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The Cotton Effect in Coordination Compounds Containing Monodentate Ligands

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In an interesting paper published in 1964, Larsen and Olsen[1] reported the absence of a Cotton effect[2] in complexes containing optically active ligands which are monodentate through nitrogen (*d*-2-aminobutane) and oxygen (*d*-α-methyl butyrate) to copper(II) and cobalt(III). These authors proposed the possibility that an induced Cotton effect in a d–d transition of a transition metal complex containing an optically active ligand will be of measurable magnitude only if the ligand is a chelate. Hawkins[3] mentions this proposal in his study of the coordination of ethambutol (N,N′-bis(2-butan-1-ol)ethylenediamine) and its derivatives to copper(II) and nickel(II) and concludes on the basis of circular dichroism spectra that at least one and probably both of the hydroxyl groups coordinate to the metal ion.

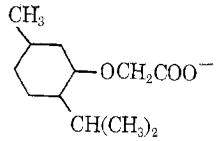
Djerassi and Geller[4] demonstrated by optical rotatory dispersion measurements that aliphatic carbonyl compounds show Cotton effects in the carbonyl-absorption region even though the nearest asymmetric center of the molecule may be several carbon atoms away from the chromophore, and there is no indication that any type of chelate or other ring formation is required for this effect to occur. In 1964, Bhatnagar and Kirschner[5] reported Cotton effects for *d*-tartrate complexes of cobalt(III) containing ammonia ($[Co(NH_3)_4(d\text{-tart})]^+$ and $[Co(NH_3)_5(d\text{-tart})]^+$) in which the tartrate is bidentate in one case and monodentate in the other, based upon optical rotatory dispersion studies of these complexes. Further, these authors indicated that the rotatory strength of the Cotton effect is markedly greater when the optically active ligand behaves as a chelate than when it is monodentate.

Discussion

This latter observation raised the question of whether ring formation is absolutely essential for the measurable appearance of the Cotton effect in these cases. The possibility exists that for some complexes containing monodentate optically active ligands, the observation of a Cotton effect may not be possible because of the weakness of the effect, but that in other similar cases the effect, though weak, may be observable. Since the ligands used by Larsen and Olsen contained one asymmetric center and those used by other workers sometimes contained two or more such centers, it is appropriate to determine whether or not the Cotton effect is observable for complexes containing monodentate ligands with one and with more than one asymmetric center.

In 1965 Fujita, Yasui, and Shimura[6] reported the appearance of a Cotton effect, utilizing both optical rotatory dispersion and circular dichroism techniques, for $[Co(NH_3)_5(l\text{-phalaH})](ClO_4)_3 \cdot H_2O$ and for $[Co(NH_3)_5(l\text{-}\alpha\text{-alaH})](ClO_4)_3 \cdot 2H_2O$ (*l*-phalaH = *l*-phenylalanine and *l*-α-alaH = *l*-α-alanine) in the d–d transition region. These authors present evidence for their proposal that coordination is through the carboxyl oxygen of the free amino acid rather than through the nitrogen. They also prepared complexes in which the same ligands behave as bidentate chelating agents toward the same metal ion, and they studied the optical rotatory dispersion, circular dichroism, and absorptions of these compounds as well.

In the present work, a cobalt(III) complex has been prepared which contains an optically active ligand having three asymmetric centers which coordinates through a carboxylate oxygen of the anionic form of the ligand. The complex synthesized is $[Co(NH_3)_5(l\text{-menac})](NO_3)_2$ (I), where *l*-menac is the *l*-menthoxyacetate anion (II). It should be emphasized that the ligand in this case is monodentate and is inside the coordination sphere of the complex ion. In an interesting study, Mason and Norman[7] point out that Cotton effect phenomena in "outer-sphere" coordination may be observable only if the ligand can be polydentate.



II

Results

The optical rotatory dispersion, circular dichroism, and absorption spectrum of the complex (I) in water are given in Figure 1, along with the optical rotatory dispersion of the sodium salt of the ligand (II) in 50% ethanol–water, in the visible region. Although the optical rotatory dispersion shows only a slight shoulder in the region of interest, the circular dichroism curve clearly indicates the presence of a distinct, positive Cotton effect in the absorption region. Further, no such effect is found for the ligand itself in this region.

Experimental Section

***l*-Menthoxyacetatopentaamminecobalt(III) Nitrate, $[Co(NH_3)_5(l\text{-menac})](NO_3)_2$ (I).**—This compound was prepared by a variation of the method used by Basolo and Murmann[8] for the synthesis of acetatopentaamminecobalt(III) nitrate. *l*-Menthoxyacetic acid[9] (8.56 g, 0.04 mole) was dissolved in 25 ml of absolute ethanol with stirring, and 3.0 ml of water and 1.00 g of carbo-

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[1] E. Larsen and I. Olsen, *Acta Chem. Scand.*, **18**, 1025 (1964).

[2] W. Heller and D. Fitts in "Physical Methods of Organic Chemistry," Vol. 1, A. Weissberger, Ed., 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1960, Part 3, Chapter 33.

[3] C. J. Hawkins, *Acta Chem. Scand.*, **18**, 1564 (1964).

[4] C. Djerassi and L. E. Geller, *J. Am. Chem. Soc.*, **81**, 2789 (1959).

[5] D. C. Bhatnagar and S. Kirschner, *Inorg. Chem.*, **3**, 1256 (1964).

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

[7] S. F. Mason and B. J. Norman, *Chem. Commun.*, 335 (1965).

[8] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 175 (1953).

[9] This compound is obtainable commercially as *l*-menthoxyacetic acid, mp 52–55°, $[\alpha]^{25}D$ $-91°$, and was used as received from the Aldrich Chemical Co., Milwaukee, Wis.

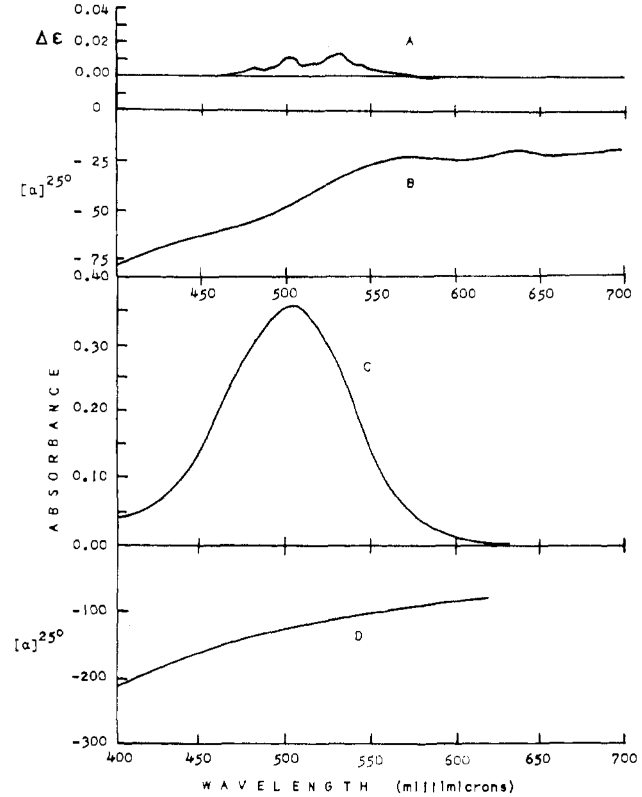

Figure 1.—A: circular dichroic absorption. B: optical rotatory dispersion of $[Co(NH_3)_5(l\text{-menac})](NO_3)_2$ (I) in water at 25° (c = 0.12 g/100 ml, 10-cm cell). C: absorption spectrum of I in water at 25° (c = 0.24 g/100 ml, 1-cm cell). D: optical rotatory dispersion of sodium l-menthoxyacetate in 50% ethanol-water at 25° (c = 0.12 g/100 ml, 10-cm cell).

natopentaamminecobalt(III) nitrate, $[Co(NH_3)_5CO_3]NO_3$ (0.0036 mole), were added to the solution. The mixture was refluxed for 5 hr with stirring and was then cooled to room temperature. The product was filtered and washed with 50 ml of absolute ethanol (the washings were added to the filtrate). The product was then washed with diethyl ether and dried at 50°; yield 0.67 g (37%), sample 1. To the filtrate was added 3.0 g of ammonium nitrate and the mixture was refluxed with stirring for 1 hr, after which it was cooled and treated as above. Additional yield 0.48 g (27%), sample 2; over-all yield 64%. *Anal.* Calcd for $[Co(NH_3)_5(l\text{-}C_{12}H_{21}O_3)](NO_3)_2$: C, 29.94; H, 7.54; N, 20.37. Found, sample 1: C, 30.12; H, 7.76; N, 20.52; sample 2: C, 30.08, H, 7.76; N, 20.44. These two samples had identical spectral properties.

Microanalyses.—These were performed by the Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany.

Optical and Spectral Measurements.—The visible absorption spectrum of the complex was determined on a Cary Model 14 spectrophotometer (c = 0.24 g/100 ml of water) at 25°. The optical rotatory dispersion of the complex was determined on a Cary Model 60 spectropolarimeter (1-dm sample tube; c = 0.12 g/100 ml of water) at 25°. The optical circular dichroism was determined on a Jasco ORD–CD instrument (1-dm sample tube; c = 0.12 g/100 ml of water) at 25°. The ordinate of the curve for circular dichroism is $\Delta\epsilon$, the circular dichroic absorption,[10] and is equal to $\Delta D/cd$, where ΔD is the circular dichroic optical density ($D_l - D_r$), c is the concentration in moles/liter, and d is the path length in centimeters. Because the circular dichroic absorption ($\Delta\epsilon$) is relatively small, it was also determined on another instrument (Roussel–Jouan Dichrograph) with substantially identical results. The authors are not prepared at this time to interpret the various peaks in Figure 1A, the important aspect in this work being to demonstrate that the sample is circularly dichroic in this region. The optical rotatory dispersion of the complex was also determined on the Jasco instrument, and it gave exactly the same shape of curve as that obtained with the Cary instrument. The optical rotatory dispersion of the sodium salt of the ligand was determined at 25° on a Perkin-Elmer Model 141 photoelectric polarimeter (1-dm sample tube; c = 0.12 g/100 ml of 50% ethanol–water) using a Bausch and Lomb high-intensity monochromator in place of the filters which are normally used with this polarimeter.

Conclusions

It is now clear that it is possible for the Cotton effect to be induced and measured in the vicinity of the d–d transition absorption band of a complex containing an optically active ligand inside the coordination sphere, even if the ligand has no absorption in this region. Further, it is possible to measure the Cotton effect for some complexes of this type whether the ligand is monodentate or polydentate and whether the ligand has several asymmetric centers or only one. Consequently, the appearance of a Cotton effect under such circumstances may be utilized as an indication of the coordination of an optically active ligand as proposed earlier[5] although the nonappearance of such an effect cannot be considered confirmatory of noncoordination of such a ligand. The work of Mason,[7] mentioned earlier, indicates that additional work is necessary on the circular dichroism induced by outer-sphere coordination of optically active ligands, in order to determine the effects of concentration and other factors on the induction of Cotton effects in the d–d transition regions of optically inactive complex ions.

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[10] L. Velluz, "Optical Circular Dichroism," Academic Press Inc., New York, N. Y., 1965, p 73.

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BATON ROUGE, LOUISIANA

The Direct Synthesis of Na_3AlH_6

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Recently, Zakharkin and Gavrilenko reported the preparation of Na_3AlH_6 by the reaction of NaH and $NaAlH_4$ at 160° in heptane.[2] Due to the insolubility

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[1] (a) Sloan Fellow, 1965–1967. (b) Requests for reprints should be addressed to this author.

[2] L. I. Zakharkin and V. V. Gavrilenko, *Dokl. Akad. Nauk SSSR*, **145**, 145, 793 (1962).