# Absolute Configurations of Octahedral Metal Complexes

## III. A Tentative Octant Rule for Cobalt(III) Complexes

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Correlations between the absolute configurations of cobalt(III)
complexes, as defined by their octant sign, and the signs of the Cotton
effects of the complexes' $d-d$ transitions are discussed. A tentative
octant rule is proposed for these complexes: if a cobalt(III) complex
of $D_3$, $D_2$, $C_2{}^a$, or $C_2{}^b$ symmetry has a $^1E$, $^1B_1$, $^1A$, or $^1B[^1B_1(D_2)]$ transi-
tion, respectively, with a negative Cotton effect, the complex will have
its absolute configuration defined by a negative octant sign.

An Octant Rule,[1] by which the absolute configuration of a cyclic carbonyl
compound is deducible from the sign of the Cotton effect of its $n \rightarrow \pi^*$
carbonyl transition has contributed greatly to the unravelling of various
stereochemical problems in organic chemistry.[2] As a preliminary to an attempt
to see if such an empirical rule could be found for the study of coordination
compounds, the present authors recently defined the absolute configurations
of complexes in terms of an octant sign.[3] Current theories of the origin of the
optical rotatory power of $d-d$ transitions of dissymmetric metal complexes,
whether based on the distortions of the donor atoms,[4,5] or their orbitals,[6,7]
or their charges,[4,8] from their regular octahedral positions or on the inter-
action of non-bonding $t_{2g}$ electrons with the chelate rings,[9] are not incompatible
with the idea that a relationship exists between the octant sign as defined
and the sign of the Cotton effects of the $d-d$ transitions.

Since circular dichroism (CD) spectra have been reported for a variety of
cobalt(III) complexes whose absolute configurations have been deduced from
X-ray analysis, stereospecificity, mechanisms of reaction or diastereoisomer
interrelationships and whose symmetries range from $D_3$ to $C_2$, it was thought
opportune to see if any correlation could be found between the octant signs
of the complexes and the signs of the Cotton effects for their $d-d$ transitions.

### DISCUSSION

An energy level diagram for low spin $d^6$ complexes possessing various
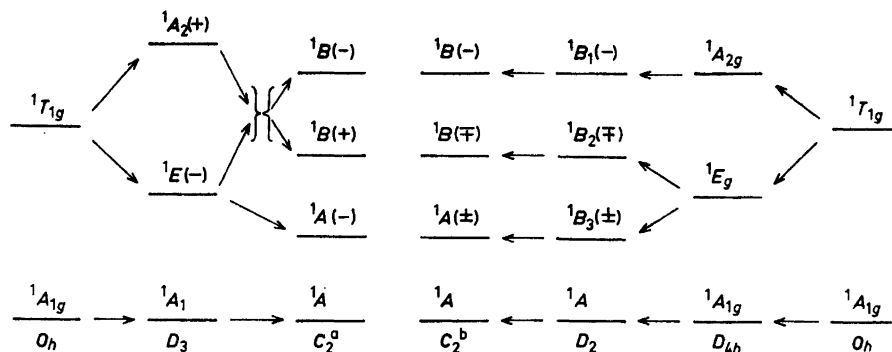symmetries is shown in Fig. 1. Only the ground state and the levels originating

*Fig. 1.* Energy level diagram for cobalt(III) complexes. Only the levels with $T_{1g}$ cubic parentage are considered. The order and size of the splittings shown are of no importance. The signs associated with the various levels indicate the signs of the Cotton effects for complexes with a negative octant sign. Details of the various transformations are given in the text. The $C_2{}^a$ column is for complexes whose octant signs are derived from the orientations of their chelate rings about the metal ion. $C_2{}^b$ refers to those complexes whose octant signs and dissymmetry are derived solely from the conformations of the chelate rings.

from the cubic $^1T_{1g}$ level are considered as they are responsible for most of the observable CD bands for the cobalt(III) complexes so far studied. The $(+)$ and $(-)$ signs in the diagram, which refer to the signs of the Cotton effects for the particular transitions for complexes with negative octant signs, were deduced from the spectral data given in the literature as discussed below.

*Complexes with* $D_3$ *symmetry.* The absolute configurations of a number of trigonal complexes are known: * $d$-[Co en$_3$]$^{3+}$, $D$,**,[10] and $l$-[Co($l$-pn)$_3$]$^{3+}$, $L$,[11] from X-ray analysis, and $l$-[Co($l$-chxn)$_3$]$^{3+}$, $L$,[12] from the stereospecificity of the ligand. Other trigonal complexes, such as $l$-[Co·ox$_3$]$^{3-}$, $D$,[13,14] and $l$-[Co·thiox$_3$]$^{3-}$, $L$[13] have been assigned absolute configurations by other methods, but these assignments are not as definite as those for the above complexes. In $D_3$ symmetry the cubic $T_{1g}$ level transforms into two components with the representations, $A_2$ and $E$. The transition of $E$ symmetry *** was identified for $D$-[Co en$_3$]$^{3+}$ as having a positive Cotton effect by a CD investigation of the uniaxial crystal, 2 $d$-[Co en$_3$]Cl$_3$·NaCl·6H$_2$O.[15] In the solution CD spectrum of $d$-[Co en$_3$]$^{3+}$, the positive CD band lies at a lower energy than a smaller negative band.[15] The sign of the splitting of the $T_1$ level is expected to be the same for $D$ or $L$-[Co en$_3$]$^{3+}$, $L$-[Co($l$-pn)$_3$]$^{3+}$, and $L$-[Co($l$-chxn)$_3$]$^{3+}$ because they are in either the $D(+, +, +)$ or $L(-, -, -)$ forms (lel[12]).

* Abbreviations for ligands used throughout this paper are: en-ethylenediamine, pn-propylenediamine, ox-oxalate, mal-malonate, chxn-*trans*-1,2-cyclohexanediamine, thiox-thiooxalate, EDTA-ethylenediaminetetraacetate, PDTA-propylenediaminetetraacetate, tart-tartrate, al-alaninate, leuc-leucinate, his-histidinate.

** The symbols, $D$ and $L$, are defined in terms of octant signs (see Ref. 3).

*** A transition is sometimes denoted in this text by the irreducible representation corresponding to the direct product of the irreducible representations of the ground and excited states.

For these three complexes the major CD band lies at the lower energy and has an opposite sign of Cotton effect to the minor band.[13,15,16] These bands have been assigned to the transition of $E$ and $A_2$ symmetries, respectively.[13] For $[Co \cdot ox_3]^{3-}$ and $[Co \cdot thiox_3]^{3-}$ the dominating CD band has also been assigned to the $A_1 \rightarrow E$ transition.[13] For the trigonal complexes discussed above the isomers with negative octant signs are found to possess transitions of $E$ and $A_2$ symmetries with negative and positive Cotton effects, respectively.

*Complexes with $D_2$ symmetry.* The *trans*-$[Co(l\text{-pn})_2X_2]^{n+}$ series provide examples of complexes with $D_2$ symmetry if the methyl groups are ignored. These complexes have an absolute configuration with a negative octant sign determined by the stereospecificity of the *l*-propylenediamine.[12] X-Ray analysis has confirmed this structure for the dichloro compound.[17] *Trans*-$[Co(l\text{-chxn})_2Cl_2]Cl$ also has a negative octant sign defined by the stereospecificity of the ligand.[18] Complexes of $D_2$ symmetry have three $B$ levels associated with the low energy $T_{1g}$ cubic band. The $B_1$ level which transforms as the $z$-coordinate, which is parallel to the $X-Co-X$ axis, has $A_{2g}$ tetragonal parentage. The transition to this level has been found to show a negative Cotton effect for the propylenediamine complexes with X equal to $Cl^-$, $Br^-$, $NO_2^-$, and $NCS^-$ and for the dichlorocyclohexanediamine complex.[18] The other two transitions originating from the $E_g$ tetragonal level have opposite signs for their Cotton effects with the positive component predominating. It is not known which of the two levels, $B_2$ (transforming as the $x$-coordinate) and $B_3$ (transforming as the $y$-coordinate passing through the chelate rings), corresponds to this major positive band.

*Complexes with $C_2$ symmetry.* The complexes with $C_2$ symmetry have been divided into two parts because the overall octant sign of a complex with this symmetry can be dependent on either (a) the relative positions of the chelate rings in the complex or (b) the conformation of the chelate ring (or rings).

(a) *Cis*-bis(bidentate) and related complexes. When the symmetry of a complex is lowered from $D_3$ to $C_2$ the $E$ level transforms in $C_2$ as $A$ and $B$ while the $A_2$ level transforms as $B$. As the two $B$ levels are expected, in general, to mix, the transition to the $A(C_2)$ level has been chosen for the comparison of the sign of the Cotton effect with the octant sign for complexes with $C_2$ symmetry. It has been proposed that the sign of the Cotton effect for this transition in complexes of the type *cis*-$[Co\ en_2L_2]^{n+}$ will be the same as that for the parent $E$ transition in a trigonal complex (say, $[Co\ en_3]^{3+}$) if the two complexes possess the same arrangement of chelate rings about corresponding $C_2$ axes.[19,20] Using this important assumption, Mason and coworkers have recently derived the absolute configuration of a number of *cis*-$[Co\ en_2L_2]^{n+}$ complexes from their CD spectra.[19,20] The *cis* complexes have also been interrelated by methods other than CD or ORD with excellent agreement between the various methods.[14] However, a method independent of CD or ORD has not yet been found to establish the absolute configuration of the *cis* complexes. If the above assumption is valid, then a complex of the type *cis*-$[Co(diamine)_2L_2]^{2+}$ with a negative octant sign will have a transition of $A$ symmetry with a negative Cotton effect.

The ligand, *l*-PDTA, is stereospecific [14] and its complex, $d_{546}$-$[Co(l\text{-PDTA})]^-$, has a negative octant sign. The absolute configuration of $d_{546}$-$[CoEDTA]^-$

has been related to that of the $l$-PDTA complex on the basis of diastereoisomer solubility data [14] supported by the marked similarity of their respective absorption and CD spectra [21] and ORD curves.[14] Thus, $d_{546}$-[CoEDTA]$^-$ also has a negative octant sign.

The configuration of $d_{546}$[Co en·mal$_2$]$^-$ has been related to that of $d_{546}$-[Co en·ox$_2$]$^-$ because of solubility and CD data.[22] These two complexes have a negative octant sign because the configuration of the latter has been related to that of $L$-[Co en$_3$]$^{3+}$.[14] The above EDTA and PDTA complexes have been related to the oxalato and malonato complexes by diastereoisomer solubility data. These four complexes have very similar crystal fields because if the chelate bridges are ignored the donor atoms and their relative positions are identical.

The CD spectrum of $d_{546}$-[Co en·mal$_2$]$^-$ showed three CD bands under the low energy absorption band, two being negative and one positive,* while only two bands were observable for the other complexes, due probably to the overlapping of the CD bands.[21,22] Douglas and his coworkers [22] has attempted to resolve the two observed CD bands for the EDTA and oxalato complexes into three "Gaussian" components.

For these four complexes, if the symmetry is approximated to $D_{4h}$, the fact that the field strength in the N,N,O,O $(xy)$ plane is greater than the $z$-coordinate field would mean that the $E$ level would lie lower in energy than the $A_2$ level. If the symmetry is now lowered to $C_2$ with the 2-fold axis bisecting the N—N edge, the $A_2$ level transforms as $B$ and the $E$ as $A$ and $B$. Thus the transition with $A$ symmetry will be either lowest or next to lowest in energy. Further, it is expected that the $A$ transition, which also originates from the $E(D_3)$ level, will have the same sign as one of the $B$ components, probably in most cases that $B$ level having essentially $E(D_3)$ as its parent state. As two negative and one positive CD bands are observed for $d_{546}$-[Co en·mal$_2$]$^-$,[22] the transition with $A$ symmetry must have a negative sign and, from above, would therefore lie lowest in energy. For $d_{546}$-[Co en·ox$_2$]$^-$ two negative bands are again observed [22] and, as for the malonato complex, the lowest energy negative band has been assigned to the transition with $A$ symmetry. This transition is the major CD band for both the oxalato and malanato complexes and it is assumed that it will also dominate the CD spectra for the other complexes. The lowest observed CD band for the EDTA and PDTA complexes is the major band [21,22] and has thus been assigned to the $A \rightarrow A$ transition. This assignment is in agreement with that of Douglas et al.[22] but is in contradiction to Gillard's assignment [21] of this transition to the negative higher energy band in the CD spectra of $l_{546}$-[CoEDTA]$^-$ and $l_{546}$-[Co($l$-PDTA)]$^-$, both of which have positive octant signs.

Thus the $d_{546}$-isomers of [CoEDTA]$^-$, [Co($l$-PDTA)]$^-$, [Co en·mal$_2$]$^-$, and [Co en·ox$_2$]$^-$, which have had their configurations related by diastereoisomer solubility data and which all have a negative octant sign, have been found to possess an $A \rightarrow A$ transition with a negative Cotton effect. This is in agree-

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* The compounds studied by Douglas and coworkers [22] were in fact $l_{546}$-[Co en.mal$_2$]$^-$, $d_{546}$-[Co en.ox$_2$]$^-$, and $l_{546}$-[CoEDTA]$^-$, but for simplicity in the present discussion the $d$ isomers with negative octant signs are considered for the three complexes.

ment with the similar correlation for the cis-[Co $en_2L_2]^{n+}$ complexes, which also have $C_2$ symmetry. If the chirality of the complexes had been the deciding factor, as is usually proposed, the above EDTA and l-PDTA complexes would have been related to the enantiomers of the other complexes.

(b) Mono(bidentate) complexes. The CD spectra of a number of complexes with the general formula, trans*-[Co(l-pn)(NH$_3$)$_2$X$_2$*]$^{n+}$ have recently been reported in the literature.[19] The absolute configurations of these complexes are known because of the stereospecificity of the ligand,[12] and the complexes have a negative octant sign.[18] It was found that these complexes have a transition, $A \rightarrow B$, corresponding to the $A \rightarrow B_1$ transition * for $D_2$ symmetrical complexes (and to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition) with a negative Cotton effect.[18]

The CD spectra of [Co(NH$_3$)$_4$($S,S$-tart)]$^{2+}$, [Co(NH$_3$)$_4$($R$-al)]$^{2+}$, [Co(NH$_3$)$_4$($S$-leuc)]$^{2+}$, and [Co(NH$_3$)$_4$($S$-his)]$^{2+}$ have been published.[23] For these complexes the absolute configurations are also determined by the stereospecific effect of the ligands. The alaninato complex has a negative octant sign,[3] opposite to that of the other complexes. If the symmetry of these complexes is approximated to $D_{4h}$, the fact that the field strength in the plane containing the chelate donor atoms and two of the ammonia nitrogen atoms ($xy$ plane) is less than the $z$-coordinate field means that the $A_{2g}$ level lies at lower energy than the $E_g$ level. The CD band of lowest energy has been thus assigned to the transition with $A_{1g} \rightarrow A_{2g}$ tetragonal parentage and is found to have a negative Cotton effect for the alaninato complex and a positive Cotton effect for the others. This is consistent with the correlation for the propylenediamine complexes.

For the trans*-[Co(l-pn)(NH$_3$)$_2$X$_2$*]$^{n+}$ complexes it is known that $A \rightarrow A(C_2)$ and $A \rightarrow B(C_2)[B_2(D_2)]$ have opposite signs for their Cotton effects. Unfortunately, at present it is not known what is the sign of the transition with A symmetry. It will be of great interest to see if this has the same sign as that for complexes of $C_2^a$ symmetry with the same octant sign.

An Octant Rule. From the above empirical correlations it is proposed that Fig. 1 be the basis of an Octant Rule for cobalt(III) complexes. Complexes of other $d^6$ metal ions are expected to also obey this rule. The rule says that, if a complex of $D_3$, $D_2$, $C_2^a$, or $C_2^b$ symmetry has a $^1E$, $^1B_1$, $^1A$, or $^1B[B_1(D_2)]$ transition, respectively, with a negative Cotton effect, the complex will have its absolute configuration defined by a negative octant sign. Such a "rule" must be held as tentative because of its limited basis. However, it will serve as a working hypothesis against which all future examples can be tested and, as such, will prove useful.

* The absorption and CD spectra of the mono(l-propylenediamine) and the corresponding trans-bis(l-propylenediamine) complexes are so similar that it is possible to characterise the transitions by their $D_2$ parent representations.

## REFERENCES

1. Moffitt, W., Woodward, R. B., Moscowitz, A., Klyne, W. and Djerassi, C. *J. Am. Chem. Soc.* **83** (1961) 4013.
2. Djerassi, C. *Optical rotatory dispersion*, McGraw-Hill, New York 1960, pp. 178—190.
3. Hawkins, C. J. and Larsen, E. *Acta Chem. Scand.* **19** (1965) 185.
4. Piper, T. S. and Karipides, A. G. *Mol. Phys.* **5** (1962) 475.
5. Karipides, A. G. and Piper, T. S. *J. Chem. Phys.* **40** (1964) 674.
6. Liehr, A. D. *J. Phys. Chem.* **68** (1964) 665.
7. Liehr, A. D. *J. Phys. Chem.* **68** (1964) 3629.
8. Shinada, M. *J. Phys. Soc. Japan* **19** (1964) 1607.
9. Mason, S. F. and Norman, B. J. *Chem. Commun.* **1965** 48.
10. Saito, Y., Nakatsu, K., Shiro, M. and Kuroya, H. *Bull. Chem. Soc. Japan* **30** (1957) 795.
11. Saito, Y., Iwasaki, H. and Ota, H. *Bull. Chem. Soc. Japan* **36** (1963) 1543.
12. Corey, E. J. and Bailar, J. C. *J. Am. Chem. Soc.* **81** (1959) 2620.
13. McCaffery, A. J., Mason, S. F. and Ballard, R. E. *J. Chem. Soc.* **1965** 2883.
14. MacDermott, T. E. and Sargeson, A. M. *Australian J. Chem.* **16** (1963) 334.
15. McCaffery, A. J. and Mason, S. F. *Mol. Phys.* **6** (1963) 359.
16. Piper, T. S. and Karipides, A. G. *J. Am. Chem. Soc.* **86** (1964) 5039.
17. Saito, Y. and Iwasaki, H. *Bull. Chem. Soc. Japan* **35** (1962) 1131.
18. Hawkins, C. J., Larsen, E. and Olsen, I. *Acta Chem. Scand.* **19** (1965) 1915.
19. McCaffery, A. J., Mason, S. F. and Norman, B. J. *Chem. Commun.* **1965** 132.
20. McCaffery, A. J., Mason, S. F. and Norman, B. J. *J. Chem. Soc.* **1965** 5094.
21. Gillard, R. D. *Spectrochim. Acta* **20** (1964) 1431.
22. Douglas, B. E., Haines, R. A. and Brushmiller, J. G. *Inorg. Chem.* **2** (1963) 1194.
23. Dunlop, J. H. and Gillard, R. D. *J. Chem. Soc.* **1964** 2822.