise. The first one is whether there exist other chiral configurations of edges on a regular octahedron for which $n_{\Delta} = n_{\Lambda}$, i.e., chiral configurations which

- (1) "Nomenclature of Inorganic Chemistry. Definitive Rules, IUPAC, 1970" ("the Red Book"); Butterworths: London, 1971 (or *Pure Appl. Chem.* 1971, 28, No. 1). A tentative version of Section 7.8 of the Red Book, the part relevant in the present paper, appeared in: *Inorg. Chem.* 1970, 9, 1-5.
- (2) Damhus, T.; Schäffer, C. E. *Inorg. Chem.*, in press.
- (3) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* 1959, 81, 549-555.
- (4) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* 1971, 6, 219-277 (Section IV.A).
- (5) Complexes of the type $[\text{Co}(\text{NH}_3)(\text{tetraen})]^{3+}$ are presently being studied by H. Yamatera and co-workers (personal communication). In addition to edge configuration chirality, further isomerism arises in these complexes because the secondary nitrogens, when coordinated, become asymmetric atoms. This does not, however, make them less useful as examples for the present discussion.

- (6) The adjective "catoptric" was used first by: Buckingham, D. A.; Maxwell, I. E.; Sargeson, A. M. *Chem. Commun.* 1969, 581-583.



Figure 1. (a) A single chiral pair of octahedron edges as encountered in *cis*-bis(bidentate) complexes. The depicted edge pair defines a right screw by the convention prescribed in ref 1 and further discussed in ref 2 and is thus a Δ pair. (b) A model of a tris(bidentate) octahedral complex. The *chiral pair index* of the enantiomer shown, defined in the main text, is (3, 0); i.e., the edge configuration contains three Δ edge pairs and no Λ pairs. We shall also alternatively write an index like (3, 0) in the form Δ_3 .



Figure 2. A chiral edge configuration with index (1, 2), i.e., containing one Δ pair and two Λ pairs. The figure models certain edta complexes (edta = ethylenediaminetetraacetate), e.g., $[\text{Co}^{\text{III}}(\text{edta})]^-$ (ref 3).



Figure 3. A chiral edge configuration with a "diagonal" chiral pair index, i.e., containing an equal number of Δ and Λ pairs. The figure might be a model of a particular enantiomer of the β -trans form of a $[\text{Co}^{\text{III}}\text{L}(\text{tetraen})]^{3+}$ complex (tetraen = 1,11-diamino-3,6,9-triazaundecane) with $\text{L} = \text{Cl}^-$ (ref 4) or $\text{L} = \text{NH}_3$ (ref 5).

contain an equal number of Δ and Λ pairs. If the answer is affirmative, the next question is whether the chirality of such configurations may in all cases be specified by a terminal-edges convention.

The present study reports an exhaustive examination of *all* possible edge configurations on an octahedron, leading to answers to these questions. It turns out that there are altogether 144 different edge configurations, counting chiral configurations only once; 74 of these are chiral, and 9 of the chiral ones have $n_\Delta = n_\Lambda$. So the first of the above questions is indeed to be answered affirmatively; regarding the second question, we shall show that, with two minor additions, the terminal-edges convention may be made to work for all these 9 cases.

We start by some general remarks about octahedral edge configurations. For any N among the numbers 0, 1, 2, ..., 11, 12, there are $\binom{12}{N} = 12! / [(12 - N)!N!]$ ways in which to occupy N edges on an octahedron, but generally many of the configurations thus obtained will be mutually superimposable under the octahedral rotation-inversion group O_h ; such configurations are counted only once here, reducing the total number of configurations from $2^{12} = 4096$ to 144. (That the number would be precisely 144 was not clear to us beforehand; this emerged from the actual examination of all the configurations.)

Further, it will be useful to have the concept of the *complementary configuration*. Given a configuration with N occupied edges, we define the complementary configuration to be the configuration made up by the remaining (i.e., the unoccupied) $12 - N$ edges. There is a remarkably simple rule, proved in the Appendix, which says that, if a configuration of N occupied edges has the chiral pair index (n_Δ, n_Λ) , then its complementary configuration has the index $(n_\Delta + 12 - 2N, n_\Lambda + 12 - 2N)$. This relationship is illustrated by the example given in Figure 4. Note, as a consequence of the rule, that the number of Δ pairs and the number of Λ pairs are equal for the configuration itself *if and only if* they are equal for the complementary configuration.

We are now ready to present the results of the investigation of all the octahedron-edge configurations. Due to the above



Figure 4. An octahedral edge configuration and its complementary configuration. The chiral pair indices given illustrate the general rule, discussed in the main text, relating the index of a configuration to that of its complement. It is noteworthy that specimen b gives the immediate impression of a left-hand screw even though the configuration contains more Δ pairs than Λ pairs.

observation regarding complementary configurations, we only need to investigate the cases $N = 0$ through $N = 6$. This was, incidentally, first done by hand but has later been redone on a computer. In the program the octahedron edges were numbered arbitrarily from 1 to 12 so that edge configurations could be represented as combinations of these numbers and symmetry operators of the group O_h as permutations of them, that is, as elements of the symmetric group of order 12!. Within each class of O_h -equivalent configurations, exactly one configuration was selected. The computer was made to plot the configurations thus found on a standard octahedral skeleton. The result is seen in Figure 5. The configurations have been numbered arbitrarily. For the chiral configurations the chiral pair index is given. The number 144 now arises in the following way: up to and including $N = 6$ there are, as shown in Figure 5, 87 configurations. Including the complementary configurations of these, we obtain a number of 174, but then the 30 configurations with $N = 6$ in Figure 5f have been counted twice. Hence the final number 144.

We see that in Figure 5 there are 6 chiral configurations with $n_\Delta = n_\Lambda$ (no. 17, 30, 42, 60, 61, and 83). Of these, no. 60 and no. 61 are mutually complementary, and no. 83 is complementary to its own mirror image. Including the complements of the 3 remaining configurations, we get the 9 configurations drawn separately in Figure 6. We shall now have a closer look at these to see whether obvious chirality descriptors offer themselves for all of them.

Figure 6c shows the configuration we already know from Figure 3. The terminal-edges suggestion mentioned in connection with Figure 3 would work here for cases c, e, g, and i, since in each of these cases the subconfiguration consisting only of terminal edges has a chiral pair index (m, n) with $m \neq n$. The resulting terminal-edges descriptors are shown in Figure 7 for the particular enantiomers of Figure 6.

Case a is not as easy. Here the subconfiguration consisting of the terminal edges has itself the chiral pair index (1, 1) and thus does not offer a chirality descriptor. It turns out, however, that a solution may be found by using a new chiral reference system, discussed in detail elsewhere,² that of chiral pairs of *oriented* lines. This reference system is much like the system based on unoriented lines. Within both systems there is a periodic variation of the assigned chirality descriptors when the two lines in a chiral pair are rotated relative to one another about their common normal; however, while the descriptor changes for every 90° in the case of *unoriented* lines—the orthogonal position being achiral—this change only occurs for every 180° in the case of *oriented* lines.

Figure 8 shows how the new reference system is applied in the present case. If we agree to orient all terminal edges *outward* from the chelate ligand, we get the situation shown in the middle of Figure 8. By the properties of the oriented-lines system, the two chiral pairs of oriented terminal edges *both* have the descriptor $\bar{\Lambda}$, so that $\bar{\Lambda}_2$ can be used as a descriptor for the whole configuration. Chiral pairs of oriented lines do not change their descriptor when both orientations are reversed, so if we instead, as shown in Figure 8 to the right, orient all the terminal edges *inward*, we still get the descriptor $\bar{\Lambda}_2$.

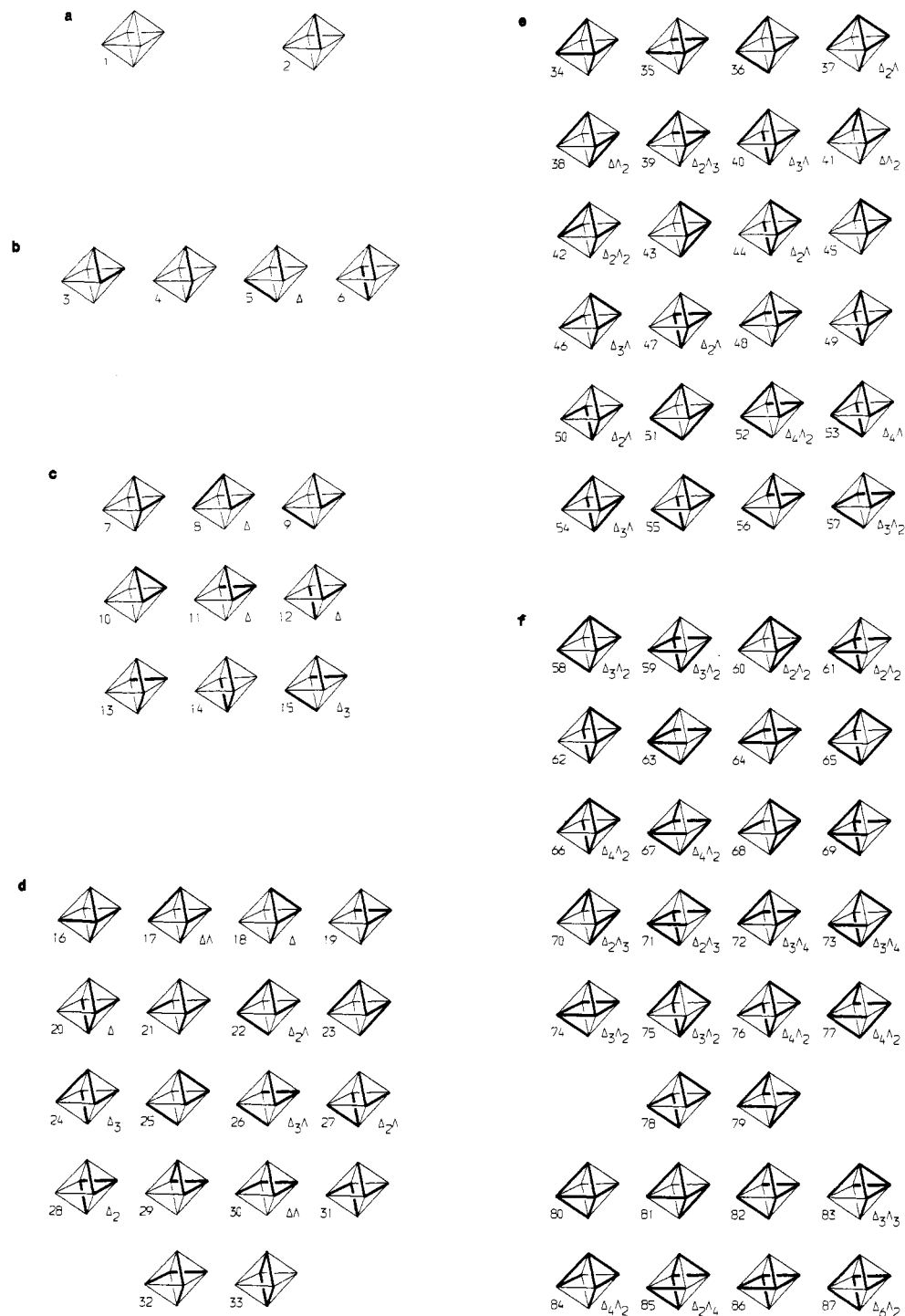


Figure 5. Complete set of octahedral edge configurations for $N \leq 6$. For chiral configurations only one enantiomer is depicted. (a) The configurations with $N = 0$ and $N = 1$. None of them are chiral. (b) The configurations with $N = 2$, i.e., with two occupied edges. No. 5 represents the *cis*-bis(bidentate) complexes and is the only chiral configuration here. (c) The configurations with $N = 3$. No. 15 represents the tris(bidentate) complexes and was also shown in Figure 1b. No. 8 and no. 11 may represent complexes of the types α - and β -[Co(trien)L₂]⁺ (ref 4), respectively (trien = 1,8-diamino-3,6-diazaoctane). (d) The 18 configurations with $N = 4$. This collection embodies 9 chiral configurations, 2 of which have $n_{\Delta} = n_{\Lambda}$ (no. 17 and no. 30). No. 30 was already shown in Figure 3 and also figures as specimen c in Figure 6; no. 17 is specimen a in Figure 6. No. 17 may model complexes like [Ni(H₂O)(edtaH₂)] (ref 9) or [Cr(H₂O)(edtaH)] (ref 10), in which (edtaH₂)²⁻ and (edtaH)³⁻ act as quinquedentate ligands. Nos. 22, 23, 28, and 30 are represented by the $\alpha\beta$, $\alpha\alpha$, $\beta\beta$, and β -trans isomers, respectively, of complexes of the [CoL(tetraen)] type^{4,5} (cf. caption to Figure 3). Nos. 24 and 26 may model complexes like [Co(trien)(bidentate)] (ref 4). No. 25 is represented by complexes of the [Co(monodentate)(bidentate)(tacn)]⁺⁺ type¹⁴ (tacn = 1,4,7-triazacyclononane). (e) The 24 configurations with $N = 5$. There are 14 chiral configurations, of which no. 42 exhibits an equal number of Δ pairs and Λ pairs. This configuration appears again as (e) in Figure 6. No. 41 is identical with the configuration shown in Figure 2. Nos. 37 and 45 may represent isomers of [Co(datn)Cl]²⁺ (ref 15) (datn = 1,4-bis(2-aminoethyl)-1,4,7-triazacyclononane). (f) The 30 configurations with $N = 6$. The upper 22 configurations (nos. 58–79) are grouped in pairs, each configuration being paired with its complementary configuration. Thus, nos. 58 and 59 are complementary, nos. 60 and 61 are complementary, etc. Of the last 8 configurations, nos. 80–82 and 84–87 are self-complementary, while no. 83 is complementary to its mirror image. Note, as a consequence of the formula presented in the main text, that any configuration with $N = 6$ has the same chiral pair index as its complementary configuration. Some of the configurations correspond to known complexes, for example no. 79 (see ref 11 and 13) and no. 87 (see ref 11–13). The rest are hereby offered as challenges to preparative chemists.

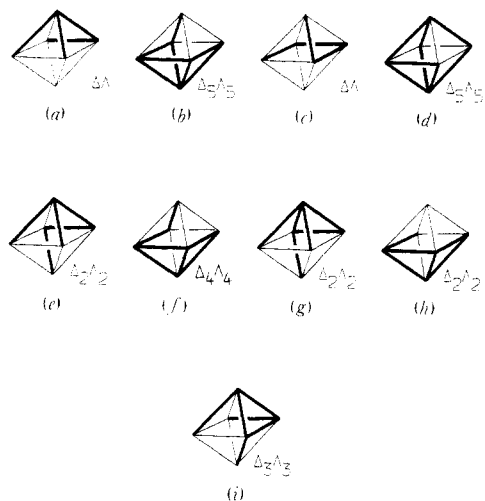


Figure 6. All the chiral configurations that contain an equal number of Δ and Λ pairs. The upper 8 configurations a–h are depicted in pairs, each pair containing a configuration and its complement. Thus a and b, c and d, etc. are complementary configurations. Specimen i is complementary to its own mirror image. Specimens a, c, e, g, h, and i are identical to no. 17, 30, 42, 61, 60, and 83, respectively, in Figure 5. The perspective is not necessarily the same as in Figure 5; it has in some cases been changed in order to facilitate the visualization of the Δ and Λ pairs of chelate-spanned edges. Furthermore, in the present perspective, the common features of configurations e and g are easily recognized (as are those of their complementary configurations f and h).

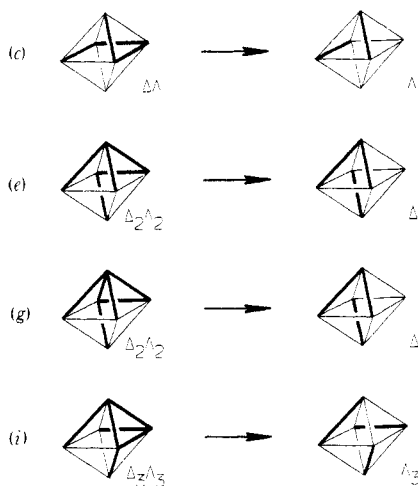


Figure 7. Of the nine configurations containing an equal number of Δ and Λ pairs, the four that can be assigned a unique chirality descriptor by means of the terminal-edges convention are shown here. The configurations have retained their letters of identification from Figure 6.



Figure 8. The configuration that is specimen a in Figure 6 has here been assigned the chirality descriptor $\bar{\Lambda}_2$ by using *oriented* terminal edges. In determining the descriptor, one can orient the terminal edges either outward or inward from the chelate ligand, whichever seems most convenient; the same descriptor is obtained in both cases.

The remaining configurations in Figure 6 have at most one terminal edge, so using terminal edges does not work in providing a chirality descriptor. Consider, however, the relation mentioned above between the chiral pair indices of a configuration and that of its complement. It follows from that relation that the quantity $n_{\Delta} - n_{\Lambda}$ is always the same for

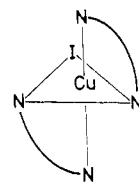


Figure 9. The trigonal-bipyramidal $[\text{CuI}(\text{bpy})_2]^+$ ion constituting an example of a nonoctahedral complex that can easily be assigned a chirality descriptor—in casu Δ —by using skew lines.

mutually complementary configurations. Thus, with respect to *this particular* property one may consider complementary configurations to have “the same sense of chirality”.⁷ Returning, with this in mind, to the remaining cases in Figure 6, we see that we may obtain a chirality descriptor for each of these if we simply *define* the chirality descriptor to be that of the complementary configuration.

In summation, *all* chiral configurations of edges on an octahedron may be given in chirality descriptor by the following simple conventions:

(1) Consider first the chiral pair index $(n_{\Delta}, n_{\Lambda})$. If $n_{\Delta} \neq n_{\Lambda}$, use the index as chirality descriptor.

(2) If $n_{\Delta} = n_{\Lambda}$, obtain a descriptor by using terminal edges, orienting them all outward (*or* all inward) if a unique descriptor is not obtained without orientation.

(3) If (1) and (2) do not solve the problem, apply (2) to the complementary configuration and use *its* chirality descriptor as the descriptor sought.

Although the present paper does not aim at making nomenclature proposals,⁷ we do note that the chirality descriptors obtained by (1)–(3) for the cases already covered by the rules in the Red Book¹ are not changed, except that in the Red Book tris(bidentate) complexes, as mentioned already, were given the descriptors Δ and Λ rather than Δ_3 and Λ_3 . Furthermore, in the Red Book Δ 's and Λ 's were allowed to appear in an arbitrary order, whereas we here group them together.

Of course it would be possible to construct consistent conventions other than (1)–(3) above; our goal has just been to show that *simple* conventions *can* be formulated. In fact, it would seem to be desirable to have a convention whereby every chiral configuration was assigned a descriptor consisting of a single Δ or Λ . We have not found any simple solution⁷ to this problem, but it is hoped that the present discussion may serve as a starting point for investigations in that direction. Note that such a “total” convention may have, in principle, the consequence that certain configurations which already in this paper obtained a single-letter chirality descriptor will get their descriptor changed to the opposite one.

The Δ/Λ system for specification of “configurational” chirality has until now been used almost exclusively in *octahedral* coordination compounds. The “Chemical Abstracts Index” has a general system for assigning *stereodescriptors*, which is applicable also to other coordination polyhedra,⁸ but as it is a little tedious to work with, it may be convenient to use, as advocated also in ref 2, the Δ/Λ and $\bar{\Delta}/\bar{\Lambda}$ systems more widely for *the restricted purpose* of quickly obtaining easily appreciated *chirality descriptors*. For example, the trigonal-bipyramidal complex shown in Figure 9 may be *immediately* described as a Δ enantiomer, whereas the Chemical Abstracts system requires one to construct a full stereodescriptor, in casu *TB-5-22'-C*, by a detailed set of rules, in order

(7) As exemplified in Figure 4b, the sense of chirality indicated by the excess of Δ pairs over Λ pairs does not necessarily coincide with the immediate screw impression of the total configuration of edges. This is one of several reasons that we at the present time hesitate to use our results as the basis for a nomenclature proposal.

(8) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* 1975, 14, 1273–1278; 1978, 17, 1563–1568.

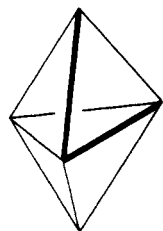


Figure 10. This edge configuration is chiral when placed on a trigonal bipyramid. The edge configuration itself, i.e., without the rest of the trigonal bipyramid, is not chiral, so a chirality descriptor cannot be found by using the Δ/Λ or $\bar{\Delta}/\bar{\Lambda}$ system.

to just obtain the chirality descriptor (in casu C).

With hindsight to such wider applications of the Δ/Λ nomenclature, we are thinking of performing investigations similar to the present one on other coordination polyhedra. However, one quickly faces new problems when leaving the regular octahedron, as we shall illustrate briefly by Figure 10.

The distinguished edge pair there forms a chiral configuration when it sits on the trigonal-bipyramidal skeleton, but it is in itself achiral and contains no skew line pairs. Thus a completely new convention is necessary if one wants to assign a chirality descriptor to this geometrical figure. (For the *concrete chemical* examples it may represent, we have the CA system mentioned above.⁸) The situation is very different from the regular octahedral case, where all edge configurations that made a chiral system when sitting on the octahedral skeleton were also chiral themselves and contained at least one chiral line pair.

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Appendix

Here we wish to prove the formula stated in the main text relating the chiral pair index of a configuration of N edges on a regular octahedron to that of its complementary configuration comprising the remaining $12 - N$ edges.

To this end, number the octahedron edges with the numbers 1, 2, 3, ..., 12 in such a way that the N edges in the given configuration receive the first N numbers (otherwise, the choice of numbering is immaterial for the following arguments).

- (9) Smith, G. S.; Hoard, J. L.; *J. Am. Chem. Soc.* **1959**, *81*, 556-561.
 (10) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316-1317.
 (11) Searle, G. H.; Dwyer, M. *Inorg. Chim. Acta* **1981**, *52*, 251-255.
 (12) Drew, M. G. B.; McCam, M.; Nelson, S. M. *Inorg. Chim. Acta* **1980**, *41*, 213-219.
 (13) Royer, D. J.; Grant, G. J.; Van Derveer, D. G.; Castillo, M. J. *Inorg. Chem.* **1982**, *21*, 1902-1908.
 (14) Fujinami, S.; Matsunami, Y.; Shibata, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2101-2106.

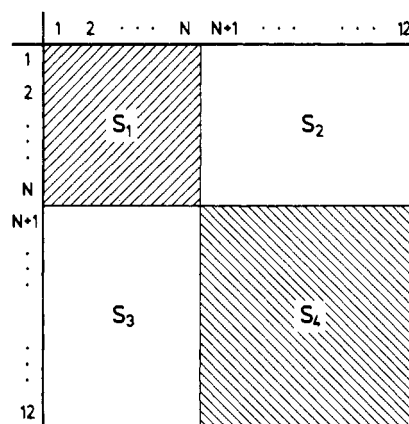


Figure 11. Structure of the matrix discussed in the Appendix.

Set up a 12×12 matrix with rows and columns numbered from 1 to 12 in order.

Fill out the matrix now by defining each element (p, q) according to the following prescription: $(p, q) = 1$ if the edges p and q form a Δ pair; $(p, q) = 0$ otherwise.

The resulting matrix is evidently symmetric and furthermore the sum of the elements in each row is 2, because a given edge forms a Δ pair with exactly 2 other edges.

Now let us partition the matrix into 4 submatrices as shown in Figure 11, the vertical line separating the first N columns from the rest and the horizontal line separating the first N rows from the rest. Let us form the sums S_1, S_2, S_3, S_4 over all elements within each of the four submatrices. From the definition of the matrix elements, it is seen that S_1 is equal to twice n_Δ for the given configuration and S_4 is equal to twice n_Δ for the complementary configuration. From the symmetry of the matrix we have

$$S_2 = S_3$$

and from the row-sum property stated above we get

$$S_1 + S_2 = 2N \quad S_3 + S_4 = 2(12 - N)$$

Altogether we have

$$S_4/2 - S_1/2 = 12 - 2N$$

which is the desired relation as far as the number of Δ pairs is concerned. Repeating the whole argument for Λ pairs obviously gives the same result for them.

Note Added in Proof. The number of O_h -equivalence classes of edge configurations may be easily calculated without carrying out the actual enumeration. Using a formula by Pólya,^{16,17} one also obtains the number 144.

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