

Tentative Proposals for Nomenclature¹ of Absolute Configurations Concerned with Six-Coordinated Complexes Based on the Octahedron²

1. Introduction

1.1. Configuration.—For spectroscopic purposes and for following the stereochemical course of substitution reactions it is of interest to consider, for example, tris- and bis-bidentate six-coordinated complexes based on the octahedron as related through the configurations depicted in Figure 1 (a) and (b). Here the edges spanned by the chelate rings are drawn as heavy lines. The chelate rings are thought of as devoid of chemical significance in the sense that the chelating ligands may be identical or different, and may be symmetrical or not. Similarly the two X's represent two monodentate ligands which may or may not be identical. It is desired, in all generality, to have a designation of chirality which is independent of the chemical nature of the chelating ligands and which only depends on the relative positions of the heavy line edges which represent the bidentate ligands or the bidentate units of polydentate ligands.

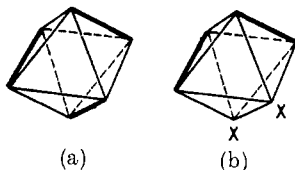


Figure 1.—General "octahedral" systems containing three (a) and two (b) bidentate ligands represented by the edges (drawn as heavy lines) which they span. It is desired to characterize these systems as having the same absolute configuration independently of their chemical significance. They have both been designated by Δ in the present proposal.

1.2. Conformation.—Further for spectroscopic purposes it is of interest to designate the conformation of chelate rings relative to the central atom or ion, but independently of the other atoms forming the chelate ring and also of the substituents of these atoms.

1.3. The Present Proposals.—All the tentative rules which follow are based on the fact that two skew

and nonorthogonal lines define a helical system. They primarily describe a nomenclature for the absolute configuration of classes comprising *cis*-bis-bidentate and tris-bidentate complexes and the absolute conformation of five-membered chelate rings. However, since the rules are based on general grounds, they lend themselves readily to application to more complicated situations, *i.e.*, polydentate chelate systems and larger chelate rings.

In the chemical literature there exist different proposals for the nomenclature of the systems, devoid of chemical significance, which are under consideration here. These proposals are generally based upon helicities about symmetry or pseudo-symmetry axes. The present proposals are independent of symmetry concepts and thereby easier to generalize to situations where symmetry is absent.

2. Basic Principle

Two skew lines which are not orthogonal to each other make up a helical system as illustrated in Figures 2 and 3. Two skew lines possess the property of having one and only one normal in common. In Figure 2 one of the skew lines AA determines the axis of a helix upon a cylinder whose radius is equal to the length of the two skew lines' common normal NN. The other of the skew lines BB makes up a tangent to the helix at N and determines the steepness of the helix. In Figure 3 the two skew lines AA and BB are seen in projection onto a plane orthogonal to their common normal.

(a) of Figure 2 and 3 illustrates a right-handed helix to be associated with the Greek letter delta (Δ referring to configuration, δ to conformation). (b) of Figure 2 and 3 illustrates a left-handed helix to be associated with the Greek letter lambda (Λ for configuration, λ for conformation).³

Because we are only interested in a qualitative measure of the helicity, the steepness of a helix is, in general,

(1) The rules proposed here are given in short form in sections 8 and 9 of this communication.

(2) Comments should be sent to the chairman of the Commission, Professor K. A. Jensen, Chemical Laboratory II of the University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, 2100 Copenhagen Ø.

(3) It should be noted that orthogonal to the common normal of the two skew lines there is a twofold axis (in fact, there are two such axes) of proper rotation which brings each one of the skew lines into coincidence with the other. This means that the helix which the first line, BB, say, determines around the second one, AA, has the same helicity as that which the second one determines around the first one.

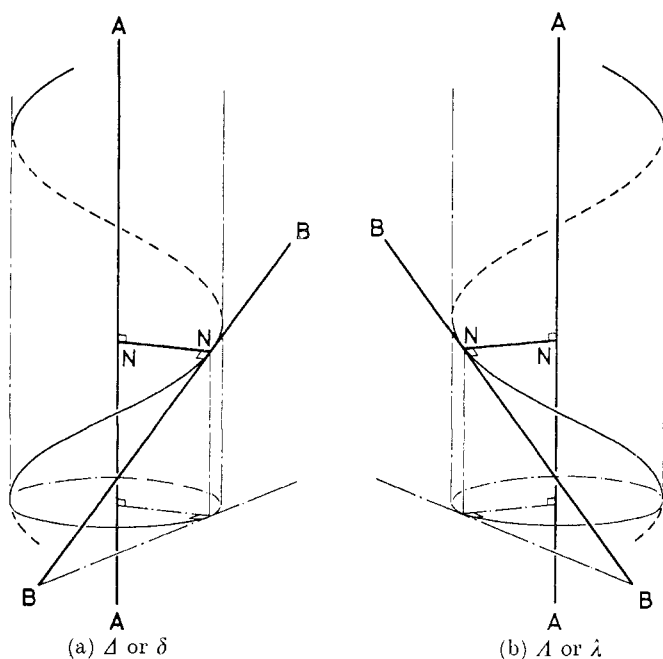


Figure 2.—Two skew lines AA and BB which are not orthogonal define a helical system. In the figure AA is taken as the axis of a cylinder whose radius is determined by the common normal NN of the two skew lines. The line BB is a tangent to the above cylinder at its crossing point with NN and defines a helix upon this cylinder by being the tangent to it at this crossing point. (a) and (b) illustrate a right- and a left-handed helix.

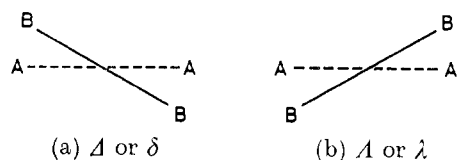


Figure 3.—The figure shows pairs of nonorthogonal skew lines in projection upon a plane parallel to both lines. The fully drawn line BB is above the plane of the paper, the dotted line AA below this plane. (a) corresponds to (a) of Figure 2 and defines a right-handed helix. (b) corresponds to (b) of Figure 2 and defines a left-handed helix.

of no importance. However, the singularities at infinite steepness, where the skew lines become parallel lines, and at vanishing steepness, where the lines become orthogonal, should be noted. Here an infinitely small rotation of one line relative to the other about their common normal will change the helicity from right-handedness to left-handedness or *vice versa*. It is obvious that as the representation of our physical situation approaches these singularities the helicity becomes undefined (see Figure 13).

3. Application to Configuration

3.1. Representation to Chelate Rings.—A chelate ring of a six-coordinated complex, whose ligators form an approximate octahedron, is represented by the edge determined by its two ligators. If two such edges are skew the pair can, without any further conventions, be associated⁴ with either (a) or (b) of Figure 3. This is the basis of the present proposal for nomenclature of absolute configurations for *cis*-bis-bidentate and tris-bidentate systems.

Two heavy line edges which are neither neighboring edges having a common vertex, nor opposite edges, will in an octahedron form a pair of skew lines. This pair always has the same relative position as that of a *cis*-bis-bidentate complex.

In Figure 4 is seen the representation of the *cis*-bis-bidentate complex of Figure 1 (b) redrawn so as to conform to Figure 3, and for the particular absolute configuration to Figure 3 (a). To the corresponding tris complex [Figure 1 (a)] is attributed the same designation because its three heavy line edges are equivalent and therefore also the three possible pairs of heavy line edges. This is illustrated in Figure 5.

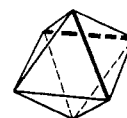


Figure 4.—The bis-bidentate complex of Figure 1 (b) redrawn so as to become associated with Figure 3 (a) and thus to become designated by Δ .

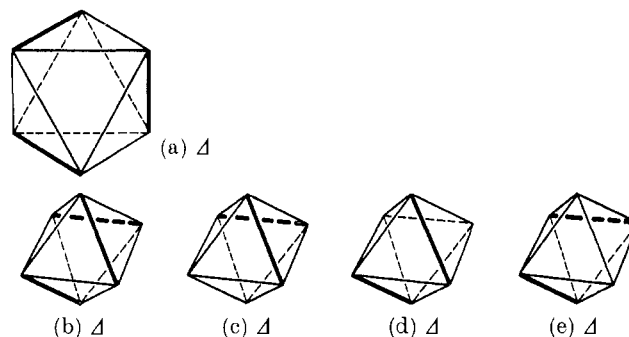


Figure 5.—(a) and (b) show the tris-bidentate system of Figure 1 (a) redrawn in two different ways. Since each of the bidentate ligands has lost its individuality by being represented only by the edge which it spans, the threefold axis of symmetry of the octahedron applies also to the present system. (a) shows the system in projection on a plane orthogonal to its threefold axis. (c), (d), and (e) each illustrates one of the three possible pairs of bidentate ligands oriented so as to refer to (b). (c) is associated with Figure 3 (a), and thus is designated by Δ . The same must hold true also for (d) and (e) because the threefold axis makes the three pairs of representations of bidentate ligands equivalent.

3.2. Some Examples of Polydentate Systems.—It is straightforward to extend the application of the above rules to more complex situations involving polydentate ligands. It is by analogy with the tris-bidentate case (Figure 5) only a matter of studying the interrelations between all the chelate rings whose corresponding edges form a pair of skew lines, *i.e.*, all the ring pairs whose relative position is the same as in a *cis*-bis-bidentate complex. Now one might count up all such contributions and designate the complex situation by Δ if the number of Δ contributions from the individual pairs exceeds the number of Λ contribu-

(4) In connection with the singularities mentioned above it should be noted that by moving the ligators away from the ideal octahedral positions a gradual transition from the situation of Figure 3 (a) to that of Figure 3 (b) is possible without a change of absolute configuration. However, for this to occur the distortions must be so great that one would no longer think of calling the complex octahedral. Further such cases are unknown.

tions and *vice versa*. This convention, which could be applied to the situations shown in Figures 6–8, will *not* be recommended here for the reason given in the next paragraph. Even though nonhelical situations will always contribute Δ and Λ an equal number of times (Figure 9), the same may be true as well for certain helical situations, as illustrated in Figure 10.

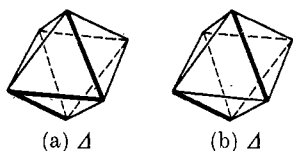


Figure 6.—A quadridentate system (a). Here only two of the heavy line edges are skew, the pair (b) being associated with Figure 5 (d) and thus being designated by Δ . The system as a whole is proposed designated “skew chelate pair, Δ .” The system may be thought of as representing the α isomer of a trien complex (trien = triethylenetetramine).

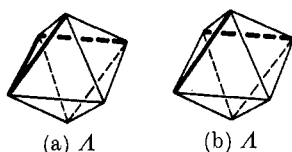


Figure 7.—Another quadridentate complex (a). As in Figure 6 there is only one helical pair (b). This is clearly associated with the mirror image of Figure 5 (c) (and, of course, therefore, also of Figure 5 (d) and (e), although this is less easy to see) and thereby gives rise to the designation Λ . The system is therefore designated “skew chelate pair, Λ .” The system may represent the β -isomer of a trien complex (see Figure 6).

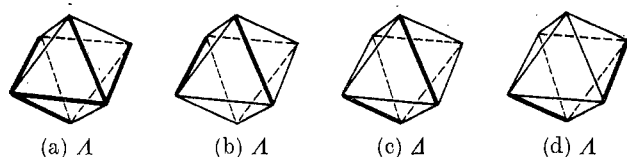


Figure 8.—A sexidentate complex (a). The pair (c) is associated with Figure 5 (d) and is therefore Δ . The pairs (b) and (d) are clearly the mirror images of Figure 5 (c) and (e), respectively, and are therefore both Λ . The whole system is designated “skew chelate pairs, $\Delta\Lambda\Lambda$ ” where the order of the symbols is immaterial. The system may represent an EDTA complex (EDTA = ethylenediaminetetraacetic acid).

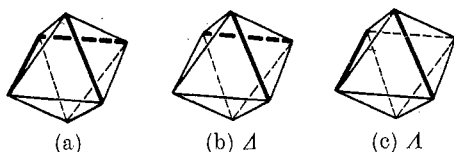


Figure 9.—A nonhelical system (a). The helical pairs (b) and (c) are mirror images of each other and contribute Δ and Λ , respectively. Nonhelical systems always have an equal number of Δ and Λ contributions. The reverse conclusion, however, is not valid (see Figure 10).

A case such as that of Figure 10 requires a further convention and here no simple one has yet been proposed. A possible convention here might conflict with the above simple counting of Δ and Λ contributions. We therefore recommend, at the present stage, for the case of Figures 6–8 where the number of Δ and Λ contributions is different, to characterize the com-

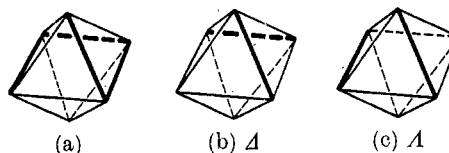


Figure 10.—A quinquidentate system (a). (b) is Δ by association with Figure 5 (c), (c) is Λ because it is the mirror image of (b). A designation for the whole helical system (a) cannot be obtained without a further convention. A preliminary designation might be “the end chelate rings form a skew chelate pair, Λ .”

plexes as follows: Figure 6, “skew chelate pair, Δ ”; Figure 7, “skew chelate pair, Λ ”; Figure 8, “skew chelate pairs, $\Delta\Lambda\Lambda$ ”. In the last example the order of the Greek letter symbols is immaterial. The case of Figure 10 might at present be characterized by (“the end chelate rings form a skew chelate pair, Λ ”).

4. Application to Conformation

In order to define the helicity of a ring conformation a convention is required for making a choice of a pair of skew lines. Here it is proposed to choose one of the lines of this pair as the edge covered by the chelate ring, *i.e.*, the line AA joining the two ligators. The other line BB is taken as that joining the two ring atoms which are neighbors to each of the ligators.

Two enantiomeric situations are shown in projection in Figure 11. The two ligators AA are in the plane of the paper, the central atom M is below this plane, and the two neighboring ring atoms BB are above it. Figure 11 (a) and (b) are associated with the corresponding Figure 3, and the proposed convention for designating the helicity is thereby given. In Figure 12 is shown a situation to which is attributed the same designation as that of the case of Figure 11 (a). In

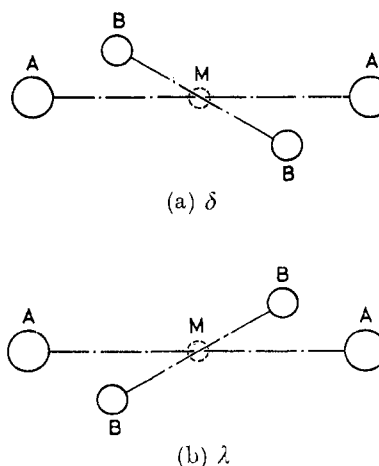


Figure 11.—Illustration of the convention for designating the helical character of the conformation of chelate rings. The ligating atoms in the plane of the paper determine one of our skew lines AA. The neighboring atoms of each ligator determine the other line BB, which here is above the plane of the paper, the central atom M being below this plane. The designations become clear by comparison with Figure 3 (a) and (b).

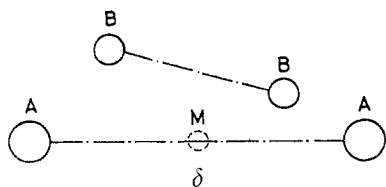


Figure 12.—Illustration of an alternative situation to that of Figure 11 (a). Both atoms BB are above the plane determined by M and AA, but this is immaterial from a nomenclature point of view. The lines AA and BB are still skew and correspond to the situation of Figure 3 (a).

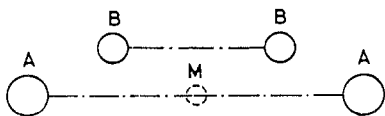


Figure 13.—Nonhelical chelate ring drawn as in Figure 11. This figure illustrates a five-membered ring in its envelope form or a six-membered ring in either its boat or its chair form.

Figure 13 BB is parallel to AA and the chelate ring will not be helical at least up to a ring size of seven or eight members, which for our purpose is without importance. The situation in which BB is parallel to AA corresponds to the case of any planar chelate ring, and in addition to this, for a five-membered ring, it corresponds to the envelope form, and for the six-membered ring, either to the chair or to the boat form. In this case only the skew-boat form has a helical character.

Nonhelical situations may still represent chiral situations when the chemical significance of the atoms, *i.e.*, their possibility of being different, is considered. The present nomenclature problem, however, is not concerned with such cases.

5. Examples of a Few Absolute Configurations

The proposals which have been put forward here dictate that the absolute configuration of the tris-(ethylenediamine)cobalt(III)ion with a positive rotation at the Na D line be characterized as upper case Λ and (–)propylenediamine in its stable chelate conformer (equatorial CH_3^-) be characterized by lower case λ .

6. Phenomenological Characterization

As well as the symbols for designating structure some phenomenological description of a mirror-image isomer is essential. The isomer might be denoted by its sign of rotation at a particular wavelength, $(+)_\lambda$

e.g., $(+)_\delta\delta\delta[\text{Co}(\text{en})_3]\text{Cl}_3$; en = ethylenediamine

When optically active ligands are coordinated they are denoted as $(+)$ and $(-)$ where the signs are the signs of the ligand at the Na D line

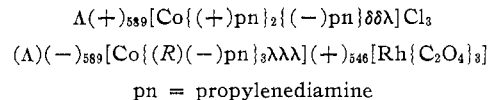
e.g., $(-)_\delta\delta\delta[\text{Co}\{(-)\text{pn}\}_3]\text{Cl}_3$; pn = propylenediamine

In those instances where the absolute configuration of the ligand is known this might also be included in the description

e.g., $(-)_\delta\delta\delta[\text{Co}\{(R)(-)\text{pn}\}_3]\text{Cl}_3$

7. Full Characterization

Examples of the use of the full nomenclature proposed here follow:



8. Rules for the Designation of Configurational Chirality Caused by Chelation in Six-Coordinated Complexes Based on the Octahedron

8.1. *cis*-Bis-Bidentate Chelation.—The two ligating atoms of a chelate ring define a line. Two such lines for the pair of chelate rings define a helix. One line is the axis of the helix and the other is the tangent of the helix at the common normal for the skew lines. The tangent describes a right-handed (Δ) or a left-handed (Λ) helix with respect to the axis and thereby defines the configuration.

8.2. Tris-Bidentate Chelation.—Any one of the three possible pairs of chelate rings is chosen to designate the configuration by rule 1.

8.3. Multidentate Chelation.—Chiral complexes of multidentate ligands are considered to contain pairs of skew lines (rule 1) and are designated by all the symbols, Δ 's and Λ 's, belonging to all the skew-line pairs. The order of citation of the symbols is immaterial.

9. Rule for the Designation of Conformational Chirality of a Chelate Ring

The line joining the two ligating atoms and the line joining the two atoms of the chelate ring adjacent to each of the ligating atoms define a helix. One line is the axis of the helix and the other is the tangent of the helix at the common normal for the skew lines. The tangent describes a right-handed (δ) or a left-handed (λ) helix with respect to the axis and thereby defines the conformation.

Appendix. Relationship between the Proposed Symbols and Those in Earlier Use

The symbols Δ and Λ were originally proposed for tris-bidentate complexes by Piper,⁵ who used the threefold axis (C_3) as reference axis. The present convention agrees with the results of Piper's proposal. The present convention for designation of conformation likewise agrees with Liehr's⁶ proposed use of δ and λ .

The absolute configuration⁷ of $(+)_\delta\delta\delta[\text{Co}(\text{en})_3]^{3+}$ (in the crystal, $\Lambda\delta\delta\delta$) is Λ and that⁸ of $(-)_\delta\delta\delta[\text{Co}\{(-)\text{pn}\}_3]^{3+}$ is $\Delta\lambda\lambda\lambda$, as determined by Saito, *et al.*, from X-ray crystallography. These two complex ions were in the X-ray papers designated by D and L, respectively. Mason pointed out that the helical configuration about a C_2 axis of a tris-bidentate or *cis*-diacidobis-bidentate complex is opposite to that about the respective C_3 or

(5) T. S. Piper, *J. Amer. Chem. Soc.*, **83**, 3908 (1961).

(6) A. D. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).

(7) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Acta Cryst.*, **8**, 729 (1955); K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957).

(8) Y. Saito, H. Iwasaki, and H. Ota, *ibid.*, **36**, 1543 (1963).

pseudo C_3 axes. He proposed⁹ the use of P (positive for right-handed) and M (minus for left-handed) as in $P(C_3)$ or $M(C_2)$ where the reference axis is indicated. The result of the present proposal is equivalent to that using the C_3 or pseudo C_3 axis and is *opposite* to that using a C_2 axis, *i.e.*, Δ for $P(C_3)$ or $M(C_2)$ and Λ for $M(C_3)$ or $P(C_2)$. Hawkins and Larsen¹⁰ defined an octant sign to characterize the helicity of configurations (also of polydentate systems) as well as for conformations. For tris-bidentate and *cis*-bis-bidentate systems and for conformations of five- and six-membered rings the relation to the present proposal is Λ (positive octant sign), λ (negative octant sign). Legg and Douglas¹¹ suggested the general use of the C_2 axis for reference of helicity and a ring-pairing method for assigning the helicity of complexes containing polydentate ligands. The ring pairs chosen to define the helicity are the same as those proposed here. However, because of the C_2 -reference axis their use of Δ and Λ is opposite to that of the present proposal. It should further be noted that both the octant-sign method and the ring-pairing method of characterizing absolute configurations need extra

(9) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965); A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 5094 (1965).

(10) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185, 1969 (1965).

(11) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).

conventions in certain cases of the type discussed here along with Figure 10.

Corey and Bailar¹² and Sargeson¹³ have discussed the concomitant interplay of conformation and configuration in tris-bidentate diamine complexes. These authors designated the conformation of the five-membered ethylenediamine ring as k and k' , but used k and k' in the opposite sense.¹⁴ With reference to our Figure 11 the interrelation of δ , λ and k , k' is

	Corey and Bailar	Sargeson
δ	k'	k
λ	k	k'

Acknowledgment.—The Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry wishes to express its appreciation of the valuable help offered by Dr. Werner Fenchel, professor of mathematics at the University of Copenhagen, by Sir Christopher Ingold and Dr. R. S. Cahn, and by several chemists working with optically active complexes.

(12) E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

(13) A. Sargeson, "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, p 303.

(14) The cause of the confusion with respect to k and k' is an error in the upper drawing of Figure 3 of Corey and Bailar's paper! The ring conformation of the unstable form, the *ob* form $\Delta\delta\delta$, is correctly given as kkk in the lower drawing of their Figure 3, but the stable form, the *lel* form $\Delta\lambda\lambda$, discussed in the text correctly as kkk , appears in the upper drawing of their Figure 3 as $\Delta\delta\delta$.