g. of 2-bromobutane was added dropwise over a period of two hours. At the end of this time the reaction mixture was allowed to come to room temperature and then to stand for twelve hours. It was then heated at 60° until the organic layer gave a negative test for halogen. The flask was then fitted with a condenser set for downward distillation and heated to 80° at 60 mm. pressure; there was obtained 61 g. of distillate. This was shaken for one hour with 75 ml. of 85% phosphoric acid, and then allowed to stand in contact with the acid overnight. The acid layer was withdrawn, the organic layer was washed with water, dried over magnesium sulfate and then rectified.[8a] There was obtained 58 g. (49% yield) of 2-butyl nitrate boiling at 59° (80 mm.). At atmospheric pressure the nitrate boils at 124° (Emich), n^{20}_{D} 1.4015, d^{20}_{4} 1.029, M_D (calcd.) 28.80, M_D (found) 28.81, lit. value,[19] b. p. 124°, d^{0} 1.0382.

Anal.[23] Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62. Found: C, 40.68, 40.34; H, 7.62, 7.79.

Racemic 2-Butyl Nitrite.—(a) Thirty-nine grams of racemic 2-butanol was treated with 38 g. of sodium nitrite and 15.5 ml. of 96% sulfuric acid according to the method of Noyes.[24] Upon rectification[8a] there was obtained 49 g. (83% yield) of a pale yellow liquid; b. p. 28° at 180 mm. At atmospheric pressure the nitrite ester boils at 68° (Emich), n^{20}_{D} 1.3710, d^{20}_{4} 0.8726, M_D (calcd.) 27.01, M_D (found) 27.02; lit. values,[20] b. p. 68°, d^{0} 0.8981.

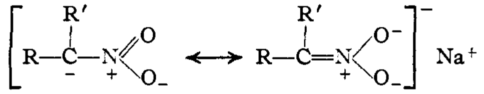
(b) Following the procedure described by Kornblum and Oliveto[25] 30 g. of racemic 2-butanol was treated with 40 g. of nitrosyl chloride. One modification was made, namely, the omission of the use of petroleum ether in working up the product; yield 21 g. (50%) boiling at 27° under 180 mm. pressure. At atmospheric pressure the nitrite boils at 68° (Emich); n^{20}_{D} 1.3710, d^{20}_{4} 0.8728.

Anal.[26] Calcd. for $C_4H_9NO_2$: N, 13.58. Found: N, 13.67, 13.70.

Summary

Contrary to an earlier report, optically active 2-nitrobutane does not give an active sodium salt upon treatment with sodium methoxide. Furthermore, 2-bromo-2-nitrobutane prepared from this salt is optically inactive.

It is concluded that the correct structure for the salts of aliphatic nitro compounds is



$$\left[\mathrm{R}-\overset{\mathrm{R'}}{\underset{-}{\mathrm{C}}}-\underset{+}{\mathrm{N}}\begin{smallmatrix}\nearrow\!\!\!\!=\mathrm{O}\\ \searrow\mathrm{O}^-\end{smallmatrix} \longleftrightarrow \mathrm{R}-\overset{\mathrm{R'}}{\mathrm{C}}=\underset{+}{\mathrm{N}}\begin{smallmatrix}\mathrm{O}^-\\ \mathrm{O}^-\end{smallmatrix}\right]^- \mathrm{Na}^+$$

The action of silver nitrite on 2-iodobutane has been shown to form 2-nitrobutane, 2-butyl nitrate, 2-butyl nitrite, 2-butanol and butanone.

LAFAYETTE, INDIANA RECEIVED AUGUST 1, 1947

---

[23] Microanalyses by Dr. Carl Tiedcke, New York, N. Y.

[24] Noyes, THIS JOURNAL, **55**, 3888 (1933).

[25] Kornblum and Oliveto, *ibid.*, **69**, 465 (1947).

[26] "The Pharmacopaeia of the United States of America," Mack Printing Co., Easton, Pa., 1942, 12 revision, p. 597.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. VIII. Configurations of Some Compounds as Revealed by Rotatory Dispersion Curves[1]

BY THOMAS D. O'BRIEN,[2] JAMES P. MCREYNOLDS[3] AND JOHN C. BAILAR, JR.

The determination of configuration of ions of the type $[M(AA)_2b_2]$ and $[M(AA)_2bc]$[4] by chemical means presents several difficult problems and no general method has yet been suggested. It is often stated that the *cis* compounds are more highly colored and more soluble than the *trans*, but there are so many exceptions to these rules that no reliance can be placed in them. Differences in reactivity of *cis* and *trans* isomers have been observed in several cases, but they are so scattered that generalization cannot be drawn from them. Finally, the fact that a compound is prepared from another of known structure is of no value in determining configuration because molecular rearrangements are common in such reactions.

Unless one or more of the coördinating groups is optically active, *trans* complexes are not resolvable, while those of the *cis* configuration are. Thus, it is definite that the optically active (violet) form of $[Co\ en_2\ Cl_2]^+$ (Ib) must have the *cis* configuration, while the inactive (green) form must be *trans* (Ia). If, on the other hand, the coördinating groups are optically active, both isomers of the complex will rotate the plane of polarized light, so that the presence of optical activity does not serve to distinguish one isomer from the other. As will be shown in this paper, however, the rotatory dispersion curves often give the desired information.

It has previously been pointed out[5] that the rotatory dispersion curves of resolved *cis*-dichloro-bis-ethylenediamine cobaltic chloride, $[Co\ en_2\ Cl_2]Cl$ (Ib) and the corresponding compound of *levo*-propylenediamine, $[Co(l\text{-}pn)_2Cl_2]Cl$, (IIb) are strikingly alike in general shape and in the positions of maxima, minima and points of zero rotation. The same is true of the carbonato complexes. Several investigators have shown that *cis* cobaltic complexes containing optically active diamines do not exist in all the possible stereo-

---

[1] Constructed from portions of the doctorate theses of James P. McReynolds (1938) and Thomas D. O'Brien (1941).

[2] Present address, Chemistry Department, University of Minnesota, Minneapolis, Minn.

[3] Died, June 19, 1943.

[4] The following abbreviations are used: AA = a group occupying two coördination positions; en = ethylenediamine; pn = propylenediamine; a, b and c = groups occupying one coördination position; Y = group occupying two coördination positions. The various compounds referred to are designated for convenience by Roman numerals, those of the ethylenediamine series being assigned odd numbers and those of the propylenediamine series, even numbers. For *trans* isomers, the Roman numeral is followed by the letter "a," for *cis* isomers, by "b."

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

chemical forms but only in certain preferred configurations.[6] The optical activity is mainly due to the arrangement of the groups about the central atom, so the rotatory dispersion curves of complexes of similar configuration should have the same characteristics whether the coördinating base be active or not. Should the non-basic constituents be in the *trans* positions in the di-active-propylenediamine compounds, then one might expect their dispersion characteristics to be similar to those of active propylenediamine itself (Fig. 2). There is, of course, the possibility of having additional isomers due to the position of the methyl group in the active propylenediamine, *i. e.*, in *cis*-$[Co(l\text{-}pn)_2Cl_2]^+$ (IIb) the methyl groups could be adjacent to the plane containing the chlorine and cobalt or distant from it. Similar relations hold for the *trans* salt. However, it is assumed here that the contribution of the methyl groups in the different positions to the rotatory dispersion curve would be very small compared to the contribution of the central atom itself. It is also possible that both diastereoisomers $[Co(l\text{-}pn)_2a_2]d^+$ and $[Co(l\text{-}pn)_2a_2]_L^+$ (or $[Co(l\text{-}pn)_2Y]^+_D$ and $[Co(l\text{-}pn)_2Y]^+_L$ might form, although it is known that these are of different stabilities. Such a pair has been reported by Bailar and McReynolds for the carbonato-bis-propylenediamine cobaltic ion (XIV).[5] They found that the rotatory dispersion curves of the two differ widely. Even if the two *cis* diastereoisomers form in equal quantity, therfore, the dispersion curve of the mixture will not resemble the curve of the *trans* isomer.

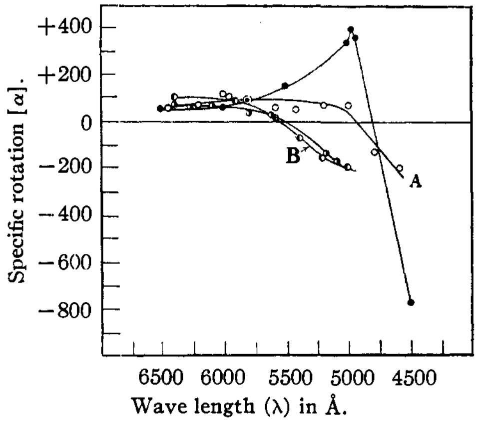


Fig. 1.—Rotatory dispersions of some complex ions of the type $[Co(AA)_2(NO_2)_2]^+$: ●, $[Co\ en_2\ (NO_2)_2]Cl$ (IIIb) according to Mathieu; ◑, $[Co\ l\text{-}pn_2(NO_2)_2]Br$ (IV) according to Hürlimann; ○, "*cis*" $[Co\ l\text{-}pn_2(NO_2)_2]^+$ (IVb); ◐, "*trans*" $[Co\ l\text{-}pn_2(NO_2)_2]^+$ (IVa).

For the purpose of this study, ethylenediamine ("en") was chosen as the reference inactive base and propylenediamine ("pn") as the optically active base because of the relative stability and ease of preparation of most of their coördination compounds, and because Mathieu[7] has determined the rotatory dispersion curves of many diethylenediamine cobaltic complexes.

Hurlimann[6a] has reported the dispersion curve of dinitro-bis-*levo*-propylenediamine cobaltic bromide, $[Co(l\text{-}pn)_2(NO_2)_2]Br$ (IV), which he obtained from the reaction of trinitro-triammine-cobalt and *levo*-propylenediamine. Hurlimann was of the opinion that his product was the pure *cis* isomer (IVb) and that none of the *trans* (IVa) form resulted from this reaction. This conclusion was based upon the fact that the compound gave a green color when heated with hydrochloric acid (a test which has been reported to distinguish the *cis* and *trans* isomers in both the ammonia and ethylenediamine series).[8] However, the dispersion curve which Hurlimann obtained (Fig. 1) shows no similarity to the one given by Mathieu for *cis*-dinitro-bis-ethylenediamine cobaltic ion (IIIb). We therefore studied Hurlimann's reaction further, and found that in addition to the product reported by him another material is formed in even larger amount. It gives a dispersion curve somewhat resembling that for *cis* $[Co\ en_2(NO_2)_2]^+$ (IIIb). The lack of greater similarity here may possibly be due to the fact that this was not the pure *cis* isomer. At least, this curve definitely differs from the curve of the *trans* isomer. The compound also gives the test which Hurlimann considered distinctive for the *cis* form. The *cis*-ethylenediamine compound is known to be slowly converted to the *trans* form on boiling in water. Our *levo*-propylenediamine complex which gave the "*cis*" rotatory dispersion curve was gradually converted by long boiling into a material which gave a curve resembling that reported by Hurlimann. As the curves show, the material which Hurlimann studied must have been largely the *trans* isomer. There are numerous examples in which *cis* compounds of the type $[Ma_4b_2]^+$ (when a and b are groups occupying one coördinate position) when heated in water are converted to the *trans* isomer. As the *cis* compound has only one form there is no possibility of getting a mixture of *cis* isomers. If A_2 groups (pn for example) are substituted for the a_4 ones, the same reaction occurs on heating in water. In addition, as no one has reported a mixture of *d* and *l* forms in which both were stable with respect to each other, it seems logical to assume that when a change occurs on refluxing the *cis* compound, it is the *trans* that is formed.

Again, it is possible that the two forms of the *levo*-propylenediamine compound might be diastereoisomers, $[Co\ l\text{-}pn_2\ (NO_2)_2]_D^+$ and $[Co\ l\text{-}pn_2(NO_2)_2]_L^+$ (IVb). To test this point, each of the diastereoisomers of $[Co\ l\text{-}pn_2\ CO_3]^+$ (XIVb)[5] was treated at room temperature with calcium nitrite. The curves for the two materials obtained were much alike, the product from the stable carbonato form apparently being all *trans*,

---

[6] (a) Hurlimann, "Dissertation," Zurich, 1918; (b) Jaeger, *Rec. trav. chim.*, **38**, 170 (1919).

[7] Mathieu, *Bull. soc. chim.*, [5] **3**, 463–475 (1936).

[8] Jorgensen, *Z. anorg. Chem.*, **17**, 468, 472 (1898); Werner, *Ber.*, **34**, 1709 (1901).

and that from the unstable form being predominately *trans*. It seems safe to say that the isomers of [Co *l*-pn$_2$(NO$_2$)$_2$]$^+$ (IV) which were obtained from trinitro-triamminecobalt were the stable *cis* form and the *trans* form.

The dispersion curve for chloro-ammino-bis-*dextro*-propylenediamine cobaltic chloride (VI) (Fig. 2) is quite smooth and regular, very similar to the curve for active propylenediamine itself, and very unlike the curve for the corresponding active ethylenediamine salt (Vb). Identical curves were obtained regardless of whether the material was prepared from the *cis* or from the *trans*-dichloro-bis-*dextro*-propylenediamine cobaltic chloride (II), and from their shape one concludes that the product has the *trans* configuration (VIa). The dichloro-bis-propylenediamine salt (II) evidently acts differently than the corresponding dichloro-bis-ethylenediamine salt (I), because the latter, whether *cis* or *trans*, always yields the *cis*-chloro-ammino salt (Vb) when treated with aqueous ammonia.

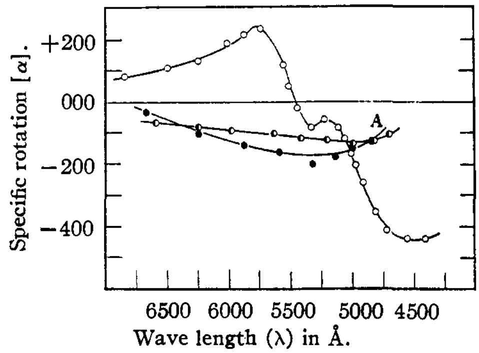


Fig. 2.—The rotatory dispersion of [Co en$_2$(NH$_3$)Cl]Cl$_2$, [Co *d*-pn$_2$(NH$_3$)Cl]Cl$_2$ and of propylenediamine: ○, [Co en$_2$(NH$_3$)Cl]Cl$_2$ (Vb) (Mathieu); ●, [Co *d*-pn$_2$(NH$_3$)Cl]Cl$_2$ (VI) prepared from *cis*-[Co *d*-pn$_2$ Cl$_2$]Cl; ◐, *levo*-propylenediamine.

The configurations of the diammino and dithiocyanato complexes [Co(AA)$_2$(NH$_3$)$_2$]$^{+++}$ and [Co(AA)$_2$(NCS)$_2$]$^+$ can be related through the conversion of the latter to the former by the action of chlorine or perhydrol. These reagents destroy the thiocyanato group, eliminating the carbon and sulfur and leaving the nitrogen (as ammonia) coordinated to the cobalt. The fact that this takes place in acid solution shows that the nitrogen-cobalt bond is not broken during the reaction, and that the diammine must therefore have the same configuration as the dithiocyanato complex from which it is derived.

No rotatory dispersion curve for [Co en$_2$(NCS)$_2$]$^+$ (IXb) was found in the literature, so a sample of the material was resolved and a curve prepared (Fig. 3). The rotations in all parts of the spectrum were low and the absorption high, so no great accuracy can be attached to the values given. However, they are sufficiently exact for our present purpose.

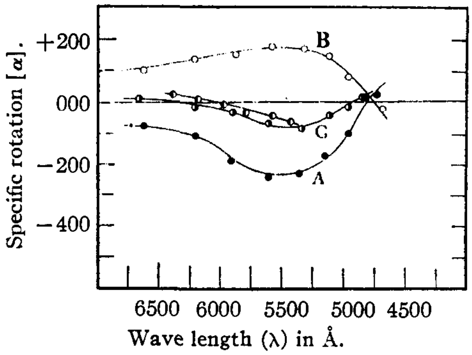


Fig. 3.—The rotatory dispersions of some complex ions of the type [M(AA)$_2$(NCS)$_2$]$^+$: ○, [Co *l*-pn$_2$(NCS)$_2$]NCS (X) prepared from *cis*-[Co *l*-pn$_2$Cl$_2$]Cl; ●, [Co *d*-pn$_2$(NCS)$_2$]NCS (X) prepared from *trans*-[Co *d*-pn$_2$Cl$_2$]Cl; ◐, *cis*-[Co en$_2$(NCS)$_2$]Cl (IX); ◑, [Cr *d*-pn$_2$(NCS)$_2$]NCS (XVI).

The dithiocyanato-bis-propylenediamine cobalt compounds (X) used in this study were prepared by the reaction of potassium thiocyanate with [Co pn$_2$ Cl$_2$]Cl (II).[9]

The products obtained from the *cis* and *trans* dichloro salts were evidently the same, as shown by the curves of Fig. 3. Here again, the rotations were low and absorptions high, so the values are not very exact. A comparison of the curves of Fig. 3, however, indicates that the propylenediamine complex (X) is quite different from the ethylenediamine compound (IXb) so must have the *trans* configuration.

Diammino-bis-*levo*-propylenediamine cobaltic chloride (VIII) was prepared by substitution of ammine groups for chlorine in *cis* and *trans* dichloro-bis-*levo*-propylenediamine cobaltic chloride (II) by allowing the salt to react with liquid ammonia at −35° and with ammonia gas at +80°, and by oxidation of the thiocyanato groups in [Co (*l*-pn)$_2$ (NCS)$_2$]NCS (X) with chlorine gas.[9] The products of all procedures gave almost identical rotatory dispersion curves. Comparison of these curves with that obtained by Mathieu for *cis*-diammino-bis-ethylenediamine cobaltic chloride (Ib) (Fig. 4) shows marked differences, in that the curve for the ethylenediamine compound shows a sharp inflection at about 5200 Å. and crosses the zero axis at about 5100 Å., while the others are positive at all wave lengths. It was therefore concluded that all of the products of our reactions were of the *trans* form. Data are given in the Experimental Section for several different reactions, but to avoid crowding on the diagram, only the results of the reaction between [Co *l*-pn$_2$Cl$_2$]Cl (II) and gaseous ammonia are shown in Fig. 4.

The sulfito salts in both series crystallize as hydrates, so might conceivably have the structure [Co(AA)$_2$(SO$_3$)H$_2$O]Cl, in which the sulfito group occupies but one coördination position, as it does,

---

[9] Werner and Dawes, *Ber.*, **40**, 791 (1907).

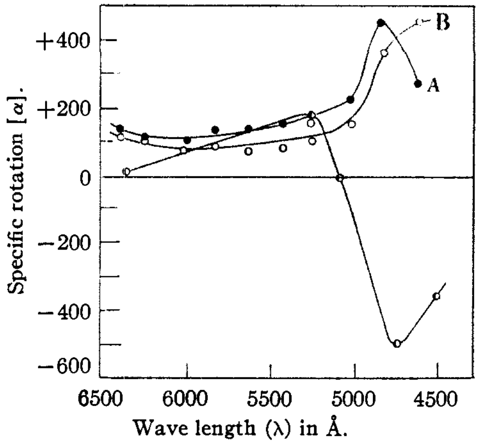


Fig. 4.—Rotatory dispersion curves of some complex ions of the type $[Co(AA)_2(NH_3)_2]^{+++}$: ●, [Co *l*-$pn_2(NH_3)_2]Cl_3$ (VIII) from *cis*-[Co *l*-$pn_2Cl_2]Cl$ and NH_3 gas; ○, [Co *l*-$pn_2(NH_3)_2]Cl_3$ (VIII) from *trans*-[Co *l*-$pn_2Cl_2]Cl$ and NH_3 gas; ◐, [Co $en_2(NH_3)_2]Cl_3$ (VII) according to Mathieu.

for example, in $NH_4[Co(NH_3)_4(SO_3)_2]$. Such a complex ion might have either the *cis* or *trans* configuration, and for a time we thought our propylenediamine complex to have the *trans* [Co $pn_2(SO_3)H_2O]^+$ structure because the dispersion curves (Fig. 5) differ markedly from the curves shown by other salts containing bidentate groups but resemble those of *trans* [Co *l*-pn_2 $X_2]^+$ salts. However, the discovery that the ethylenediamine compound is optically active proved that it must have the *cis* configuration; the striking similarity of the curves for the two series indicates that the propylenediamine compounds are also *cis*. Finally, the fact that the ethylenediamine sulfito compound can be dehydrated without change in color or loss of optical activity indicates that the water is not an integral part of the complex ion, which must, therefore, have the structure [Co en_2 $SO_3]^+$ (XI). On account of the great solubility of the corresponding propylenediamine salt, pure samples could not be obtained. The similarities between the members of the two series are so great, however, that there is little doubt that they have the same structure.

The physical properties of corresponding complex ions of cobalt and chromium are strikingly similar, as many investigators have observed. While we have not studied the reactions of chromic complexes in detail, the curves of Figs. 3 and 6 indicate that the rotatory dispersion curves of complex ions of the two elements are of the same general shape. Even though the points of inflection and points of zero rotation differ by several hundred Ångstrom units, the similarity of the curves is great enough to allow one to decide whether a complex ion of either metal is *cis* or *trans* if the configuration of an analogous complex of the other is known.

It is interesting to note that the thermal decomposition of tris-propylenediamine chromic thiocyanate leads to *cis*-dithiocyanato-bis-propylenediamine chromic thiocyanate. The corresponding reaction in the ethylenediamine series apparently yields the *trans* dithiocyanato compound.[10] This reaction is being investigated further.

Experimental

Rotatory Dispersion Curves.—The observed rotations were taken on a Schmidt–Haensch polarimeter with a prism monochromator and using a 1000-watt projection bulb as a light source. The wave lengths reported are not strictly monochromatic, but represent an average which covers about 100 Å. The polarimeter scale is graduated to 0.001°, although an accuracy of 0.01° was the best that could be obtained due to the high light adsorption by the colored solutions. Every time the wave length setting was changed the zero point of the instrument was checked, and it was found that there was some change due to the change in focus of the light source and to the different openings of the monochromator slit. The observed rotations are an average of at least five readings, and in some cases, where the light adsorption was high and the accuracy low, as many as ten readings were taken. A 1-dm. tube was used unless otherwise noted.

Dichloro-bis-ethylenediamine cobaltic chloride (I) was prepared by the usual method,[11] and the corresponding propylenediamine compound according to the directions given earlier [12]

***cis*-Dinitro-bis-*levo*-propylenediamine cobaltic nitrite** (IVb) was prepared from *levo*-propylenediamine and trinitro-triammine-cobalt as carried out by Watts.[13] The first fraction only was used. As has been pointed out in the discussion, this reaction leads to a mixture of *cis* and *trans* forms which can be separated by careful fractionation. The *trans* form was obtained in solution by refluxing the *cis* form in water for twenty-six hours. The *trans* form was also prepared by allowing the stable carbonato-bis-*levo*-propylenediamine complex (XIV) to stand in solution with a 10% excess of calcium nitrite for one week at room temperature. A mixture of *cis* and *trans* forms was obtained from a similar procedure using the unstable diastereoisomer of the carbonato compound.[5]

***cis*-Dinitro-bis-*levo*-propylenediamine Cobaltic Nitrite** (IVb).—The readings were taken upon a solution containing 0.16 g. of the salt in 100 cc. of water in the regions of higher transmission and upon a solution of one-half this concentration for the regions of higher absorption. This solution was found to be stable over several days so that all the readings could be taken upon a single solution (readings taken with 0.16% are marked with an asterisk), Curve A, Fig. 1.

Wave length	Observed rotation	Specific rotation
6400*	+0.08	+ 50
6200*	+ .09	+ 56
6000*	+ .17	+106
5900*	+ .16	+100
5800*	+ .15	+ 94
5600*	+ .10	+ 63
5400*	+ .08	+ 50
5200*	+ .12	+ 75
5000	+ .06	+ 75
4800	− .10	−125
4600 (0.04%)	− .08	−200

---

(10) Rollinson and Bailar, THIS JOURNAL, **66**, 641 (1944).

(11) Bailar, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 222.

(12) Bailar, Stiegman, Balthis and Huffman, THIS JOURNAL, **61**, 2402 (1939).

(13) Watts, "Dissertation," Zurich, Switzerland, 1912.

A solution containing 0.16 g. per 100 cc. of the *cis* dinitro compound was refluxed in water for seven hours. The rotation was then taken at selected wave lengths.

Wave length	Observed rotation	Specific rotation
5400	+0.07	+ 45
5200	+ .04	+ 25
5000	− .14	− 88

The solution was then refluxed for another ten hours.

5400	+ .04	+ 25
5200	− .06	− 38
5000	− .16	−100

The solution was then refluxed for another nine hours (Curve B, Fig. 1).

Wave length	Observed rotation	Specific rotation
6400	+0.16	+100
5900	+ .13	+ 80
5800	+ .11	+ 70
5600	+ .03	+ 20
5400	− .05	− 30
5200	− .26	−160
5000	− .32	−200

Further refluxing gave no further change. This material is evidently the pure *trans* isomer (IVa).

Dinitro-bis-*levo*-propylenediamine cobaltic nitrite (IV), prepared from the stable diastereoisomer of carbonato-bis-*levo*-propylenediamine cobaltic carbonate (XIV), was used in a solution of 0.2% concentration. Readings were taken only in the range at which the values changed from positive to negative.

Wave length	Observed rotation	Specific rotation
5800	+0.14	+ 70
5600	+ .04	+ 20
5400	− .06	− 30
5200	− .33	−165

It will be noted that this series of readings checks well with those given above for the *trans* form (IVa).

Dinitro-bis-*levo*-propylenediamine cobaltic nitrite (IV) prepared from the unstable diastereoisomer of carbonato-bis-*levo*-propylenediamine cobaltic carbonate (XIV) was used in a solution of 0.3% concentration. It was found necessary to dilute this solution for the reading at 5200 Å.

Wave length	Observed rotation	Specific rotation
6000	+0.27	+90
5600	+ .15	+50
5400	+ .10	+30
5200 (0.15%)	− .09	−60

The dispersion characteristics of the solution indicate that this reaction leads to a mixture of *cis* and *trans* forms. From the shape of the curve at the point at which the sign of the rotation changes it would seem that more of the material is of the *trans* form than the *cis*.

Chloro-amino-bis-*dextro*-propylenediamine cobaltic chloride (VI) was prepared by the method of Watts.[13] This consisted of adding aqueous ammonia to *cis*-dichloro-bis-*dextro*-propylenediamine cobaltic chloride (IIb) until the resulting solution turned deep red. This was evaporated to dryness and the residue extracted with alcohol. The extract was then evaporated to dryness, and the resulting purple-red powder dried at 105° for two hours. The salt contains one molecule of water of hydration.

Anal. Calcd.: Cl, 30.58; N, 20.10. Found: Cl, 30.56; N, 20.09.

The rotatory dispersion curve was measured on a 0.05% solution (Curve A, Fig. 2). Due to the high adsorption at the lower wave lengths, reproducible readings could not be obtained below 4800 Å.

Wave length in Å.	Observed rotation	Specific rotation
6625	−0.02	− 40
6225	− .06	−120
5892	− .07	−140
5615	− .08	−160
5360	− .10	−200
5160	− .09	−180
4985	− .08	−160
4850	− .07	−140

Dithiocyanato-bis-*dextro*-propylenediamine cobaltic thiocyanate (X) was made from dichloro-bis-*dextro*-propylenediamine cobaltic chloride (II) and potassium thiocyanate by the method of Werner and Dawes.[9] Both the *cis* and the *trans* starting material were used, and, as was shown later, both yielded the *trans* dithiocyanato salt (Xa).

Anal. Calcd.: C, 28.35; H, 5.25. Found: C, 28.57; H, 5.50. The optical rotations were taken on a 0.1% solution in a 0.5-dm. tube (Curve A, Fig. 3).

Wave length in Å.	Observed rotation	Specific rotation
6625	−0.035	− 70
6225	− .05	−100
5892	− .095	−190
5615	− .12	−240
5360	− .11	−220
5160	− .09	−180
4985	− .045	− 90
4850	00	00
4720	+ .01	+ 20

Readings were also taken on a 0.1% solution of dithiocyanato-bis-*levo*-propylenediamine cobaltic thiocyanate (X), Curve B. At the wave length marked with one asterisk, the solution was diluted with an equal volume of water, giving a 0.05% solution. At those wave lengths marked with two asterisks, the solution was again diluted with an equal volume of water, resulting in a 0.025% solution.

Wave length in Å.	Observed rotation	Specific rotation
6625	+0.10	+100
6225	+ .13	+130
5892	+ .15	+150
5615	+ .18	+180
5360	+ .17	+170
5160*	+ .07	+140
4985**	+ .02	+ 80
4850**	.00	00
4720**	− .005	− 20

Diammine-bis-*levo*-propylenediamine cobaltic chloride (VIII) was prepared from dithiocyanato-bis-*levo*-propylenediamine cobaltic thiocyanate (X) by oxidation with chlorine as reported by Werner and Dawes.[9] Further samples of diammino-bis-*levo*-propylenediamine cobaltic chloride (VIII) were prepared from *cis* and *trans* dichloro-bis-*levo*-propylenediamine (II) by allowing them to react with liquid ammonia at −33°. Samples were also prepared by passing ammonia gas over the dry *cis* and *trans* dichloro compounds at 80°. After recrystallization, the compound contains one molecule of water. *Anal.* Calcd. N, 23.01. Found for sample from *cis* dichloro and ammonia gas: N, 22.70; for sample from *trans* dichloro and liquid ammonia: N, 22.62.

The complete curves for the samples prepared from the

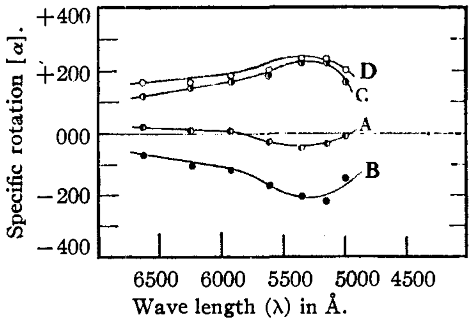


Fig. 5.—The rotatory dispersion of some complex ions of the type $[Co(AA)_2SO_3]^+$: ○, $[Co\ l\text{-}pn_2SO_3]^+$ (XII) prepared from *cis*-$[Co\ l\text{-}pn_2Cl_2]Cl$ and Na_2SO_3; ◑, $[Co\ l\text{-}pn_2SO_3]^+$ (XII) prepared from *trans*-$[Co\ l\text{-}pn_2Cl_2]Cl$ and Na_2SO_3; ●, $[Co\ d\text{-}pn_2SO_3]^+$ (XII) prepared from *trans*-$[Co\ d\text{-}pn_2Cl_2]Cl$ and Na_2SO_3; ◐, $[Co\ en_2SO_3]^+$ (XI) prepared from *levo-cis*-$[Co\ en_2Cl_2]Cl$ and Na_2SO_3.

dichloro compounds with dry ammonia at 80° were obtained. The other samples were examined only at intervals throughout the spectrum. The product of the reaction of dry ammonia upon the *cis* dichloro compound was run at a concentration of 0.1% at all wave lengths except those marked with an asterisk. The marked wave lengths were run at a concentration of 0.05% (Curve A, Fig. 4).

Wave length in Å.	Observed rotation	Specific rotation
6400	+0.13	+130
6200	+ .11	+110
6000	+ .10	+100
5800	+ .12	+120
5600	+ .13	+130
5400	+ .15	+150
5200	+ .10	+100
5000	+ .23	+230
4800*	+ .23	+460
4600*	+ .14	+280

The product prepared from the *trans* dichloro compound with dry ammonia was studied in the same manner. All readings except those marked with an asterisk were taken at 0.1%. Those marked were taken at 0.05% (Curve B, Fig. 4).

Wave length, Å.	Observed rotation	Specific rotation
6400	+0.11	+110
6200	+ .11	+110
6000	+ .08	+ 80
5800	+ .09	+ 90
5600	+ .08	+ 80
5400	+ .09	+ 90
5200	+ .16	+160
5000*	+ .08	+160
4800*	+ .19	+380
4600*	+ .23	+460

The product from the liquid ammonia and *trans* dichloro reaction was examined in a 0.1% solution. Only three wave lengths were used since the points fell well within the range of error for the curves already found.

Wave length, Å.	Observed rotation	Specific rotation
5800	+0.11	+110
5200	+ .20	+200
4800	+ .38	+380

The product of the liquid ammonia and *cis*-dichloro reaction was not isolated from the solution as it had been contaminated with sodium dithionate in an unsuccessful attempt to isolate the *trans* form as the dithionate. The concentration was approximately 0.1%. This solution was examined at only four wave lengths as the readings checked well with the curves already obtained.

Wave length, Å.	Observed rotation	Specific rotation
6400	+0.11	+110
5600	+ .12	+120
5200	+ .19	+190
4800	+ .45	+450

The product from the oxidation of the dithiocyanato complex was not isolated from solution since it was found that the solution was strongly acid and the compound decomposed on evaporation. The concentration used was approximately 0.16%. Only three wave lengths were examined since the points found fall close to the curves already obtained.

Wave length, Å.	Observed rotation	Specific rotation
6000	+0.15	+ 90
5400	+ .21	+130
4800	+ .60	+360

Sulfito-bis-ethylenediamine cobaltic chloride (XI) was prepared by the procedure of Werner and Pokrowska,[14] using optically active dichloro-bis-ethylenediamine cobaltic chloride (Ib). The material can be recrystallized from warm water and dried at 100° with only partial loss of optical activity. In order to get the largest readings possible, however, the material on which the dispersion curve was obtained was not isolated from the solution. Two hundred milligrams of optically active $[Co\ en_2Cl_2]Cl$(Ib) in 100 cc. of water was treated with 1 g. of sodium sulfite and the solution was diluted to 204 cc. Readings were taken as soon as the characteristic brown-yellow color of the sulfito salt appeared (Curve A, Fig. 5).

Wave length, Å.	Observed rotation	Specific rotation
6625	+0.04	+40
6225	+ .02	+20
5892	+ .02	+20
5615	− .02	−20
5360	− .04	−40
5160	− .02	−20
4985	− .01	−10

All attempts to isolate the sulfito propylenediamine salt (XII) in pure crystalline form proved fruitless, so the readings were made on a solution prepared by adding 1 g. (an eight-fold excess) of sodium sulfite to 200 mg. of *trans*-dichloro-bis-*dextro*-propylenediamine cobaltic chloride (II). This should yield 209 mg. of the sulfito complex, and it was on this assumption that the solution was diluted to 209 cc. to give a 0.1% solution (Curve B, Fig. 5).

Wave length in Å.	Observed rotation	Specific rotation
6625	−0.07	− 70
6225	− .10	−100
5892	− .11	−110
5615	− .17	−170
5360	− .20	−200
5160	− .22	−220
4985	− .14	−140

The same procedure as described above was used to prepare sulfito-bis-*levo*-propylenediamine cobaltic ion (XII). A 0.1% solution was used (Curve C).

---

[14] Werner and Pokrowska, *Ann.*, **386**, 81 (1912).

Wave length in Å.	Observed rotation	Specific rotation
6625	+0.11	+110
6225	+ .14	+140
5892	+ .16	+160
5615	+ .19	+190
5360	+ .22	+220
5160	+ .22	+220
4985	+ .17	+170

The following points were obtained from a 0.1% solution of sulfito-bis-*levo*-propylenediamine cobaltic ion (XII) made by the above procedure, with the exception that the *cis*-dichloro-bis-*levo*-propylenediamine cobaltic chloride (IIb) was used as a starting material rather than the *trans* (Curve D).

Wave length in Å.	Observed rotation	Specific rotation
6625	+0.16	+160
6225	+ .16	+160
5892	+ .18	+180
5615	+ .20	+200
5360	+ .24	+240
5160	+ .24	+240
4985	+ .20	+200

Dithiocyanato-bis-*dextro*-propylenediamine chromic thiocyanate (XVI) was prepared accordingly to the directions of Rollinson and Bailar.[14] Readings were taken on a 0.1% solution (Curve C, Fig. 3). At those wave lengths marked with an asterisk the solution had to be diluted with an equal volume of water because of high absorption.

Wave length in Å.	Observed rotation	Specific rotation
6625	+0.01	+10
6225	− .01	−10
5892	− .04	−40
5615	− .07	−70
5360	− .08	−80
5160*	− .02	−40
4985*	− .01	−20
4850*	+ .01	+20

While the rotations of the chromic salt (Fig. 3) are less negative at all wave lengths than those of the corresponding cobalt salt, the similarity of the curves is striking.

The curves for the dichloro-bis-ethylene (XVb) and bis-propylenediamine chromic (XVI) salts are shown in Fig. 6. The salts were prepared according to Rollinson and Bailar[10] and the former was resolved by the method of Werner.[15] Readings were taken on a 0.083% solution. At those wave lengths marked with an asterisk a 0.042% solution was used, made by diluting the original solution with an equal volume of water (Curve A, Fig. 6).

Wave length in Å.	Observed rotation	Specific rotation
6625	−0.15	−160
6225	− .07	− 84
5892	+ .03	+ 36
5615	+ .15	+180
5360	+ .33	+396
5160*	+ .18	+432
4985*	+ .10	+240
4850*	− .05	−120

Rotations of the dichloro-bis-*levo*-propylenediamine chromic salt (XVI) were taken on a 0.033% solution (Curve B).

Wave length in Å.	Observed rotation	Specific rotation
6625	+0.04	+120
6225	+ .02	+ 60
5892	− .01	− 30
5615	− .02	− 60
5360	− .12	−360
5160	− .13	−390
4985	− .06	−180
4850	+ .02	+ 60

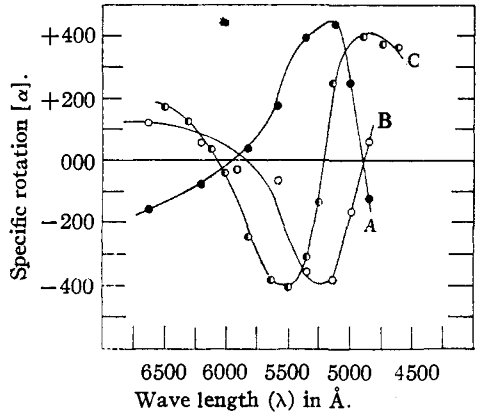


Fig. 6.—The rotatory dispersions of some complex ions of the type *cis*-$[M(AA)_2Cl_2]^+$: ○, [Cr *l*-pn_2Cl_2]Cl (XVIII); ●, *levo*-[Cr en_2Cl_2]Cl (XVII); ◐, [Co *l*-pn_2Cl_2]Cl (II) (for data, see ref. 5).

Summary

Rotatory dispersion curves have been plotted for several ethylenediamine and propylenediamine cobaltic complexes of the types $[Co(AA)_2a_2]^+$ and $[Co(AA)_2Y]^+$. These can be used to distinguish between *cis* and *trans* isomers in the propylenediamine series.

It is shown that the reaction of $[Co(NH_3)_3(NO_2)_3]$ with propylenediamine leads to a mixture of *cis* and *trans* [Co $pn_2(NO_2)_2$]NO_2(IV). Either *cis* or *trans* [Co pn_2Cl_2]Cl(II), reacting with potassium thiocyanate, leads to *trans* [Co $pn_2(NCS)_2$]$^+$ (Xa). The reaction of either *cis* or *trans* [Co pn_2Cl_2]Cl (II) with aqueous ammonia yields *trans* [Co $pn_2(NH_3)Cl$]Cl_2 (VIa) and with anhydrous ammonia, *trans* [Co $pn_2(NH_3)_2$]Cl_3 (VIIIa). The reaction with aqueous ammonia is particularly interesting, as the corresponding reaction in the ethylenediamine series leads to the *cis* isomer (VIIb).

The reaction of sodium sulfite with *trans* [Co pn_2Cl_2]Cl (IIa) gives [Co pn_2SO_3]$^+$ (XII), in which the sulfite ion acts as a bidentate group.

The similarity between the rotatory dispersion curves shown by analogous complexes of cobalt and chromium is pointed out, with the suggestion that it may serve as a means of determining configurations.

URBANA, ILLINOIS RECEIVED DECEMBER 26, 1946

---

[15] Werner, *Ber.*, **44**, 3132 (1911).