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The Application of Optical Rotatory Dispersion Techniques to the Determination of Coordination of Optically Active Ligands

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The comparison of optical rotatory dispersion curves is utilized as a technique to determine whether or not an optically active ligand is outside the coordination sphere of complexes having absorption bands at wave lengths different from those of the ligand. It is also noted that the rotatory strength (magnitude of optical rotation) of a complex containing an optically active substance which behaves as a bidentate ligand is noticeably greater than the rotatory strength observed when the same substance behaves as a monodentate ligand.

Discussion

While studying both the effects of optically inactive ions on the optical rotatory dispersion (wave length dependence of optical rotation) of optically active complex ions[2–4] and the applicability of spectropolarimetry to the titrimetry of acids and bases using asymmetric indicators (*e.g.*, tartaric acid)[5] the authors decided to study the differences in the optical rotatory dispersion between a complex containing an optically active ligand inside the coordination sphere as opposed to one containing the same ligand outside this sphere. Further, the authors considered the possibility of studying the differences in the optical rotatory dispersion of complexes containing an optically active ligand inside the coordination sphere, where the ligand can be made to be either bidentate or monodentate.

The compounds chosen for study were: $[Co(NH_3)_4(d\text{-tart})]ClO_4 \cdot H_2O$ (I), $[Co(NH_3)_5(d\text{-tart})]ClO_4$ (II), and $[Co(NH_3)_6]_2(d\text{-tart})_3 \cdot 6H_2O$ (III), where *d*-tart is the dinegative *d*-tartrate anion. These were chosen so as to have asymmetric centers in the ligand and to avoid the complications which would be introduced by including the type of configurational dissymmetric center which occurs at the metal ion in compounds such as $[Co(l\text{-pn})_3]^{+3}$ (*l*-pn is *l*-propylenediamine). In addition, it is possible to prepare complexes with *d*-tartrate in which the ligand is bidentate, monodentate, and not coordinated at all.

Experimental

Compounds. *d*-Tartratotetraamminecobalt(III) Perchlorate Monohydrate, $[Co(NH_3)_4(d\text{-tart})]ClO_4 \cdot H_2O$.—This was prepared from the chloride salt, $[Co(NH_3)_4(d\text{-tart})]Cl \cdot H_2O$, which was in turn synthesized from the carbonato complex $[Co(NH_3)_4CO_3]Cl$ according to the method of Lamb.[6] To 6.0 g. of the carbonato complex dissolved in 100 ml. of water there was added a solution of 4.12 g. of *d*-tartaric acid in 100 ml. of water at room temperature (constant stirring). Stirring was continued until the evolution of carbon dioxide ceased. The product of the synthesis of the chloride, a dark red, viscous paste, was washed with 100 ml. of absolute ethanol, ground in a mortar with 25 ml. of absolute ethanol, filtered, washed with ether, and dried under vacuum for 48 hr. *Anal.* Calcd. for $[Co(NH_3)_4(C_4H_4O_6)]Cl \cdot H_2O$: C, 14.61; H, 5.48; N, 17.05; Cl, 10.80. Found: C, 14.60; H, 5.48; N, 17.02; Cl, 10.80. The dark red, crystalline product was then treated with the stoichiometric quantity of freshly prepared silver perchlorate and the silver chloride was filtered off. The complex was recovered by evaporation of the filtrate in a stream of dry air.

***d*-Tartratopentaamminecobalt(III) Perchlorate, $[Co(NH_3)_5(d\text{-tart})]ClO_4$.**—This was prepared from the chloride salt, $[Co(NH_3)_5(d\text{-tart})]Cl \cdot 2H_2O$, which was synthesized according to the method of Duff.[7] *Anal.* Calcd. for $[Co(NH_3)_5(C_4H_4O_6)]Cl \cdot 2H_2O$: C, 13.20; H, 6.33; N, 19.26. Found: C, 13.26; H, 6.08; N, 18.99. The chloride was converted to the perchlorate just as described above for the tetraammine complex.

Hexaamminecobalt(III) *d*-Tartrate Hexahydrate, $[Co(NH_3)_6]_2(d\text{-tart})_3 \cdot 6H_2O$.—This was prepared from the choride salt, $[Co(NH_3)_6]Cl_3$, which was synthesized according to the method of Bjerrum and McReynolds.[8] In this case 5.0 g. of the chloride was dissolved in 250 ml. of water and the solution was treated with 10.2 g. of freshly prepared silver *d*-tartrate. The silver chloride produced during the reaction was filtered off and the complex was recovered by evaporation of the filtrate in a stream of dry air. The yield of the orange, needle-like crystals was quantitative. *Anal.* Calcd. for $[Co(NH_3)_6]_2(C_4H_4O_6)_3 \cdot 6H_2O$: C, 16.48; H, 6.85; N, 19.22. Found: C, 16.80; H, 7.20; N, 18.79.

Instrumentation: Visual Polarimetry.—Determinations of optical rotation at the sodium D-line were made with a Rudolph Model 80 high precision visual polarimeter, using 1-dm. tubes.

Spectropolarimetry.—Optical rotatory dispersion curves were determined with a photoelectric spectropolarimeter constructed in this laboratory (W.S.U.). The instrument is described in detail in a previous paper.[2] The 1-dm. polarimeter tubes were of the center-fill type and were fitted with optically inactive fused quartz end plates.

Results and Conclusions

Table I gives the observed optical rotations at the sodium D-line of solutions of six compounds in which *d*-tartrate is present in the same concentration. The rotations are different and no definite conclusion can be drawn from these data alone about the coordination or

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[2] M. J. Albinak, D. C. Bhatnagar, S. Kirschner, and A. J. Sonnessa in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., Inc., New York, N. Y., 1961, p. 154 ff.

[3] M. J. Albinak, D. C. Bhatnagar, S. Kirschner, and A. J. Sonnessa, *Can. J. Chem.*, **39**, 2360 (1961).

[4] S. Kirschner, D. C. Bhatnagar, M. J. Albinak, and A. J. Sonnessa in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, New York, N. Y., 1964, p. 63 ff.

[5] S. Kirschner and D. C. Bhatnagar, *Anal. Chem.*, **35**, 1069 (1963).

[6] A. Lamb, *J. Am. Chem. Soc.*, **59**, 385 (1937).

[7] J. Duff, *J. Chem. Soc.*, **123**, 563, 569 (1923).

[8] J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1946).

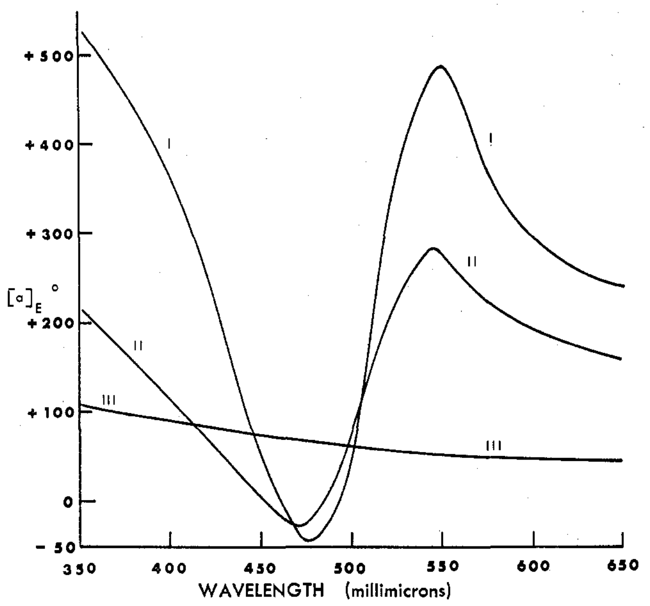

Fig. 1.—Optical rotatory dispersions of: I, $[Co(NH_3)_4(d\text{-}tart)]ClO_4 \cdot H_2O$; II, $[Co(NH_3)_5(d\text{-}tart)]ClO_4$; III, $[Co(NH_3)_6]_2(d\text{-}tart)_3 \cdot 6H_2O$.

noncoordination (or the degree of "dentateness") of the tartrate ligand. The similarity of rotation of compounds III and VI implies that the tartrate may not be coordinated in III, although this similarity could also be attributed to coincidence.

TABLE I

OPTICAL ROTATIONS OF *d*-TARTRATE COMPOUNDS

Compounds		Concn., M	α_{obsd} (Na D), deg.
$[Co(NH_3)_4(d\text{-}tart)]ClO_4 \cdot H_2O^a$	(I)	0.2×10^{-2}	0.053 ± 0.003
$[Co(NH_3)_5(d\text{-}tart)]ClO_4$	(II)	0.2×10^{-2}	0.030
$[Co(NH_3)_6]_2(d\text{-}tart)_3 \cdot 6H_2O$	(III)	0.0666×10^{-2}	0.011
$H_2(d\text{-}tart)$	(IV)	0.2×10^{-2}	0.007
$NaH(d\text{-}tart)$	(V)	0.2×10^{-2}	0.009
$Na_2(d\text{-}tart)$	(VI)	0.2×10^{-2}	0.012

[a] *d*-tart = *d*-tartrate anion.

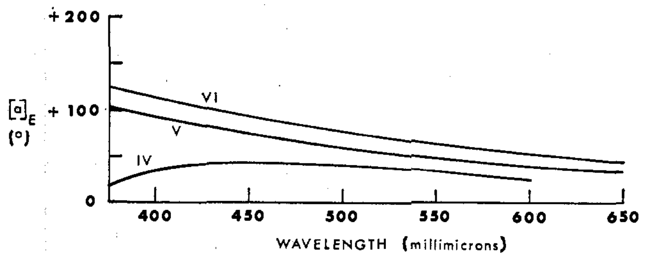

Fig. 2.—Optical rotatory dispersions of: IV, *d*-tartaric acid; V, sodium monohydrogen *d*-tartrate; VI, sodium *d*-tartrate.

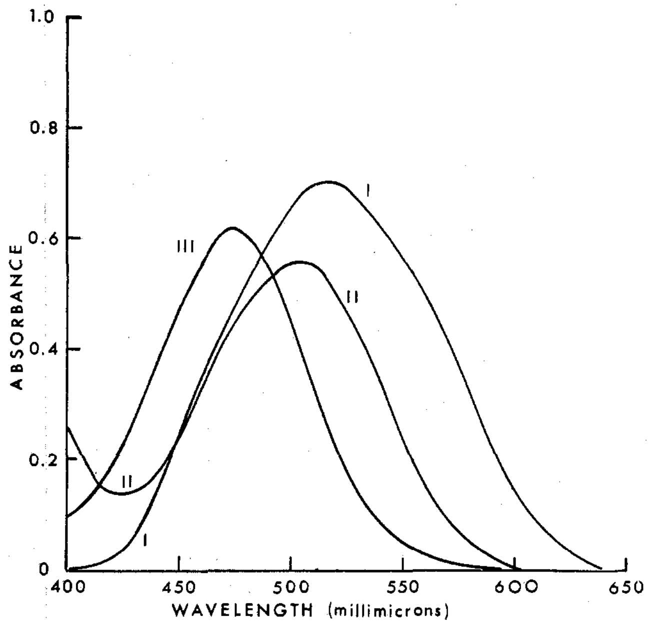

Fig. 3.—Absorption spectra of: I, $[Co(NH_3)_4(d\text{-}tart)]ClO_4 \cdot H_2O$; II, $[Co(NH_3)_5(d\text{-}tart)]ClO_4$; III, $[Co(NH_3)_6]_2(d\text{-}tart)_3 \cdot 6H_2O$.

Figures 1 and 2 give the optical rotatory dispersions of compounds I-VI and Fig. 3 gives the absorption spectra of compounds I-III (compounds IV-VI are colorless). The ordinates of Fig. 1 and 2 are expressed as *equivalent rotation* ($[\alpha]_E$) which is defined[9] as

$$[\alpha]_E = [\alpha]_M/n = [\alpha]M/100n$$

where $[\alpha]_M$ is the molecular (or molar) rotation and $[\alpha]$ the specific rotation of the optically active compounds, n is the number of optically active ions per molecule (or formula unit), and M is the molecular (or formula) weight of the compound. The equivalent rotation is used in order to eliminate any nonreal differences in calculated rotations which would appear if molecular or specific rotations were used in comparing compounds having different numbers of optically active groups per molecule or formula unit of complex compound.

From Fig. 1-3 it can be observed that the complex I, in which the tartrate ion is bidentate, and the complex II, in which the tartrate is monodentate, have absorption spectra which are similarly shaped. They also have optical rotatory dispersions which are similarly shaped but which differ in rotational strength (magnitude of optical rotation at the peaks and troughs). Most noticeable, however, is the fact that although the complex III, in which tartrate is not coordinated, has an absorption peak at 476 mμ, it does not exhibit any anomalous rotatory dispersion in that region whatsoever. In fact, the shape of the optical rotatory dispersion curve of III closely resembles that of sodium *d*-tartrate (VI).

That compounds I and II exhibit anomalous rotatory dispersions in the vicinity of their absorption bands is indicative of interaction of the "colorless" optically active tartrate ligand with the chromophoric center of the complex, resulting in an optically active absorption band. This effect is not unexpected for complexes where there is a covalent or partially covalent link between optically active ligands and the metal ion. Since

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(9) Equivalent rotation is defined herein as molar rotation divided by n. There is some disagreement in the literature about the definition of molar rotation, some authors using specific rotation times molecular weight and others dividing this product by 100. The latter definition seems to be the most used and the definition of equivalent rotation herein carries this factor of 100, which did not occur in previous papers.[2-4]

this effect does not occur in III, it is apparent that the lack of a coordinate link of the tartrate to the metal ion results in the rotatory dispersion being similar to that of the free tartrate ion. Figures 1 and 2 indicate no observable interaction between the tartrate and the chromophoric center of III.

Optical rotatory dispersion has therefore indicated the noncoordination of a colorless (visible region) optically active coordinating agent in a system containing a colored complex. Further, there is a noticeable decrease in the rotational strength of the optical rotatory dispersion when the bidentate ligand becomes monodentate (Fig. 1), indicating that optical rotatory dispersion may also be a technique which can be utilized to differentiate between monodentate and polydentate character of optically active ligands. Similar studies on other systems are now in progress with a view toward testing this observation.

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Polymeric Zinc Derivatives of Simple Bis-Chelating Agents

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Infrared end-group analysis indicates a degree of polymerization of at least 20 for a zinc derivative of dithiooxamide prepared by the interfacial polymerization reaction of zinc acetate with dithiooxamide. The degrees of polymerization of zinc derivatives of 2,5-dihydroxy-*p*-benzoquinone prepared by two-stage reactions from diethylzinc and 2,5-dihydroxy-*p*-benzoquinone are estimated to be 4 and 27 by chemical end-group analysis. The conditions of the second step, the heating of the intermediate $C_2H_5ZnO_2C_6H_2O_2H$, determine the degree of polymerization.

Although considerable effort has been devoted to the synthesis of coordination polymers involving bis-chelating agents,[1] their characterization as polymers has not developed apace. This is undoubtedly due to the insolubility and intractability of most of the products. Typically these materials have been formulated as polymers from steric considerations and assigned a degree of polymerization on the basis of elemental analysis. Recently there have been attempts to estimate the degree of polymerization of some coordination polymers based on simple bis-chelating agents by other techniques.[2-6] We wish to record here the results of our efforts in this direction. We selected for study the one-to-one zinc derivatives of 2,5-dihydroxy-*p*-benzoquinone ($H_2C_6H_2O_4$) and dithiooxamide ($H_2C_2H_2N_2S_2$). $ZnC_6H_2O_4$ is a novel composition. Although $ZnC_2H_2N_2S_2$ has since been reported,[7] no attempt was made to measure its degree of polymerization.

Experimental

(A) **Apparatus.**—The reactions involving $(C_2H_5)_2Zn$ were carried out by standard manipulative techniques in a high vacuum apparatus. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer.

(B) **Reactants.**—With the following exceptions all chemicals and solvents were reagent grade and were not further purified.

(1) A sample of $H_2C_2H_2N_2S_2$ supplied by Mallinckrodt Chemical Works was used without further purification. *Anal.* Calcd. for $C_2H_4N_2S_2$: C, 20.0; H, 3.3; N, 23.3. Found: C, 20.0; H, 3.4; N, 23.1.

(2) Technical grade $H_2C_6H_2O_4$ was purified by vacuum sublimation. *Anal.* Calcd. for $C_6H_4O_4$: C, 51.5; H, 2.8. Found: C, 51.7; H, 3.0.

(3) Commercial $(C_2H_5)_2Zn$ was purified by fractional distillation in the vacuum apparatus. Its vapor-phase infrared spectrum (bands observed at 2933–2882 (vs), 2809 (sh), 2740 (sh), 1468 (m), 1418 (m), 1379 (m), 1185 (m), 985 (s), and 949 (m) cm.$^{-1}$) correlated well with the reported liquid-phase spectrum.[8] Attempts to determine the exact purity by vapor-phase chromatography were unsuccessful because we were unable to elute the $(C_2H_5)_2Zn$ from the columns tried. A combination of vapor-phase chromatography and mass spectroscopy, however, revealed that the major impurity, diethyl ether, was present in larger amounts than all the other impurities combined. Comparison of the vapor-phase infrared spectrum of the sample with that of a low-pressure standard sample of diethyl ether indicated that the diethyl ether impurity (as represented by a very small peak in the 9.7 μ region) was approximately 0.2 mole % of the $(C_2H_5)_2Zn$ sample. The purity of the $(C_2H_5)_2Zn$ was therefore in excess of 99.5 mole %.

(C) **Reactions.** (1) **Preparation of $ZnC_2H_2N_2S_2$.**—A solution of 25 mmoles of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 50 ml. of water was added to a suspension of 25 mmoles of $H_2C_2H_2N_2S_2$ in 300 ml. of benzene in a Waring blendor. The mixture was agitated for 15 min. and then filtered. The precipitate, a pale yellow solid, weighed 3.2 g.

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(1) Much of this work has been reviewed recently. See, for example, J. C. Bailar, Jr., "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, p. 51; B. P. Block, Chapter 8 in "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, New York, N. Y., 1962; I. Haiduc, *Russ. Chem. Rev.*, **30**, 498 (1961); or C. N. Kenney, Chapter 9 in "Developments in Inorganic Polymer Chemistry," M. F. Lappert and G. J. Leigh, Ed., Elsevier Publishing Company, New York, N. Y., 1962.

(2) F. W. Knobloch, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1959.

(3) D. N. Chakravarty and W. C. Drinkard, Jr., *J. Indian Chem. Soc.*, **37**, 517 (1960).

(4) R. N. Hurd, G. DeLaMater, G. C. McElheny, and L. V. Peiffer, *J. Am. Chem. Soc.*, **82**, 4454 (1960).

(5) S. Kanda, *Nippon Kagaku Zasshi*, **81**, 1347 (1960), from *Chem. Abstr.*, **55**, 2294*e* (1961).

(6) S. Kanda, *Nippon Kagaku Zasshi*, **83**, 282, 560 (1962), from *Chem. Abstr.*, **58**, 13,404*gf* (1963).

(7) V. N. Odnoralova and G. I. Kudryavtsev, *Vysokomolekul. Soedin.*, **4**, 1314 (1962).

(8) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **14**, 360 (1959).