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The Stereochemistry of Complex Inorganic Compounds. XII. The Diastereoisomers of Carbonato Bis-levo-propylenediamine Cobalt(III) Ion[1]

BY SR. MARY MARTINETTE, B.V.M. AND JOHN C. BAILAR, JR.

In studies on the carbonato bis-levo-propylenediamine cobalt(III) ion a series of 0.1% solutions was prepared and found to be optically unstable. When a solution of the complex was evaporated to dryness at room temperature the specific rotation of a 0.1% solution of the complex formed was +130°. When it was evaporated to dryness on a steam-cone at 80–85° the specific rotation was −430° for a 0.1% solution. On standing at room temperature both solutions underwent a change in rotation. These data seem to indicate the preparation of the diastereoisomers; this is supported by measurements of the electrical conductivity of their solutions. Absorption curves were determined for these two carbonato solutions. The shape of the two curves was very similar but the light absorption for the dextrorotatory isomer was lower at all wave lengths than for the levorotatory isomer. Rotatory dispersion curves were determined for each solution and were found to differ markedly. Superimposition of the absorption curves on the rotatory dispersion curves showed the rotatory power to increase strongly as one approached the region of maximum absorption and to change sign within this region. These results are those predicted for colored complex molecules and exemplify the Cotton effect.

The optical behavior of cobaltic complex compounds containing active diamines has presented a number of interesting problems. Evidence has been advanced to indicate that all of the possible stereochemical forms do not exist but, rather, that only certain preferred configurations are to be found. Hurlimann,[2] working with dinitro-bis-propylenediamine cobalt(III) compounds and Jaeger,[3] using active cyclopentylenediamine, substantiated this observation. Jaeger concluded from studies with the carbonato bis-levo-propylenediamine cobalt(III) ion, $[\mathrm{Co}_{\mathrm{D}}l\text{-}\mathrm{pn}_2\mathrm{CO}_3]^+$, that it would exist in only one form. However, Stiegman[4] offered good evidence for the existence of two isomers and Bailar and McReynolds[5] prepared each in impure form and determined their respective rotatory dispersion curves. Their preparation of the two diastereoisomers was effected by a Walden inversion method and they designated the inverted form as "unstable" and the non-inverted form as "stable." Following the convention established by Jaeger[8] they assigned the formulas $[\mathrm{Co}_{\mathrm{D}}l\text{-}\mathrm{pn}_2\mathrm{CO}_3]^+$ to the more stable form and $[\mathrm{Co}_{\mathrm{L}}l\text{-}\mathrm{pn}_2\mathrm{CO}_3]^+$ to the less stable form. They also determined the absorption spectra.[5]

Further confirmation of this earlier work and other interesting observations are presented here. The diastereoisomers have been prepared separately, their rotatory dispersions and absorption spectra have been determined, and observations have been made on the changes in rotation exhibited by their solutions. Conductivity data have been obtained further to confirm the nature of the complex ions.

The designation of the diastereoisomeric forms as "stable" and "unstable" is not entirely correct, for the relative stabilities of the isomers seems to depend upon the conditions of the experiment.[6] Apparently the conditions under which evaporation of the solution takes place during the course of preparation directs orientation within the complex ion. It has been found that when the carbonato complex is prepared according to the usual procedure, division of the solution into two parts and subsequent evaporation of these under two different sets of conditions will yield compounds of widely different specific rotations. On analysis, these compounds are shown to have essentially the same composition, differing only in that one has two molecules of water of hydration and the other has one molecule of water of hydration.

A study of the absorption spectra and of the rotatory dispersion of these two compounds shows them to be diastereoisomers. Superimposition of the absorption curves on the rotatory dispersion curves for the diastereoisomers gives interesting and conclusive evidence for this (Fig. 1). The Cotton effect[7] is immediately apparent. The absorption curves of the diastereoisomers show different degrees of light absorption within an "optically active" absorption band. When these curves are super-imposed on the rotatory dispersion curves the rotatory power is shown to increase strongly as one approaches an appropriate band and to change sign within the region of absorption.

Solutions of the two diastereoisomers change rotation on standing, the direction of change being the same in both cases. Conductivity studies and precipitation studies indicate that this is not due to any breakdown of the complex ion. Partial conversion of one diastereoisomer to the other appears to be possible on heating even in the solid state. A change from a specific rotation of +130 to 0° (0.1% solutions) can be effected by heating one of the diastereoisomers in the solid state for 70 hours at 80–85°. Heating for another 70 hours produces no further change. Heating of the solid complex at 110° brings about decomposition as evidenced both by a change in the color of the compound—red to dark brown—and by a change in the rotation consistent with results due to

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[1] Most of the work reported in this article was abstracted from the dissertation of Sister Mary Martinette, B.V.M., presented to the Faculty of the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1949. The remainder was done by Sister Mary Martinette at Mundelein College. The work at Mundelein College was made possible by a Cottrell grant-in-aid from Research Corporation.

[2] Hans Hurlimann, Dissertation, Zurich, 1918.

[3] F. M. Jaeger, and H. B. Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928).

[4] C. A. Stiegman, Thesis, University of Illinois, 1934.

[5] J. C. Bailar, Jr., and J. P. McReynolds, THIS JOURNAL, **61**, 3199 (1939).

[6] J. C. Bailar, Jr., *Record of Chemical Progress, Winter Issue*, **10**, 21 (1949).

[7] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946, p. 881.

decomposition. Repeated evaporation of solutions of the complex and determinations of the specific rotation of 0.1% solutions of the product show the configuration of the dextrorotatory complex to be readily changed to that of the levorotatory complex.

Characteristic behavior of solutions of these diastereoisomers may be seen from the following observations: (All rotations taken on 0.1% solutions.)

A. Repeated evaporation to dryness of a 0.1% D isomer solution

$$\begin{tikzcd}
\begin{array}{c}[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}\\ {[\alpha]_D} +130^\circ\end{array} \arrow[r, "\text{standing at room}", "\begin{array}{c}\text{temperature for}\\ \text{18 days}\end{array}"'] & {[\alpha]_D +240^\circ} \arrow[d, "\begin{array}{c}\text{evaporated}\\ \text{at 85–90°}\end{array}"', "\text{to dryness}"] \\
{[\alpha]_D +150^\circ} & {[\alpha]_D +190^\circ} \arrow[l, "\text{Evaporated to}"', "\begin{array}{c}\text{dryness again}\\ \text{at 85–90°}\end{array}"]
\end{tikzcd}$$

B. 0.1% solutions of the D and L isomers allowed to stand at room temperature over a period of time

$$\begin{array}{c}[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}\\ {[\alpha]_D} +130^\circ\end{array} \xrightarrow{\text{14 days}} [\alpha]_D +240^\circ$$

$$\begin{array}{c}[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}\\ {[\alpha]_D} -410^\circ\end{array} \xrightarrow{\text{14 days}} [\alpha]_D +210^\circ$$

Experimental

Preparation of Compounds. (1).—Levo-propylenediamine was obtained by resolving 85% *racemic*-propylenediamine according to the method of Bauman,[8] as modified by Bailar and co-workers[9] and further modified by Jonassen.[10]

(2).—Dichloro bis-levo-propylenediamine cobalt(III) chloride was prepared by a modification[10] of the method of Werner and Frohlich.[11]

(3).—Solutions of carbonato bis-levo-propylenediamine cobalt(III) chloride $[\mathrm{Co}(l\text{-pn})_2\mathrm{CO_3}]\mathrm{Cl}$ were produced by grinding silver carbonate with the dichloro complex,[12] $[\mathrm{Co}(l\text{-pn})_2\mathrm{Cl_2}]\mathrm{Cl}$, the molar ratio being changed to produce the chloride rather than the carbonate salt.

(4).—D- and L-carbonato bis-levo-propylenediamine cobalt(III) chloride diastereoisomers were prepared by evaporation of the carbonato complex solutions under different conditions. The prepared solution was divided into two portions. One portion was evaporated to dryness in an air stream at room temperature; this yielded a red crystalline compound, $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$. This substance, in 0.1% solution, showed a $[\alpha]_D$ of +130°. The other portion was evaporated to dryness on a steam-cone at 85–90° yielding a red crystalline compound, $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$. A 0.1% solution of this isomer showed a $[\alpha]_D$ of −430°. Both samples were then dried for one hour in an oven at 80–85°.

Anal. Calcd. for $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$: Co, 17.40; C, 24.81; H, 7.09; N, 16.55. Found: Co, 16.94; C, 24.45; H, 7.24; N, 16.47. Calcd. for $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$: Co, 18.20; C, 26.2; H, 6.67; N, 17.48. Found: Co, 18.52; C, 26.02; H, 6.90; N, 17.38.

The cobalt analysis was carried out by the method of Callis[13] as adapted from Mellan.[14]

Optical Rotation Measurements.—The specific rotations were determined in one-decimeter tubes at room temperature. This temperature varied little in the course of several days since the instrument was housed in an inside room. The concentration of the solution investigated was 0.1%. A sodium vapor lamp served as a nearly monochromatic light source for the specific rotations observed at the D line of sodium. In the rotatory dispersion studies a 1000-watt projection bulb served as a polychromatic light source. A Schmidt–Haensch polarimeter equipped with a prism monochromator was used. The resulting light was not strictly monochromatic and the wave lengths indicated represent an average for a band covering approximately 100 Å. Since the color of the solutions of the complex compounds being studied was very intense, polarimeter reading across the spectrum was exceedingly difficult. Though the polarimeter scale was calibrated to 0.001° the specific rotations reported here are for the most part based on readings accurate to 0.01°.

The maximum positive specific rotation obtained for solutions of the L isomer at the sodium D line was +360°. This was found after a 0.1% solution had stood for 6 months. To eliminate the possibility that this marked change might be due to aquation of the complex ion this specific rotation was compared with that of a 0.1% solution of $[\mathrm{Co_D}l\text{-pn}_2\text{-}(\mathrm{H_2O})_2]\mathrm{Cl_3}$. The aquated ion solutions gave a specific rotation of +70°.

Absorption Spectra Measurements.—The absorption spectra data were obtained by measuring the optical densities of 0.05% solutions. A Beckman quartz spectrophotometer, model D, was used and from it optical densities were then converted to extinction coefficients, *E*, and the curves plotted were those of *E versus* wave lengths.

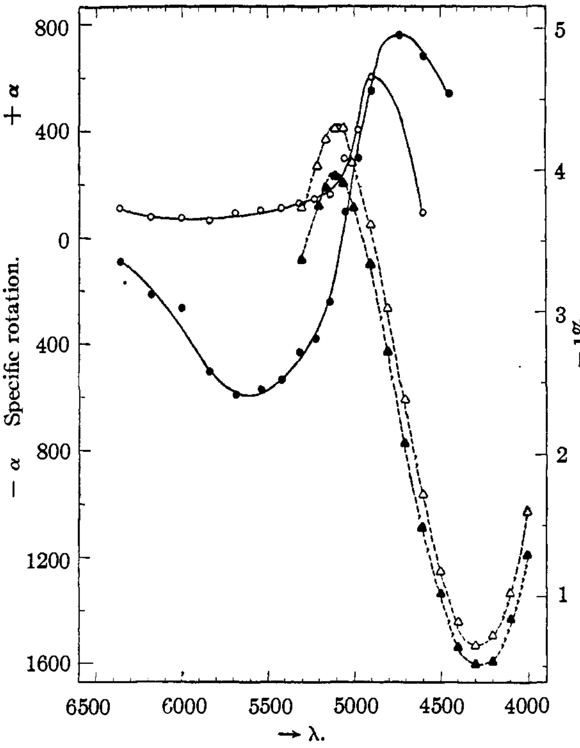

Fig. 1.—Rotatory disperson and absorption: ○, rotation of $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$; ●, rotation of $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$; △, extinction coefficient of $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$; ▲, extinction coefficient of $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$.

Conductance Studies.—Two samples were used. An Industrial Instruments Type RC conductivity bridge and

Sample I

A freshly prepared 0.1% solution of the L isomer.
$[\alpha]_D$ −440°
Cell constant, 0.3920
Measured resistance, 1650 ohms
Specific conductance, 2.375×10^{-4}
Molar conductance, mhos/cm. 80.5

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[8] G. Bauman, *Ber.*, **28**, 1180 (1895).

[9] J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, THIS JOURNAL, **61**, 2402 (1939).

[10] H. B. Jonassen, Thesis, University of Illinois, 1946.

[11] A. Werner and A. Frohlich, *Ber.*, **40**, 2225 (1907).

[12] J. C. Bailar, Jr., and J. P. McReynolds, THIS JOURNAL, **61**, 3801 (1939).

[13] C. F. Callis, Thesis, University of Illinois, 1948.

[14] Ibert Mellan, "Organic Reagents in Organic Analysis," Blakiston Co., Philadelphia, Penna., 1941, p. 326.

Sample II

A 0.1% solution of the L isomer which had stood 8 months.
$[\alpha]_D$ +360°
Cell constant, 0.3920
Measured resistance, 1050 ohms
Specific conductance, 3.74×10^{-4}
Molar conductance, mhos/cm. 126.5

a Freas conductivity cell were used. The determinations were run at 18°.

TABLE I

These data are shown graphically in Fig. 1.

Wave length, Å.	Specific rotation $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$	Specific rotation $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$
6360	+109°	− 91°
6180	+ 75	−215
6000	+ 71	−273
5840	+ 62	−504
5680	+ 90	−594
5540	+100	−566
5420	+111	−536
5320	+127	−433
5230	+143	−380
5140	+160	−245
5060	+294	+ 92
4980	+400	+294
4900	+600	+550
4740	....	+758
4600	+ 94	+690
4450	....	+536

TABLE II

These data are shown graphically in Fig. 1

Wave length, Å.	Extinction coefficient $[\mathrm{Co_D}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$	Extinction coefficient $[\mathrm{Co_L}l\text{-pn}_2\mathrm{CO_3}]\mathrm{Cl}\cdot \mathrm{H_2O}$
3500	3.28	3.88
3550	3.54	4.08
3600	3.62	4.10
3700	3.26	3.72
3800	2.62	2.96
3900	1.96	2.20
4000	1.30	1.60
4100	0.84	1.02
4200	0.54	0.72
4300	0.52	0.66
4400	0.64	0.82
4500	1.02	1.18
4600	1.48	1.72
4700	2.08	2.38
4800	2.72	3.02
4900	3.34	3.62
5000	3.74	4.08
5080	3.92	4.30
5100	3.96	4.30
5160	3.88	4.22
5200	3.78	4.04
5300	3.38	3.78

Werner[15] carried out conductivity determinations on a series of coördination compounds to find the molar conductance values. He showed the values for solutions of 2 ion complexes to be in the neighborhood of 105. If, on standing in solution, the L isomer was aquated, rather than converted to the D isomer as the authors propose, the molar conductance would have been in the neighborhood of 450, the approximate value for a 4 ion complex. Even after standing 8 months the molar conductance values of the complex indicate only slight aquation.

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(15) A. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Vieweg, Braunschweig, ed. 4, 1920, page 46; D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 381.

[CONTRIBUTION NO. 1612 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Diffusion–Convection. A New Method for the Fractionation of Macromolecules

BY JOHN G. KIRKWOOD[1a] AND RAYMOND A. BROWN[1b]

A new method of fractionation of macromolecules in solution based upon the principles of the Clusius column is proposed. Horizontal transport of the macromolecular components in a vertical convection channel is produced by thermodynamic interaction with a diffusing low molecular weight substance to which the channel walls are permeable. Vertical convective transport under gravity is produced by the horizontal density gradient of the solution arising from the concentration gradient of the diffusible components. Preliminary experiments on the transport of serum albumin, which demonstrate the practical possibilities of the method, are described.

We wish to describe a new method of fractionation of macromolecules in solution, which we shall call diffusion–convection. Like the method of electrophoresis convection,[2] the new method is based upon the principles of the Clusius column. A solution of the macromolecular components is contained in two reservoirs connected by a vertical convection channel, the walls of which are impermeable to the passage of the macromolecules but permeable to a diffusible component of low molecular weight, the concentration of which is maintained at a level $C_1^{(1)}$ in an exterior reservoir on one side of the convection channel and at a concentration $C_1^{(2)}$ in a similar reservoir on the other side. The low molecular weight component, diffusing horizontally across the channel under its concentration gradient, produces by virtue of its effect on the density of the solution, a horizontal density gradient leading under the action of gravity to countercurrent convective circulation in the channel between the top and bottom reservoirs. If the diffusible component interacts thermodynamically with a macromolecular component, the concentration gradient of the former will produce a horizontal chemical potential gradient of the latter. As a consequence, the macromolecular component will diffuse horizontally toward the channel wall at which its chemical potential is the lowest. Such transport may also be produced in part by codiffusion arising directly from the chemical po-

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[2] J. R. Cann, J. G. Kirkwood, R. A. Brown and O. Plescia, THIS JOURNAL, 71, 1630 (1949).