The Stereochemistry of Complex Inorganic Compounds. XXXI.[1] Optical Inversions in the Reactions of Some Optically Active α-Dihalotriethylenetetraminecobalt(III) Cations with Ammonia and Ethylenediamine

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Abstract: The reaction of optically active α-$[CoX_2(trien)]^+$ with liquid ammonia at low temperature or with ethylenediamine under various conditions at room temperature leads to an optical inversion. On the other hand, ammonation by gaseous ammonia at higher temperatures leads chiefly to a retention of configuration but with a great loss of optical activity. The reaction with 1,10-phenanthroline in pyridine solution at its boiling point also leads chiefly to retention of configuration with much racemization. Optically active β-$[CoX_2(trien)]^+$ reacts with ethylenediamine at room temperature with retention of configuration. The optical inversions are believed to take place by a "back-side attack" by the incoming group, which is NH_2^- or $NH^-CH_2CH_2NH_3^+$.

In the previous paper,[1] it was pointed out that an optical inversion can take place only in reactions of a complex having a geometrical structure which allows a "back-side attack." Since *cis*-$[CoCl_2(en)_2]^+$ undergoes an optical inversion in its reaction with ammonia at low temperature,[2] a similar reaction would be expected with $[CoX_2(trien)]^+$. An analogous result might be anticipated with ethylenediamine at room temperature. The complex $[Co(en)(trien)]^+$ has been prepared,[3] but its structure is unknown.

The mechanism and stereochemistry of the reactions are probably essentially the same as for the optical inversion in the base hydrolysis of *cis*-$[CoX_2(en)_2]^+$. It has been proposed that the optical inversion results from a "back-side attack" by OH^- as the incoming group.[1,4,5] Thus since the presence of $[Ag(NH_3)_2]^+$ has no effect in the base hydrolysis of *cis*-$[CoCl_2(en)_2]^+$,[6] a similar behavior would be expected in the ammonation of α-$[CoX_2(trien)]^+$ with liquid ammonia due to the easy formation of $[Ag(NH_3)_2]^+$ from the silver salt and liquid ammonia.

A comparison of the reactions of α- and β-$[CoX_2(trien)]^+$ under similar reaction conditions is interesting. We wish to report here the optical inversions observed in the reactions of both liquid ammonia and anhydrous ethylenediamine with α-$[CoX_2(trien)]^+$.

Results and Discussion

The ammonation of either α- or β-$[CoX_2(trien)]^+$ leads to $[Co(NH_3)_2(trien)]^{3+}$. The ammonation of D*-α-$[CoX_2(trien)]^+$ in liquid ammonia at −33°, like the base hydrolysis,[5] proceeds with inversion of configuration. The presence of silver nitrate exerts no effect on the reaction. In the ammonation with gaseous ammonia, the degree of retention of configuration is small, but definite. The product showed a low optical activity, probably because the reaction mixture was kept at an elevated temperature for a long time. In general, the rate of ammonation in liquid ammonia is much faster than that in gaseous ammonia.

The optical rotatory dispersion curves for L*-β-$[Co(NH_3)_2(trien)]^{3+}$, L*-β-$[Co(en)(trien)]^{3+}$, and L*-β-$[CoCl_2(trien)]^+$ are shown in Figure 1.

The reaction of D*-α-$[CoCl_2(trien)]^+$ with anhydrous ethylenediamine, like that with liquid ammonia at −33°, leads to a product with inverted configuration, L*-β-$[Co(en)(trien)]^{3+}$. But L*-β-$[CoCl_2(trien)]^+$, under the same conditions, gave the same product, with retention of configuration. These results resemble those observed in the base hydrolysis of α- and β-$[CoX_2(trien)]^+$. The reaction of D*-α-$[CoCl_2(trien)]Cl$ with gaseous ethylenediamine at 120° gave a completely inactive product. The data are summarized in Table II.

The reaction of D*-α-$[CoCl_2(trien)]Cl$ with 1,10-phenanthroline (phen) in pyridine gives D*-α-$[Co(phen)(trien)]Cl_3$ with a low optical activity. At 115.5°, the reaction was completed in 12 hr and showed $\alpha^{25}D$ $+0.004 \pm 0.001°$ and $[\alpha]^{25}D$ $+20 \pm 5°$. The steric course of the reaction may depend upon the fact that the nitrogen atoms of phen cannot become negative by loss of a proton. This allows the phen to make a "front-side attack."[1]

The amide ion in liquid ammonia or the zwitterion of ethylenediamine can play the role of a base in these systems just as the hydroxide ion does in aqueous solution. The scheme of reactions is outlined in Figure 2.

The postulate of a "back-side attack" by OH^-, NH_2^-, or $NH^-CH_2CH_2NH_3^+$ gives a logical explanation for the inversion. A possible mechanism of the optical inversion in liquid ammonia is shown in Figure 3. There is a possibility of a "front-side attack" by the positive end of the zwitterion, but this reaction is very slow, as is the acid hydrolysis of $[CoCl_2(trien)]^+$. The reaction with ammonia at room temperature, the *cis* product from which is mostly of the configuration of the starting material, is believed to proceed by a "front-side attack" by neutral ammonia molecules.

It is unknown whether the intermediate $[CoCl(NH_3)(trien)]^{2+}$ gives $[Co(NH_3)_2(trien)]^{3+}$ with preponderance

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[1] Paper XXX: E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1120 (1966).

[2] R. D. Archer and J. C. Bailar, Jr., *ibid.*, **83**, 812 (1961).

[3] F. Basolo, *ibid.*, 70, 2034 (1948).

[4] L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 3658 (1964).

[5] E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *ibid.*, **87**, 4458 (1965).

[6] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *ibid.*, **85**, 1215 (1963).

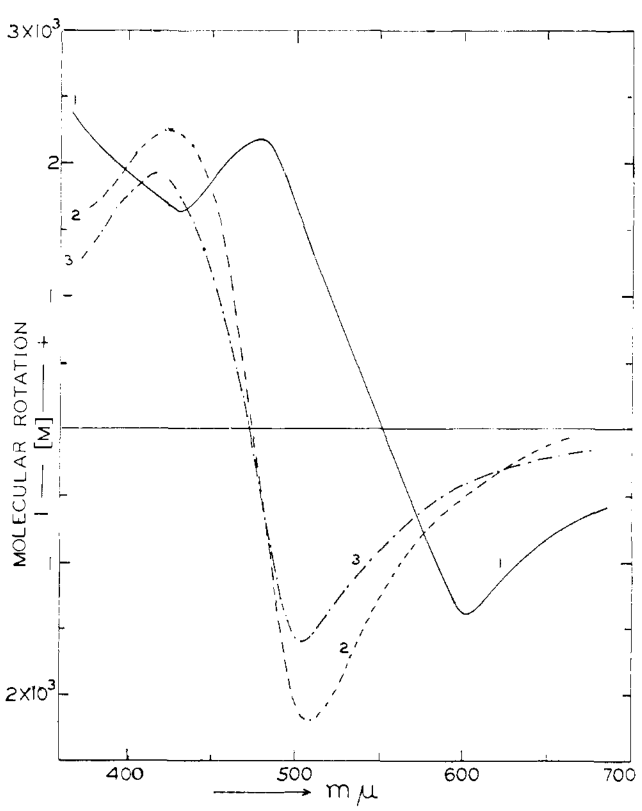

Figure 1. Optical rotatory dispersion of (1) (−)-D-β-[CoCl$_2$(trien)]Cl, (2) (−)-D-β-[Co(en)(trien)]Cl$_3$, and (3) (−)-D-β-[Co(NH$_3$)$_2$(trien)]Cl$_3$.

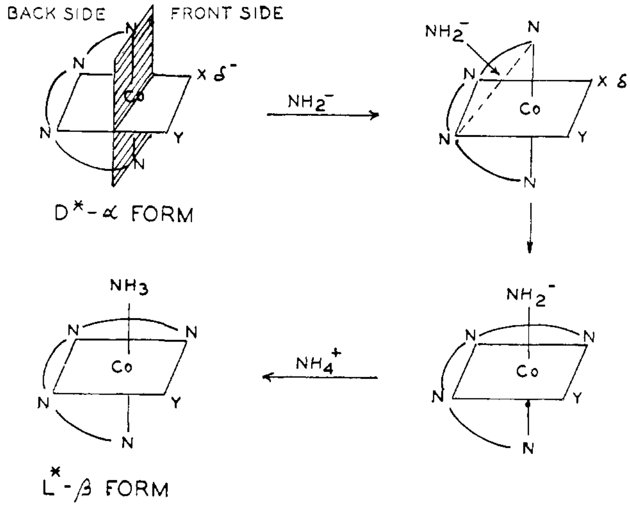

Figure 3. A possible mechanism of the optical inversion in liquid ammonia.

of optical inversion. It would be expected to give inversion, as the second step in the base hydrolysis does.[5] The repulsion between the attacking amide anion and the negatively charged chloro ligand favors "back-side attack" over "front-side attack." Also, "back-side attack" is favored by the possibility of temporary ion-pair formation through a hydrogen bond between the lone pair of the amide ion and the hydrogen atoms of the coordinated amine.

One other factor, undoubtedly, is important in the geometry of the complex in these reactions. According to crystal-field theory, an optical inversion requires the formation of a pentagonal bipyramid or square pyramid with lower crystal field splitting energy than an intermediate.[7] Therefore it is proposed that only complexes having suitable geometry and CFSE will undergo reactions with optical inversion. No examples of inversion have been found in the reactions of complexes of chromium, rhodium, or platinum. A search for such inversion is now underway.

Experimental Section

The preparation and resolution of the following materials were carried out according to standard procedures: D*-α-[CoCl$_2$(trien)]Cl,[5] L*-β-[CoCl$_2$(trien)]Cl,[1] and L*-β-[CoBr$_2$(trien)]Br.[1]

D*-α-Dibromotriethylenetetraminecobalt(III) Bromide (D*-α-[CoBr$_2$(trien)]Br. A finely powdered and dried sample of D*-α-[Co(ox)(trien)]NO$_3$[5] (3.6 g, 0.01 mole) was suspended in 80 ml of absolute ethanol and cooled in an ice bath; dry HBr gas was bubbled into the solution for 15 min. The solution was kept for 2 days at room temperature. It was then filtered, and the product was washed with small amounts of ethanol and ether: yield 2.4 g (77%), $[\alpha]^{25}\mathrm{D}$ +1900°, $[M]^{25}\mathrm{D}$ +8455° (0.1% aqueous solution).

Anal. Calcd for [CoBr$_2$C$_6$H$_{18}$N$_4$]Br: C, 16.19; N, 12.59; H, 4.08. Found: C, 16.21; N, 12.52; H, 3.94.

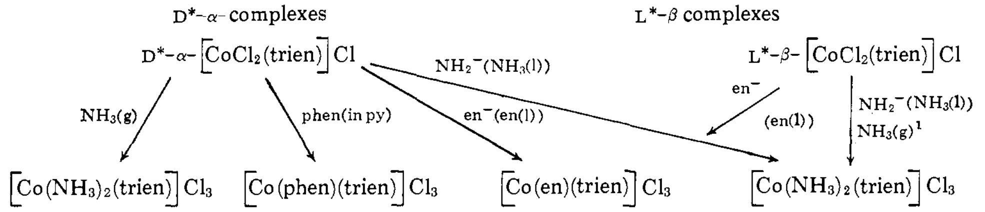

Figure 2. Reactions of *cis*-[CoCl$_2$(trien)]$^+$ with ammonia, anhydrous ethylenediamine, and 1,10-phenanthroline.

The chief bands in the infrared spectrum for D*-α-[CoBr$_2$(trien)]Br are 3130 (m), 3100 (m), 1570 (s), 1305 (m), 1193 (w), 1183 (m), 1053 (s), 1030 (m), 790 (m), 768 (w), 670 (s), 637 (m), 575 (m), 550 (m), 483 (s), and 425 (s).

Ammonation in Liquid Ammonia. The data reported in Table I were obtained as follows.

Conversion of D*-α-[CoCl$_2$(trien)]Cl to L*-β-[Co(NH$_3$)$_2$(trien)]Cl$_3$. A finely powdered sample of D*-α-[CoCl$_2$(trien)]Cl (1.6 g, 0.005 mole) was added to 20 ml of liquid ammonia in a Dry Ice-acetone bath. Moisture was excluded by the use of soda lime traps. When the temperature rose to the boiling point of ammonia, the solution changed from violet to orange. At the end of the reaction period the excess ammonia was allowed to evaporate. About 30 ml of ethanol was added to the yellow residue and the mixture was filtered. The product was washed with ethanol and ether and air dried: yield 1.4 g (81%); for a 0.2% aqueous solution, $\alpha^{25}\mathrm{D}$ −0.020 ± 0.002°, $[\alpha]^{25}\mathrm{D}$ −100 ± 10°.

Anal. Calcd for [CoC$_6$H$_{24}$N$_6$]Cl$_3$: C, 21.14; N, 24.04; H, 7.00. Found: C, 21.16; N, 24.20; H, 7.03.

Ammonation of D*-α-[CoBr$_2$(trien)]Br. The ammonation of D*-α-[CoBr$_2$(trien)]Br (2.2 g, 0.005 mole) was carried out in the same way: yield 2.0 g (83%); for a 0.2% aqueous solution, $\alpha^{25}\mathrm{D}$ −0.015 ± 0.002°, $[\alpha]^{25}\mathrm{D}$ −75 ± 10°.

Anal. Calcd for [CoC$_6$H$_{24}$N$_6$]Br$_3$: N, 17.12. Found: N, 17.20.

The reaction of D*-α-[CoCl$_2$(trien)]Cl and D*-α-[CoBr$_2$(trien)]Br in the presence of AgNO$_3$ was carried out in the same way except

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(7) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 5.

Table I. Ammonation of D*-α-[CoX$_2$(trien)]$^+$

State of ammonia	Reaction temp, °C	Complex	Other metal ion	Reaction time, days	Product	
					α^{25}D^a	[α]^{25}D^a
Liquid	−33	D*-α-[CoCl$_2$(trien)]Cl	. . .	1	−0.020 ± 0.002	−100 ± 10
Liquid	−33	D*-α-[CoCl$_2$(trien)]Cl	Ag NO$_3$	1	−0.020	−100
Liquid	−33	D*-α-[CoBr$_2$(trien)]Br	. . .	1	−0.015	−75
Liquid	−33	D*-α-[CoBr$_2$(trien)]Br	Ag NO$_3$	1	−0.016	−80
Gas	+100	D*-α-[CoCl$_2$(trien)]Cl	. . .	10	+0.008 ± 0.001	+40 ± 5
Gas	+100	D*-α-[CoBr$_2$(trien)]Br	. . .	10	+0.006	+30

[a] Throughout the paper, the values of α^{25}D are expressed in degrees/centimeter and those of [α]^{25}D, in degrees × 100/decimeters × grams of solute.

Table II. Reactions of α- and β-[CoCl$_2$(trien)]$^+$ with Ethylenediamine

State of ethylenediamine	Reaction temp, °C	Complex	Product	
			α^{25}D	[α]^{25}D
Anhydrous	40	D*-α-[CoCl$_2$(trien)]Cl	−0.030 ± 0.002	−150 ± 10
Anhydrous	4	D*-α-[CoCl$_2$(trien)]Cl	−0.032	−160
50% aqueous soln	25	D*-α-[CoCl$_2$(trien)]Cl	−0.028	−140
Anhydrous	40	L*-β-[CoCl$_2$(trien)]Cl	−0.038	−190
Anhydrous	8	L*-β-[CoCl$_2$(trien)]Cl	−0.034	−170
50% aqueous soln	25	L*-β-[CoCl$_2$(trien)]Cl	−0.030	−150

that 1.7 g (0.01 mole) of AgNO$_3$ was added to the liquid ammonia.

For 0.2% aqueous solutions of purified product from D*-α-[CoCl$_2$(trien)]Cl, the following values were obtained: α^{25}D −0.020 ± 0.002°, [α]^{25}D −100 ± 10°; from D*-α-[CoBr$_2$(trien)]Br, α^{25}D −0.016 ± 0.002°, [α]^{25}D −80 ± 10°.

Ammonation in Gaseous Ammonia. Ammonation of D*-α-[CoCl$_2$(trien)]Cl. A slow stream of ammonia gas was passed over 1.6 g (0.05 mole) of finely powdered D*-α-[CoCl$_2$(trien)]Cl which was heated to about 100°. The reaction was completed in 10 days as was indicated by the change in the color of the complex from blue-violet to yellow. The product was dissolved in a small amount of water and was then reprecipitated by the addition of a large amount of absolute ethanol. The reprecipitated product was filtered and washed with ethanol and ether, and dried in a vacuum desiccator: yield 1.3 g (74%); for a 0.2% aqueous solution, α^{25}D +0.008 ± 0.001°, [α]^{25}D +40 ± 5°.

Anal. Calcd for [CoC$_6$H$_{24}$N$_6$]Cl$_3$: C, 21.14; N, 24.02; H, 7.00. Found: C, 21.22; N, 24.26; H, 6.89.

The ultraviolet spectrum in aqueous solution of D*-α-[Co(NH$_3$)$_2$-(trien)]Cl$_3$ showed the following absorption maxima (10^3 cm^{-1} (log ε)): ν_1, 21.05 (1.99); ν_2, 29.41 (1.98); ν_3, 40.94 (4.03).

The chief bands in the infrared spectra are for D*-α-[Co(NH$_3$)$_2$-(trien)]Cl$_3$: 3120 (sh), 1690 (s), 1320 (sh), 1120 (w), 1063 (s), 1038 (m), 1015 (sh), 848 (w), 770 (m), 721 (m), 670 (m), 645 (m), 570 (s), 501 (s), 434 (s), 366 (s), and 310 (s); for L*-β-[Co(NH$_3$)$_2$-(trien)]Cl$_3$: 3110 (sh), 3080 (sh), 1650 (s), 1335 (s), 1300 (sh), 1280 (m), 1180 (w), 1170 (w), 1136 (w), 1080 (m), 1055 (s), 1030 (sh), 818 (w), 781 (m), 664 (w), 606 (m), 550 (m), 513 (m), 488 (m), 392 (w), 374 (m), 351 (m), and 324 (m).

The ammonation of D*-α-[CoBr$_2$(trien)]Br (2.2 g, 0.005 mole) was carried out in the same way; yield 1.8 g (77%); for a 0.2% aqueous solution, α^{25}D +0.006 ± 0.001°, [α]^{25}D +30 ± 5°.

Anal. Calcd for [CoC$_6$H$_{24}$N$_6$]Br$_3$: N, 17.12. Found: N, 17.30.

Reaction with Anhydrous Ethylenediamine. The data reported in Table II were obtained as follows.

Reaction with D*-α-[CoCl$_2$(trien)]Cl. A finely powdered sample of D*-α-[CoCl$_2$(trien)]Cl (1.6 g, 0.005 mole) was added to 10 ml of anhydrous ethylenediamine[8] at room temperature. When the mixture was ground with a glass rod, an exothermic reaction took place. The violet color of the complex changed to dark brown and its temperature rose to 40°. After cooling the product, 30 ml of absolute ethanol was added and the mixture filtered. The product was washed with ethanol and ether in turn. The material was purified by reprecipitating it from aqueous solution by the addition of a mixture of 2 ml of concentrated HCl and a large amount of ethanol: yield 1.5 g (81%); for a 0.2% aqueous solution, α^{25}D −0.030 ± 0.002°, [α]^{25}D −150 ± 10°.

Anal. Calcd for [CoC$_8$H$_{26}$N$_6$]Cl$_3$: C, 25.85; N, 22.59; H, 7.05. Found: C, 25.66; N, 22.49; H, 7.01.

In another experiment, the materials were cooled in an ice bath, but the temperature rose to 4° because of the heat of reaction: for 0.2% aqueous solution, α^{25}D −0.032 ± 0.002°, [α]^{25}D −160 ± 10°.

Anal. Calcd for [CoC$_8$H$_{26}$N$_6$]Cl$_3$: C, 25.85; N, 22.59; H, 7.05. Found: C, 25.66; N, 22.49; H, 7.01.

Reaction of Anhydrous Ethylenediamine with L*-β-[CoCl$_2$(trien)]Cl. In a similar way, L*-β-[CoCl$_2$(trien)]Cl was converted to L*-β-[Co(en)(trien)]Cl$_3$ at 40°; yield 1.5 g (81%); for a 0.2% aqueous solution, α^{25}D −0.038 ± 0.002°, [α]^{25}D −190 ± 10°.

Anal. Calcd for [CoC$_8$H$_{26}$N$_6$]Cl$_3$: N, 22.59. Found: N, 22.69.

Even when the reactants were cooled in an ice bath, the temperature rose to 8°; for a 0.2% aqueous solution, α^{25}D −0.034 ± 0.002°, [α]^{25}D −170 ± 10°.

Reaction of 50% Ethylenediamine Aqueous Solution. This experiment was carried out in the same way, using 50% ethylenediamine in place of anhydrous ethylenediamine. D*-α-[CoCl$_2$-(trien)]Cl was converted to L*-β-[Co(en)(trien)]Cl$_3$. Absorption ultraviolet and infrared spectra were identical with those of L*-β-[Co(en)(trien)]Cl$_3$ prepared from L*-β-[CoCl$_2$(trien)]Cl and anhydrous ethylenediamine: for a 0.2% aqueous solution, α^{25}D −0.030 ± 0.002°, [α]^{25}D −150 ± 10°. The ultraviolet spectrum in aqueous solution of L*-β-[Co(en)(trien)]Cl$_3$ showed the following absorption maxima (10^3 cm^{-1} (log ε)): ν_1, 21.37 (1.95); ν_2, 29.42 (1.92); ν_3, 45.05 (4.69). The infrared spectrum of L*-β-[Co(en)(trien)]Cl$_3$ showed bands at 3140 (sh), 3020 (sh), 1730 (sh), 1600 (s), 1420 (sh), 1320 (w), 1275 (w), 1170 (m), 1153 (m), 1090 (w), 1060 (s), 1032 (m), 832 (w), 789 (m), 736 (s), 610 (m), 575 (w), 560 (s), 530 (m), 513 (m), 483 (s), 466 (s), 378 (m), 345 (w), and 310 (m).

Reaction of Ethylenediamine Vapor. A slow stream of dry air was bubbled into anhydrous ethylenediamine which was kept at about 80°. The stream containing ethylenediamine vapor was passed over 1.6 g (0.05 mole) of finely powdered D*-α-[CoCl$_2$-trien)]Cl which was heated to about 120° (3.5° above the boiling point). The reaction was completed in 1 week, as was indicated by the change in color of the complex from blue-violet to yellow.

The product was dissolved in a small amount of water and was precipitated by the addition of a large amount of ethanol.

The purified product was dried in a vacuum desiccator, yield 1.5 g (81%); an aqueous solution was completely inactive.

Anal. Calcd for [CoC$_8$H$_{26}$N$_6$]Cl$_3$: N, 22.59. Found: N, 22.70.

Reaction of D*-α-[CoCl$_2$(trien)]Cl with 1,10-Phenanthroline in Pyridine. A mixture of finely powdered D*-α-[CoCl$_2$(trien)]Cl

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[8] Prepared from a mixture of 10 g of sodium metal and 100 ml of ethylenediamine (98-99%) which was allowed to stand for 1 day at room temperature. The ethylenediamine was distilled and collected at 116.5°.

(1.0 g, 0.005 mole) and 1,10-phenanthroline (1.5 g, 0.0075 mole) in 80 ml of anhydrous pyridine was heated to reflux for 12 hr. The yellow product was washed with ethanol and ether and air dried, yield 2.2 g (90%). Purification was carried out as before: for a 0.2% aqueous solution, α^{25}D +0.004 ± 0.001, $[\alpha]^{25}$D +20 ± 5°.

Anal. Calcd for $[CoC_{18}H_{20}N_6]Cl_3$: C, 43.96; N, 17.09; H, 5.33. Found: C, 44.22; N, 17.2; H, 5.14.

The ultraviolet spectrum (in aqueous solution) of D*-α-[Co(phen)(trien)]Cl_3 showed the following absorption maxima (10^3 cm^{-1} (log ϵ)); ν_1, 21.28 (2.10); ν_2, 28.49 (2.82); ν_3, 29.8 (3.01) (sh); ν_4, 31.47 (3.41) (sh); ν_5, 36.36 (4.18); ν_6, 44.64 (4.48). The infrared spectrum of D*-α-[Co(phen)(trien)]Cl_3 showed bands at 3050 (sh), 1610 (m), 1340 (sh), 1230 (w), 1140 (m), 1065 (s), 1045 (s), 1025 (m), 870 (sh), 850 (s), 792 (m), 776 (m), 695 (w), 645 (sh), 621 (w), 580 (w), 488 (s), 394 (w), 374 (w), 322 (w), and 306 (s).

Apparatus. The apparatus used was the same as described in an earlier paper.[1]

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The Stereochemistry of Complex Inorganic Compounds. XXXII. The Stereochemistry of the Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Ion and the Bis(diaminobiphenyl)platinum(II) Ion

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Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois. Received August 16, 1965

Abstract: The ethylenediamine-2,2′-diaminobiphenylplatinum(II) ion has been resolved into optically active forms. The asymmetry arises from the noncoplanarity of the two phenyl rings, which is maintained by their attachment to the metal ion. Aqueous solutions of the isomers show no loss of optical activity in 140 min at room temperature. Dichloro-2,2′-diaminobiphenylplatinum(II) and its isomer, bis(diaminobiphenyl)platinum(II) tetrachloroplatinate(II), were prepared and characterized. The bis(diaminobiphenyl)platinum(II) ion might exist in both racemic and *meso* forms, but no evidence for the existence of such isomerism was seen. The ion proved to be too unstable for resolution.

It has long been known that derivatives of biphenyl having bulky substituents in the 2,2′, 6, and 6′ positions exist in the form of optical isomers because the two rings of the biphenyl cannot be in the same plane and are not free to rotate about their common axis. If there are substituent groups in only the 2 and 2′ positions, the rings can rotate and racemization is rapid.

If a metal ion is coordinated to substituents in the 2,2′ positions of the biphenyl derivatives, it should be possible to separate the resulting complex compound into optically active isomers, because coordination with the metal ion prevents rotation of the phenyl rings. McCollough and Bailar[1] prepared bis(ethylenediamine-2,2′-diaminobiphenyl)cobalt(III) chloride and resolved it into four isomeric forms, which can be designated as D*d*, D*l*, L*d*, and L*l*, the capital letters representing the optical activity inherent in the complex and the small letters the activity of the ligand. Although their evidence is quite clear, the demonstration of the asymmetry of the diaminobiphenyl group might be considered to be more solidly established if it were the only asymmetry in the complex, so it was decided to attempt the preparation and resolution of complexes of this type. The complexes chosen for study were the ethylenediamine-2,2′-diaminobiphenylplatinum(II) ion and the bis(2,2′-diaminobiphenyl)platinum(II) ion.

Experimental Section

Preparation of Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Chloride. Dichloroethylenediamineplatinum(II) was prepared by the method of Heneghan and Bailar,[2] and diaminobiphenyl by the method of Lloyd and McDougall.[3] From these two, ethylenediamine-2,2′-diaminobiphenylplatinum(II) chloride was prepared as follows. Diaminobiphenyl (4.65 g, 0.025 mole) and $[Pt(en)Cl_2]$ (5.65 g, 0.025 mole) were placed in a flask containing 200 ml each of alcohol and water. The mixture was stirred mechanically at 75–85° for 2 hr on a steam bath. The suspended yellow crystals of $[Pt(en)Cl_2]$ slowly dissolved to give a colorless solution. This solution was evaporated to dryness at 30° by use of a rotary evaporator. The crystals were washed with absolute alcohol and ether and air dried. They were then recrystallized from water, washed with alcohol and ether, and dried at 50° for 8 hr *in vacuo*. The resulting white crystalline product (yield 85.3%) melted with decomposition at 260°.

Anal. Calcd for $[Pt(en)(dabp)]Cl_2$: C, 32.95; H, 3.95; N, 10.98; Pt, 38.23; Cl, 13.89. Found: C, 33.00; H, 4.07; N, 11.29; Pt, 38.10; Cl, 14.40. The infrared spectrum of $[Pt(en)(dabp)]Cl_2$, which was taken on the Beckman IR5A, is given in Table I.

The Resolution of Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Ion. Equimolar amounts of $[Pt(en)(dabp)]Cl_2$ (2.1 g or 0.041 mole) and silver tartrate[4] (1.5 g, 0.041 mole) were dissolved in 500 ml of water. The silver chloride was filtered off, and the filtrate was concentrated to saturation (200 ml). The desired $[Pt(en)(dabp)][C_4H_4O_6]$ was then precipitated by adding alcohol, filtered, washed with alcohol, and dried at 50° *in vacuo* (yield 74.7%).

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