Absolute Configuration of Octahedral Metal Complexes:

The Octant Sign

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The terminology for the absolute configuration of octahedral metal complexes is discussed and the symbols D and L are redefined in terms of an octant sign. The derivation of the octant sign for a variety of structures is given. The possibility of a correlation between the octant sign and the sign of the Cotton effects for identified transitions within certain symmetry groups is mentioned.

For tris-bidentate, *cis*-bis-bidentate and certain multidentate complexes, the absolute configuration of the complexes can be described by referring to the chirality of the helical arrangement of chelate rings about one or more of the symmetry axes. Two sets of symbols, D or L[1] and Δ or Λ,[2] have been used to define this chirality. However, for compounds that do not possess such an array of chelate rings, *e.g.* $[Co(NH_3)_4(l\text{-pn})^*]^{3+}$, these notations, if defined in terms of this molecular spirality, are not applicable. In this paper, the historically important D and L symbols have been made generally applicable by redefining them in terms of an octant sign, which allows the absolute configuration to be more easily visualised than by considering imaginary 'screws'. Jones and Eyring[3] have briefly mentioned an octant sign for $[Coen_3]^{3+}$. However, their method of positioning the complex in a coordinate system would severely limit its application to other complexes.

Moffitt and his co-workers[4] have proposed the use of an octant sign to define the absolute configuration of organic carbonyl compounds. The relationship that was found to exist between this term and the sign of the Cotton effect for the $n \to \pi^*$ carbonyl transition has facilitated the assignment of the absolute configuration to these compounds.[5] Although much has been

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* Traditionally, the isomer under consideration has been specified by the sign of rotation at the sodium D line or at another suitable wavelength by means of the symbols d, l or $(+)$, $(-)$. The authors prefer the d, l notation for both ligands and complexes because of the possible confusion of $(+)$ or $(-)$ with the octant sign. Thus, *laevo* rotatory propylenediamine has been given the abbreviation l-pn.

written recently about the absolute configuration of metal complexes and its assignment on the basis of the sign of the Cotton effect for particular transitions (for a review see Woldbye [6]), at present there is no general rule for assigning absolute configurations to coordination compounds on this basis. It is hoped that the definition of absolute configuration in terms of an octant sign, as presented in this paper, will lead to a general *Octant Rule* for metal complexes.

THE OCTANT SIGN

The octant sign of a complex is derived by positioning the complex in a right-handed coordinate system so that the central atom is at the zero point and the ligands are distributed in the manner given below. The sign of each octant is given by the sign of the product of its coordinates. The octant sign of a complex is obtained by adding the octant signs of the atoms that compose the chelate rings, the sign of each atom, of course, being that of the octant in which it is situated. The substituents on the chelate rings as well as any monodentate ligands are not considered as they are thought to be of minor importance in determining the dissymmetry of the electronic field and, thus, the optical activity of the complex. However, the positions of the ring atoms are thought to be important because they determine the static or vibrationally-induced asymmetry of the donor atoms, which gives rise to the dissymmetry of the electronic field.

(a) Mono-bidentate complexes

For convenience and uniformity the first chelate ring is so placed that the donor atoms lie in the xy plane and have the coordinates, $(+x, +y)$ and $(-x, +y)$.* As an example we will consider the most stable form of $[MX_4(l\text{-pn})]^{n+}$. l-Propylenediamine has the absolute configuration, I.[7] According to conformational analysis,[8] the most stable form of the above complex would have the methyl group in an 'equatorial' position and thus the chelate ring would have the conformation, II.** Both the carbon atoms lie in negative octants while the nitrogen atoms, being in the xy plane, do not contribute to the octant sign. Thus the complex has an overall negative octant sign. The most stable complex of d-propylenediamine, on the other hand, would


I   II   III

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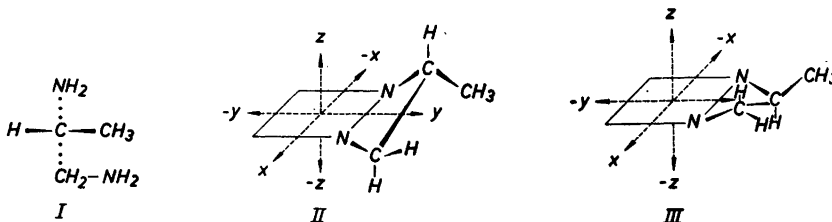
* It should be emphasised that the positions of the donor atoms in the coordinate system differ from the usual positions on the x, y, and z axes.

** For simplicity, the hydrogens on the nitrogens have been omitted in this and other structures.

have the structure III which is enantiomeric with II and has a positive octant sign.

For complexes with α-amino acids, it had been thought that the chelate ring would be approximately planar.[8] However, X-ray analysis of the bis-glycinatocopper(II) complex has shown that the chelate ring is puckered in such a way that the nitrogen and copper atoms are on opposite sides of the C—CO—O plane.[9] From Dreiding atomic models it becomes evident that even small deviations of the chelate ring from planarity give the substituent on the α-carbon atom an 'axial' or 'equatorial' character. Thus, the most stable form for the complexes of D-α-amino acids, whose anions have the absolute

IV   V   VI
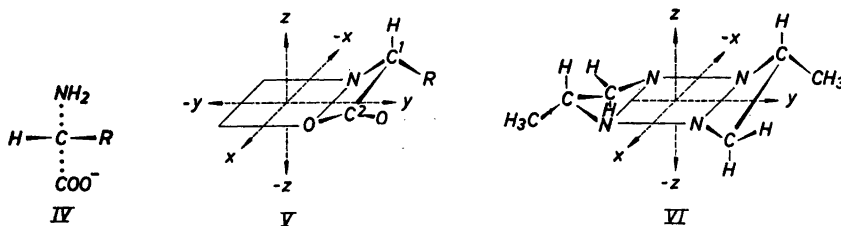
configuration IV,[10] has the structure V, in which the substituent on the α-carbon is 'equatorial'. The atoms, C_1 and C_2, are in the $(-x,+y,+z)$ $(-)$ and $(+x,+y,+z)$ $(+)$ octants, respectively. If only the signs of the two carbon atoms are considered, the complex would have no octant sign. However, as C_2 lies almost in the xy plane, the sign of C_1 would predominate. Thus, the complex would be given a negative octant sign.

(b) Bis-bidentate complexes

(i) *Trans*. The octant signs of *trans*-bis-bidentate complexes are obtained in a similar manner to that for the mono complexes. Corey and Bailar[8] have postulated from conformational analysis that the most stable form of a *trans*-bis-(*l*-propylenediamine) complex would have the structure VI, in which the two methyl groups are in equatorial positions. X-Ray analysis has confirmed the above structure for *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl· HCl·2H$_2$O.[7] For this structure, all the ring carbon atoms lie in the negative octants and so the complex has a negative octant sign. The conformation of the rings in structure VI is completely described by the notation, $(-,-)$, which is equivalent to the term, kk, as proposed by Corey and Bailar.[8]


VII   VIII
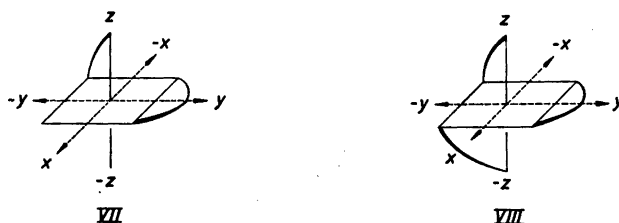
(ii) *Cis*. To completely define the absolute configuration of *cis*-bis-bidentate complexes, both the distribution of the chelates around the metal and the conformation of the two chelate rings need to be described. The octant sign resulting from the former is independent of which ring is considered in the xy plane. For example, in the complex, *cis*-[M(en)$_2$X$_2$]$^{n+}$ with the structure VII, no matter which ring is in the xy plane, both carbon atoms of the other ring are together contained in a positive octant. However, the octant signs of the two rings must be determined by considering both rings separately in the xy plane. For the above complex, there are three possible conformations for the two rings, (+,+), (+,−) and (−,−), respectively.

(c) Tris-bidentate complexes

The tris-bidentate complexes have to be considered in a manner similar to that for the *cis*-bis complexes. Using this method, [M(en)$_3$]$^{n+}$ with the structure VIII has a positive octant sign; the two rings that do not lie in the xy plane are completely contained in positive octants.

(d) Multidentate complexes

The absolute configuration of complexes with multidentate ligands can also be described by octant signs. We will consider three examples, *cis* α-[Co trien X$_2$]$^{n+}$, *cis* β-[Co trien X$_2$]$^{n+}$ (where trien stands for triethylene-tetramine) and [Co EDTA]$^{-}$, having the structures, IX, X, and XI, respectively.

IX   X   XI
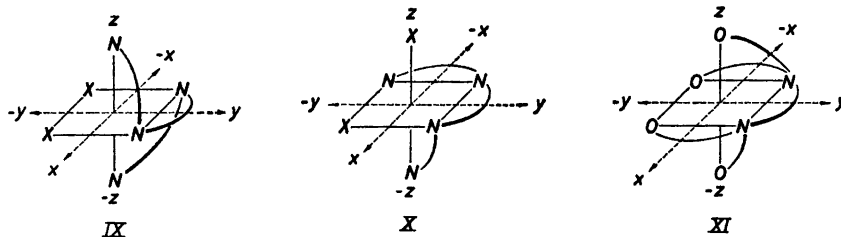
To arrive at the octant sign for a multidentate complex, each chelate bridge must be placed in turn in the xy plane, the octant sign assessed for each position, and the signs, so obtained, added. For the particular *cis* α trien complex under consideration, the octant signs for the three positions are +, 0 and 0, giving a resultant positive sign. Similarly, for the *cis* β trien and EDTA complexes, resultant positive octant signs are obtained as the signs for the individual positions are −,+,+ and −,+,0,+,0, respectively.

(e) Dissymmetric complexes with neither positive nor negative octant signs

There are certain dissymmetric complexes which have neither positive nor negative octant signs according to the present definition. For example, an octahedral compound possessing six different monodentate ligands, or a

complex such as cis-$[Mx_2y_2aa]^{n+}$, where x and y are monodentate ligands and where M-aa is a planar chelate ring, have no octant sign. However, when more is known about the stereochemistry of these compounds, an octant sign could perhaps be assigned on the basis of the positions of the monodentate ligands, which probably would have octant signs due to distortions from the regular octahedral positions.

SYMBOLISM FOR DESCRIBING ABSOLUTE CONFIGURATIONS

The absolute configuration of the d-$[Co(en)_3]^{3+}$ complex ion, which has been traditionally ascribed the symbol D, was determined by Saito and his coworkers [11] from the X-ray analysis of 2 d-$[Co(en)_3]Cl_3 \cdot NaCl \cdot 6H_2O$ to be that given in structure VIII. This has the form of a right-handed helical screw when viewed along any of the C_2 axes but a left-handed screw if the C_3 axis is taken as the line of reference. Thus, Mason [12] has suggested the use of symbols such as $D(C_2)$ or $L(C_3)$ to describe the absolute configuration of this complex whereas Piper [2] has introduced the symbol Λ (and Δ to describe the enantiomer).

The absolute configuration of a complex, whether it possesses a helical arrangement of chelates or does not, can be defined by the octant sign of the complex. The actual position of the complexes in the above coordinate system was chosen so that the octant sign of d-$[Co(en)_3]^{3+}$ would be positive. This has enabled compounds with a positive octant sign to be assigned the historically important symbol D and those with a negative octant sign the symbol L. However, as was discussed above, the conformations of the chelate rings need to be defined before the absolute configuration of some complexes are completely described. Therefore, it is proposed that, where necessary, the octant signs of such chelate rings are incorporated with the D or L symbol. In this way, the various forms of $D[Co(en)_3]^{3+}$ would have the symbols $D(+,+,+)$, $D(+,+,-)$, $D(+,-,-)$, and $D(-,-,-)$, respectively.

CORRELATION OF THE OCTANT SIGN WITH THE SIGN OF COTTON EFFECT FOR $d-d$ TRANSITIONS

For the determination of the absolute configuration of cyclic ketones, an Octant Rule was formulated on the basis of an empirically found relationship between the octant sign and the sign of the Cotton effect for the isolated carbonyl $n \rightarrow \pi^*$ transition.[4] Unfortunately, metal complexes do not have an isolated non-degenerate transition which is common to all complexes. Further, the observed $d-d$ transitions have not been accurately assigned for the majority of complexes.

The $A \rightarrow E$ and $A \rightarrow A$ components of the lowest energy absorption band for $D[Co(en)_3]^{3+}$ and other trigonal metal complexes have been assigned following the circular dichroism investigations of their uniaxial crystals.[12] For these complexes, which possess a D_3 symmetry, the signs of the Cotton effect for their $A \rightarrow E$ transitions are found to correspond with the octant signs of the complexes. A polarised crystal spectrum of $trans$-$[Co(en)_2Cl_2]^+$, which has an effective symmetry of D_{4h}, has shown that the $^1A_{1g} \rightarrow {}^1E_g$ band for this complex is at a lower energy than the $^1A_{1g} \rightarrow {}^1A_{2g}$.[13] This pattern

would be reproduced in $trans$-[Co(l-pn)$_2$Cl$_2$]$^+$, whose lower energy transition ($^1A_{1g} \rightarrow {}^1E_g$) has a positive Cotton effect.[14] This has to be correlated with the negative octant sign of the most stable form of this complex. It will be from such correlations as these within various symmetry groups that an Octant Rule for metal complexes will emerge.

The complexes, d-cis α[Co trien Cl$_2$]$^+$,[15] d-cis β[Co trien Cl$_2$]$^+$,[15] and l_{546}-[Co EDTA]$^-$,[16,17] have been assigned the absolute configurations IX, X, and XI, respectively, on the basis of comparisons of the signs of the Cotton effects for these compounds with those for complexes whose configurations had been assigned previously. These conclusions were supported by diastereoisomer solubility data. The three compounds were given the symbol D as their circular dichroism spectra were related back to that for D-[Co en$_3$]$^{3+}$. The octant signs of these three structures are also the same (positive) and according to our definition would be given the symbol, D. This consistency supports the introduction of the octant sign nomenclature as the "handedness" nomenclatures would have given the l_{546}-[Co EDTA]$^-$ complex a symbol opposite to that for the d-α and β[Co trien Cl$_2$]$^+$ complexes.

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