It is possible that the following types of couplings also have the signs indicated.

$$\underset{+}{\text{H—C—N—P}} \qquad \underset{+}{\text{H—C—O—P}}$$

The available data concerning the signs and magnitude of the H–C–P coupling have caused some confusion. The changes of this coupling seem to be well described by the following two rules: (1) in the H–C–P fragment the geminal coupling becomes either less positive or more negative as the s character of the phosphorus atom bonding orbitals to carbon increases; (2) in the H–C–P fragment the geminal coupling becomes either more positive or less negative as the s character of the carbon atom bonding orbital to phosphorus increases.

We take the trends described by these rules as evidence that these couplings involving phosphorus and protons result primarily from at least two large Fermi contact contributions which nearly cancel. Such a situation appears to prevail also in the cases of the H–C–H and ^{13}C–C–^{1}H couplings. The proton–phosphorus couplings between nuclei separated by three bonds appear to be positive, and the multiplicity of coupling contributions existing for the geminal coupling do not seem evident for these vicinal couplings. All the results discussed here are consistent with the ^{31}P–^{1}H coupling being positive, and the changes of this coupling with phosphorus orbital s character are qualitatively in the same absolute direction as those observed for changes of the ^{13}C–^{1}H coupling with carbon orbital s character changes.

A General Method for Relating the Absolute Configurations of Octahedral Chelate Complexes[1]

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Abstract: A ring-pairing method is proposed for relating the absolute configurations of octahedral chelate complexes of different symmetries. The method utilizes pairs of chelate rings as they occur in *cis*-$[Co(en)_2X_2]^{n+}$. The method is demonstrated for several complexes, and it is shown to be consistent with spectroscopic (circular dichroism) data.

Confusion has arisen in the designation of the absolute configurations of optically active chelate complexes of different symmetries, *e.g.*, $[Co(en)_3]^{3+}$ and $[Co(EDTA)]^-$, because of the lack of a common basis for relating their chiralities. Absolute configurations of cobalt(III) chelate complexes have been related through optical rotatory dispersion[2] (ORD) and circular dichroism (CD) spectra[3-6] to optically active $[Co(en)_3]^{3+}$ for which the absolute configuation is known.[7] It has been suggested that the most intense CD band (or Cotton effect curve) found in the $A_{1g} \rightarrow T_{1g}$ region (16,000 to 21,000 cm^{-1} for Co(III) complexes)[8] of a given enantiomorph should have the same sign as the dominant E_a (T_{1g} parentage) transition found for the configurationally related enantiomorph of $[Co(en)_3]^{3+}$.[6] The dominant CD band has been assigned E_a parentage even when an inversion of states occurs. Such inversions resulting from changes in the crystal field strengths of the ligands sometimes are observable in CD spectra even though obscured in ORD spectra.[9]

Reference Axis

The configurations of many chelate complexes can be related to the helix described by the chelate ligands of $[Co(en)_3]^{3+}$ about the major axis, C_3. This so-called chirality is left-handed for $(+)_{589}$-$[Co(en)_3]^{3+}$, and the isomer is designated Λ (Δ is used for the mirror image isomer) using Piper's convention,[10] Figure 1. Complexes with $\mathbf{C}_3$ symmetry are much less common than those with $\mathbf{C}_2$ symmetry, *e.g.*, *cis*-$[Co(en)_2X_2]^{n+}$. The configuration of such a $\mathbf{C}_2$ complex can be designated using the pseudo-C_3 axis (X's connected by imaginary line) to relate it to $[Co(en)_3]^{3+}$, or the helix can be designated using the C_2 axis. Changing the reference axis from C_3 to C_2 changes the handedness of the helix described by the chelate rings. For example, the enantiomorph of $[Co(en)_3]^{3+}$ shown in Figure 1 could be designated $\Lambda(C_3)$ or $\Delta(C_2)$, depending on whether the reference axis is C_3 or C_2.[6,11]

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(1) This work was supported by a research grant (GM10829-08) from the Division of General Medical Studies, Public Health Service.

(2) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(3) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

(4) R. A. Haines and B. E. Douglas, *ibid.*, **4**, 452 (1965), and other papers in this series.

(5) A. M. Sargeson and G. H. Searle, *ibid.*, **4**, 45 (1965).

(6) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(7) Y. Saito, K. Nakatsu, M. Skiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

(8) T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 291.

(9) K. Garbett and R. D. Gillard, *Chem. Commun.*, 76 (1965).

(10) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(11) Before his untimely death, Piper suggested using notation such as Δ_2 or $\Delta(C_2)$ to remove the ambiguity regarding the choice of axis when it is not the major axis. The IUPAC nomenclature commission has yet to make a recommendation concerning the symbols to be used to describe the chirality, *i.e.*, Δ and Λ or P and M. Any notation system adopted can be used for the designation of configurations by the method proposed here.

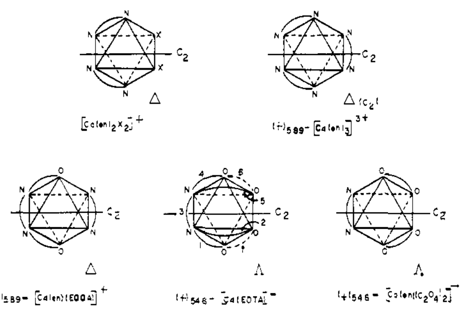

Figure 1. Absolute configurations of some cobalt(III) complexes related to $[Co(en)_3]^{3+}$

Because this system of two chelate rings is common to $\mathbf{C}_2$, $\mathbf{C}_3$, and $\mathbf{D}_3$ complexes and to others for which the optical activity arises from the spiral pattern of the chelate rings, reference to the C_2 or pseudo-C_2 axis provides a more common basis for relating configuration of chelate complexes. In complexes containing multidentate ligands the chelate rings can be easily paired to define the chirality about a pseudo-C_2 axis as will be shown, whereas to use a C_3 axis it is often necessary to insert an imaginary ring to define the chirality. Consequently the Λ and Δ designations used in this paper are made with reference to the C_2 or pseudo-C_2 axes, and it is suggested that this convention be adopted in the future.

The Ring-Pairing Method

The chirality of the *cis*-$[Co(en)_2X_2]^{n+}$ complexes can be easily related to $[Co(en)_3]^{3+}$ since there are only two chelate rings and these coincide with rings of $[Co(en)_3]^{3+}$, Figure 1. On the other hand the chirality of $[Co(EDTA)]^-$ is not so easily defined.

We have recently resolved the two geometric isomers of $[Co(en)(EDDA)]^+$ [EDDA = ethylenediamine-N,N′-diacetate ion) and related complexes.[12] These complexes are of particular interest with respect to the assignment of absolute configurations since they form a new link between the absolute configurations of $[Co(EDTA)]^-$ and $[Co(en)_3]^{3+}$. Comparison of *trans*-$[Co(en)(EDDA)]^+$ to $[Co(EDTA)]^-$, Figure 1, shows that the complexes can be related through the EDDA "backbone" which is common to both, and these two isomers might be expected to have the same chirality, defined by the two sets of acetate rings common to both (1 and 4 of $[Co(EDTA)]^-$). In their study of the reaction of active $[Co(EDTA)]^-$ with anhydrous ethylenediamine to give $[Co(en)_3]^{3+}$, Busch and Cooke[13] also chose to relate the absolute configurations of these two complexes through acetate rings 1 and 4 of $[Co(EDTA)]^-$, Figure 1.

The absolute configuration of active $[Co(EDTA)]^-$ has also been determined by comparison of its ORD curve to that of the analogous $(+)_{546}$-$[Co(PDTA]^-$ [PDTA = 1,2-propylenediaminetetraacetate ion) whose absolute configuration is known from conformational analysis.[2] Experimental evidence strongly supports the supposition that the $(+)_{546}$ isomers of $[Co(EDTA)]^-$ and $[Co(en)(AA)_2]^-$ (AA = oxalate and malonate), which in turn are related through CD spectra to $(-)_{589}$-$[Co(en)_3]^{3+}$) are configurationally related.[14] Thus, $[Co(EDTA)]^-$ should have the chirality shown in Figure 1 using imaginary rings 6 and 7 with 3, with the opposite label to the one suggested by Busch and Cooke.[13] (Note that these earlier discussions referred the chirality of these complexes to the C_3 or pseudo-C_3 axis.) It should be stressed that all the papers concerning the absolute configuration of $[Co(EDTA)]^-$ agree on the same structure for a particular isomer. They differ only in the designation used.

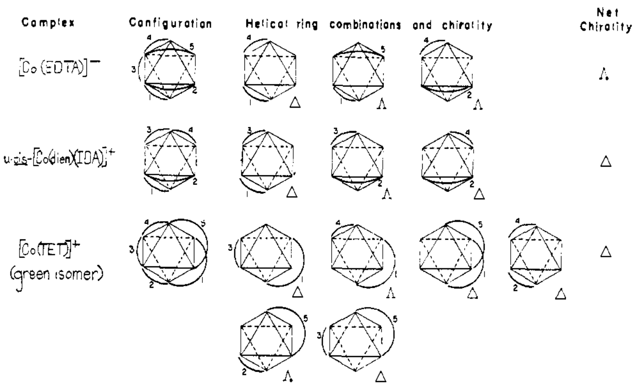

Figure 2. Determination of chirality of some complexes by examining helical ring combinations.

Although the choice of chirality for $[Co(EDTA)]^-$ would appear somewhat arbitrary, a method for assigning the chirality to this complex and to the many related cobalt(III) chelate complexes is needed to avoid further confusion. The method should be unambiguous, easily applied, inclusive, and consistent with the ORD and CD spectral properties of the complex to which chirality is closely related.

Such a method is suggested as follows. For a given enantiomorph of a complex all possible two-ring (bidentate chelate rings) combinations which form a helical set are written down, and the chirality (Δ or Λ related to that about C_2 for *cis*-$[Co(en)_2X_2]^{n+}$) of each set is determined. The dominant or net chirality and consequent optical activity of the complex should be governed by the chirality which occurs the greatest number of times. This process is illustrated for $[Co(EDTA)]^-$ in Figure 2. The ring pairs are shown with respect to the configuration being examined. The chirality is then determined for each pair (treating the rings as equivalent) using the C_2 axis defined by the pair. Sets such as adjacent rings 1 and 2 or 3 and 5 and *trans* rings in the same plane such as 2 and 4 are not counted. Such pairs together do not define a spiral pattern. The chirality suggested by this method for $[Co(EDTA)]^-$ is in agreement with that suggested by CD[14] and ORD[2] spectra.

The contribution of the helical sets to the optical activity is considered to be more important than that from ring conformations. Attempts have been made to relate the CD of a complex to the conformation of the rings for both complexes with a helical distribution of chelate rings[15] and complexes lacking such a distri-

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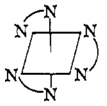
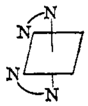
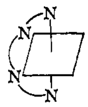
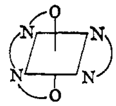
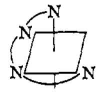
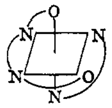
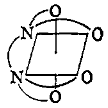
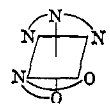
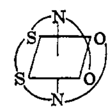
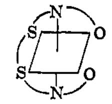
[12] J. I. Legg, B. E. Douglas, and D. W. Cooke, presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[13] D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, 23, 145 (1961).

[14] B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, 2, 1194 (1963).

[15] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

Table I. Absolute Configurations Resulting from an Examination of Possible Helical Ring Combinations

Complex	Configuration	Designation (net chirality)	Sign of CD component related to E_a
$(+)_{589}$-$[Co(en)_3]^{3+}$		$\Delta(C_2)$	$+(E_a)^{6}$
$(+)_{589}$-*cis*$[Co(en)_2(H_2O)_2]^+$		Δ	$+(A_2)^{6}$
$(+)_{589}$-α-$[Co(trien)Cl_2]^+$		Δ	$+(A_2)^{5}$
$(+)_{589}$-*trans*-$[Co(en)(EDDA)]^+$		Δ	$+(A_2)^{10}$
$(+)_{546}$-β-$[Co(trien)Cl_2]^+$		Λ	$-^{5}$
cis-$[Co(en)(EDDA)]^{+\ 10}$		Λ	$-^{a,c}$
$(+)_{546}$-$[Co(EDTA)]^-$		Λ	$-(A_2)^{12}$
u-*cis*-$[Co(dien)(IDA)]^{+\ 14,b}$		Δ	$+^{a}$
$[Co(TET)]^{+\ 2}$ Green isomer		Δ	$+^{a}$
Brown isomer		Λ	$-^{a}$

[a] Predicted sign. [b] dien = diethylenetriamine, IDA = iminodiacetic acid. [c] This assignment has been confirmed by the nmr study of the complex where EDDA has been replaced by the analogous ligand *l*-ethylenediamine-N,N′-di-α-propionate, which is of known absolute configuration.[18]

bution.[16] It has been demonstrated, though, that the relative conformations of the rings need not be considered to explain changes in the CD spectra but that the presence of optically active ligands in these complexes can account for these changes in the spectra.[17]

The absolute configuration of *trans*-$[Co(en)(EDDA)]^+$ has been established independently by the preparation and nmr study of the complex where EDDA has been replaced by the analogous ligand *l*-ethylenediamine-N,N′-di-α-propionate which is of known absolute configuration.[18] This confirms the assignment made by relating the CD spectra of *trans*-$[Co(en)(EDDA)]^+$ to $[Co(EDTA)]^-$.[12] The designations of the configurations of the *trans*-$[Co(en)(EDDA)]^+$ isomers by using the ring-pairing method are consistent with the assignments made from CD spectra and nmr studies.

Figure 2 also illustrates this method as applied to bis-tridentate chelate complexes which have recently been prepared.[19] The change from α-$[Co(trien)(acido)_2]^+$ (trien = triethylenetetramine) to the β isomer has been likened to an inversion of configuration.[5] Such an observation is supported if the ring combinations are examined, and the results are summarized in Table I. A more complex example could be the conversion of the green isomer of $[Co(TET)]^+$ (TET = 1,10-bis(salicylideneamino)-4,7-dithiadecane, a hexadentate chelate) to the brown isomer which ORD data suggest as being comparable to an inversion of configuration.[2] This observation is also supported if the ring combinations are worked out (Figure 2 and Table I).

The results of applying the method of ring pairing to a series of complexes are summarized in Table I along with the sign expected or found for the CD or ORD component which may be related to the dominant low energy E_a transition found for $\Delta(C_2)$-$(+)_{589}$-$[Co(en)_3]^{3+}$. The results are consistent with the CD or ORD data available.

The results obtained by this method are the same as those obtained using an octant sign method suggested by Hawkins and Larsen.[20] The latter method is somewhat more difficult to apply, involving a number of reorientations of the isomer coincident with the number of chelate rings present, and does not enable an easy visualization of the chirality of the complex.

Finally, it can be seen that the ring-pairing method for relating absolute configurations is applicable to any series of octahedral metal chelate complexes containing two or more chelate rings which can be related to *cis*-$[Co(en)_2X_2]^{n+}$, although the interpretation of the related electronic properties will depend on the electronic configuration of the metal ion.

Acknowledgments. We thank D. W. Cooke and T. E. MacDermott for helpful comments.

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(16) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

(17) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965).

(18) L. Schoenberg, D. W. Cooke, and C. F. Liu, private communication; presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(19) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

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