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COTTON EFFECTS AND CONFIGURATION IN ACIDOPENTAMMINE-COBALT (III) COMPLEXES OF ASYMMETRIC ACIDS

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Abstract—A method for comparing the optical configurations of carboxylic acids is outlined, using their complexes with the pentamminecobalt (III) residue. The spectroscopic basis of this method is outlined, and other methods for relating configurations using metal complexes are discussed from the spectroscopic viewpoint.

RULES are available for deducing the optical configurations of several classes of asymmetric molecule directly from the measured ORD or CD spectra. Such rules were, at first, usually empirical, but many have subsequently been shown to have a sound spectroscopic basis. For many important classes of compound, unfortunately, the transitions giving rise to optical activity are of such high energy that direct observation of Cotton effects for the native molecule is not possible, or at least experimentally difficult with currently available instruments, which do not operate in the vacuum UV region. A case in point is that of the carboxylic acids, where only recently has one extremum of the Cotton effect in dispersion been found. The present work refers to a method of relating configurations of acids using their cobalt (III) complexes; these show Cotton effects in the easily accessible visible region when they contain an asymmetric carboxylic acid.

Several applications of the Cotton effects of metal complexes of asymmetric organic molecules have been made. Karrer[1] and Pfeiffer[2] in 1937 independently used the signs of Cotton effects in copper (II) complexes of optically active α-amino acids to deduce relative configurations of the ligands. A number of similar complexes of copper (II) with amino acids have since been studied by ORD and by CD.[3] Recently, the use of the so-called vicinal effect (the Cotton effects induced in the visible absorption bands of a transition metal ion in its complexes with an asymmetric ligand) was extended to other systems. These were complexes[4] of α-amino acids and α-hydroxy acids with the tetrammine cobalt (III) fragment, $[Co(NH_3)_4(\alpha\text{-}RCH\cdot(NH_2)COO)]^{2+}$, complexes[5] of 1,2-diamines with nickel (II) and cobalt (III), and complexes[6] of 1,2-amino-ols with copper (II). Several other types of organic molecules such as dithiocarbamates,[7] have since been employed as ligands, and the Cotton effects induced

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in the electronic absorption bands of the metal ion used to relate configurations. To date, all results refer to chelating ligands.

We now report some results on non-chelated ligands, bonded to cobalt (III) through the carboxylate group, of the type $R{\cdot}CHX{\cdot}CO_2H$. Complexes of cobalt (III) are particularly suitable for the purpose, since they are kinetically rather inert to substitution, and their spectroscopy is well understood.

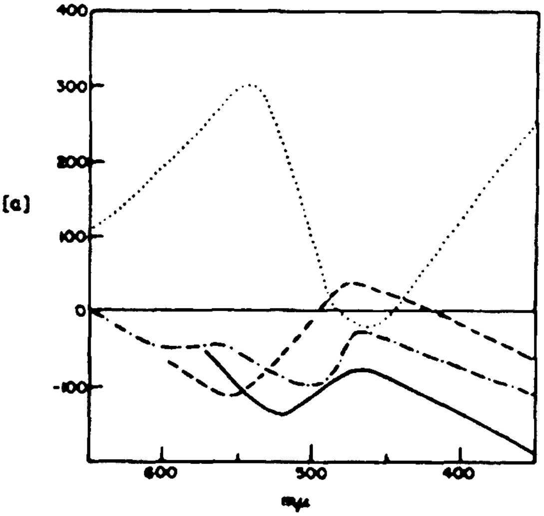

FIG. 1. ORD spectra of complexes $[Co(NH_3)_5(A)]^{n+}$.
— A = L(+)-lactate
······ A = L(−)-malate
. . . A = D(+)-tartrate. (cf. Ref. 17)
- . - . - . A = L(+)-alaninate (cf. Ref. 8)

When a carboxylic acid is allowed to react under controlled conditions (ca. 40°, pH ca. 5) with the readily available carbonatopentamminecobalt (III) ion, the product is the carboxylatopentamminecobalt (III) ion, i.e.

$$RCO_2H + (CoNH_3)_5(OCO_2)]^+ \rightarrow [Co(NH_3)_5(O{\cdot}CO{\cdot}R)]^{2+} + OH^- + CO_2$$

To obtain the stated product where the acid is a potential chelator, the temperature must be kept below 45°, else ammonia is lost, and the chelated tetrammine complex formed. When R is such that the acid is asymmetric, the visible absorption bands of the product now have Cotton effects associated with them. For example, the rotatory dispersion curve of {(+) lactato} pentamminecobalt (III) nitrate is given in the Figure.

The signs of the Cotton effects induced in the visible absorption bands of the cobalt ion reflect the chirality about the carboxyl group, that is, the optical configuration of the acid. The Figure shows the rotatory dispersion curves of the complexes of L(+)-lactate, L(+)-malate, and D(+)-tartrate. The complex ion containing L(+)-alaninate, $[(NH_3)_5Co(OOC{\cdot}CH{\cdot}CH_3(NH_2)]^{2+}$, bonded through the carboxylate, was known[8] from earlier work, and its Cotton effects are also shown in the figure. Clearly, the configurational relationships between the acids are reflected in the sign of the Cotton effect in rotatory dispersion for the longer wavelength absorption band of the derived cobalt (III) complex. An empirical rule may be stated:

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[8] J. Fujita, T. Yasui and Y. Shimura, *Bull. Chem. Soc., Japan* **38**, 654 (1965).

if the dominant Cotton effect for the longer wavelength spin-allowed transition of an acido-pentammine cobalt (III) ion (formed from a carboxylic acid with an asymmetric carbon atom in the α-position) is negative, then the acid has the L-configuration, related to that of L(+)-lactic acid.

Similar complexes may readily be made with carboxylic acids where the asymmetric centre is β, γ. . . to the carboxyl group, but it is rather doubtful whether the induced Cotton effects in the resulting cobalt (III) complex would be large enough to be useful in correlating configurations.

The spectroscopic basis of the method is as follows. In a perfectly regular octahedral complex of cobalt (III), belonging to the point group O_h, the longest wavelength spin-allowed transition corresponds to ${}^1T_{1g} \leftarrow {}^1A_{1g}$, which is magnetic-dipole-allowed and hence contributes strongly to optical activity. (The band in the present complexes at ca. 350 mμ is descended from ${}^1T_{2g} \leftarrow {}^1A_{1g}$ of O_h, which is magnetic-dipole-forbidden, and therefore makes little contribution to optical activity, as shown in the Figure). In the six-coordinated complexes of lower symmetry considered here, $[Co(NH_3)_5(OOCR)]^{2+}$, the local microsymmetry at the cobalt atom is C_{4v}; the threefold degeneracy is removed, giving an A and an E component. Now, in all the carboxylate complexes studied, the splitting will be similar, and like that in the acetatopentamminecobalt (III) ion, so that the transitions being studied are of the same type and in the same order of energies in all the complexes, irrespective of the substituents on the asymmetric carbon atom. Thus, although the method is designed as an empirical means of studying configurations, it has a firm spectroscopic foundation.

From the spectroscopic standpoint, the use of complexes of the type discussed here is more satisfactory than those earlier employed, for two distinct reasons. In the case[2–5] of the kinetically labile complexes of copper (II), their stereochemistry in solution is uncertain, and may vary within such a series as the apparently similar bis-α-amino-acid complexes. A stereochemical variation probably causes the marked divergence[3,9] of the Cotton effects of the L-proline complex from those of the L-alanine and L-valine complexes. Further, the ordering of energy levels in such complexes is not yet settled,[10] so that the spectroscopic basis of comparisons using copper (II) complexes is not entirely rigorous, though the method is empirically useful. In the series of chelated complexes we discussed earlier,[6] $[Co(NH_3)_4RCH(X)COO]^{2+}$, where X = OH or NH_2, the point groups of the complexes (though both formally C_1) may be regarded in terms of local microsymmetry as C_{2v} (for X = OH) and C_{4v} (for X = NH_2). The first order splittings of the threefold degenerate level of the parent octahedron are different (${}^1T_{1g}$ giving ${}^1A + {}^1E$ for C_{4v}, but ${}^1A + {}^1B + {}^1B$ for C_{2v}). Thus, while comparisons within the series (i.e. for X = OH, *or* for X = NH_2) were satisfactory, inter-relations between compounds where X = OH and X = NH_2 were not possible, since the Cotton effects observed did not arise from analogous transitions. This is a distinct advantage of the present method using non-chelated compounds, that, irrespective of the substituents X, Y, and Z in (X, Y, Z) C·CO_2H, the transitions in $[Co(NH_3)_5$ (X, Y, Z) C·COO] are directly comparable. One point for which we have, at present, no evidence, is the possible effect of ion-pairing in these systems, which could conceivably modify the nature of the Cotton effect obtained.

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[10] C. Dijkgraaf., *Spectrochim. Acta* **20**, 1227 (1964).

The present observation of Cotton effects in these non-chelated compounds raises a general point. It has been said[11] that chelate rings must be present before *d-d* absorption bands will show Cotton effects. This is not so. It is quite true, as was pointed out[12] some time ago, that the size of a Cotton effect for a *d–d* transition of a chelated metal complex is a function of the number of chelate rings present, but any chromophore in an asymmetric environment will show Cotton effects—the difficulty arises in the detection of small effects, as pointed out recently[13] for the case of L-phenylalanine.

EXPERIMENTAL

Microanalyses: Microanalytical Laboratory, Sheffield University. Electronic spectra: a Unicam SP 700 spectrophotometer, and ORD spectra: Bendix N.P.L. "Polarmatic" spectropolarimeter.

Preparations of complexes involved adding two equivs of the carboxylic acid to one equiv of carbonatopentamminecobalt (III) nitrate in water. The sols were evaporated to small volume at temps not exceeding 45°. With the exception of the malato-complex, products were obtained as crystalline solids, and characterized by their analyses and electronic spectra. Carboxylate-pentammine cobalt (III) complexes aquate rather readily in aqueous soln (the rate of aquation of several C-substituted acetato-pentammine cobalt (III) ions is related[14] to the base strength of the coordinated ligand.) The observed Cotton effects confirm that the conjugate base of the acids is coordinated to the metal. Refs to previous preparations are in Table 1.

TABLE 1. ELECTRONIC SPECTRA OF CARBOXYLATO-PENTAMMINECOBALT (III) IONS

Complex[a]	*b*	λ	ϵ	λ	ϵ
Acetate	16	504	66	352	50
(+)-Lactate	*c*	501	55	350	47
(−)-Malate	*c*	501	—	349	—
(+)-Tartrate	17	505	—	—	—
(+)-Alaninate	8	500	68	350	54

[a] The anion in $[Co(NH_3)_5(carboxylate)]^{2+}$; [b], Ref. to prep.
[c] This work.

{(+) *Lactato*} *pentamminecobalt* (III) *nitrate*. An aqueous soln containing two equivs of L(+)-lactic acid, and one equiv of carbonatopentammine cobalt (III) nitrate was evaporated at 45° when red crystals of the desired product were obtained, which were washed with alcohol and ether. (Found; C, 10·3; H, 5·5; N, 28·8; calc. for $C_3H_{20}CoN_7O_9$: C, 10·1; H, 5·7; N, 28·1%.) The IR spectrum showed bands (due to co-ordinated carboxylate) at 1608 and 1325 cm^{-1} (in good agreement with values[15] for the analogous acetato-complex).

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