Geometric and Optical Isomers of Cobalt(III) Complexes Containing Two Moles of the Cyclic Tridentate Ligand Derived from *o*-Aminobenzaldehyde[1]

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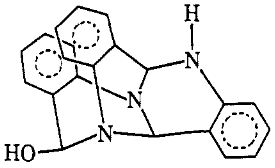
Abstract: A study of the self-condensation of *o*-aminobenzaldehyde in the presence of cobalt ions has led to the isolation of two series of compounds which have been characterized as geometric isomers of the cobalt(III) complex, $Co(TRI)_2X_3 \cdot nH_2O$, where TRI is the closed tridentate macrocyclic ligand, tribenzo[*b,f,j*][1,5,9]triazacycloduodecine, X is NO_3, Cl, Br, I, NCS, BF_4, PF_6, and ClO_4, and *n* is 1–5. The racemic isomer *dl*-$Co(TRI)_2^{3+}$ has been resolved into its optical antipodes. ORD and CD data are reported. Evidence is presented which suggests that the other isomer should be formulated as *meso*-$Co(TRI)_2^{3+}$. The observed isomerism depends on the relative progression of ring members in the two cyclic ligands.

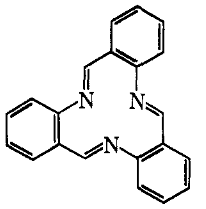
It is known that *o*-aminobenzaldehyde condenses with itself to form two products: a bisanhydro trimer, 13-hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline, structure I, and a trisanhydro tetramer, whose structure can be obtained from I by replacing the -OH group with a $-NHC_6H_4CHO$ moiety.[2]



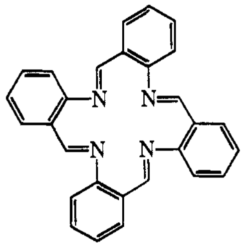
I

In the presence of metal ions, the self-condensation proceeds in a different manner, and metal complexes with macrocyclic Schiff base ligands are formed. Complexes containing either a closed tridentate ligand, tribenzo[*b,f,j,*][1,5,9]triazacycloduodecine, abbreviated TRI, structure II, and/or a cyclic tetradentate ligand, tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, abbreviated TAAB, structure III, have been prepared and characterized.[3–6] X-Ray crystal studies of the nickel(II) complexes have confirmed the existence of the two Schiff base ligands.[7,8]

Since the products formed *via* self-condensation of *o*-aminobenzaldehyde in the presence of metal ions are different from those formed in their absence, the condensation must be governed by coordination template effects. By looking at the reaction products obtained in the presence of different metal ions, certain characteristics of the metal ion template may be inferred.



II



III

Initial studies of the metal ion induced condensation emphasized reaction with nickel(II) and copper(II) ions. Both $Ni(TRI)^{2+}$ and $Ni(TAAB)^{2+}$ complexes were isolated from the reaction of *o*-aminobenzaldehyde with nickel(II) ions.[4,6] Exclusive synthesis of $Ni(TRI)^{2+}$ complexes was achieved by rearrangement of one equivalent of the bisanhydro trimer, structure I, in the presence of nickel, while $Ni(TRI)_2^{2+}$ complexes were formed in the metal ion induced rearrangement of two equivalents of the bisanhydro trimer.[9] The nickel(II) complex containing one TRI ligand was separated into its optical antipodes by resolution on columns packed with potato starch.[10] Attempts to resolve the bis(tridentate)–nickel complex were unsuccessful.

In contrast to these results, self-condensation of *o*-aminobenzaldehyde, as well as rearrangement of the bisanhydro trimer, in the presence of copper(II) ions produces complexes containing exclusively the tetradentate ligand, $Cu(TAAB)^{2+}$.[9] This result had been predicted in view of the usual stereochemistry of the copper(II) ion, and illustrates the stereoselectivity of the metal ion acting as a template for the ring-forming reaction.

Investigations of the *o*-aminobenzaldehyde condensation have now been extended to include reaction in the presence of cobalt(II) ions, with subsequent isolation of the cobalt(III) complexes. As in the nickel(II) case, evidence has been found for complexes with both the TAAB and TRI ligands. Cobalt complexes containing the TAAB ligand will be discussed in a later publication. This report describes the synthesis and characterization of two geometric isomers of the bis tridentate complex, $Co(TRI)_2^{3+}$. One of the geometric isomers has been successfully resolved into its optical antipodes. This marks the first example of geometric isomerism noted among the macrocyclic complexes derived from *o*-aminobenzaldehyde, and the first successful resolution of a metal complex containing two TRI ligands.

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(1) Abstracted in part from the Ph.D. Dissertation of S. C. Cummings, The Ohio State University, 1968.

(2) S. G. McGeachin, *Can. J. Chem.*, **44**, 2323 (1966).

(3) G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

(4) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4830 (1964).

(5) G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

(6) G. A. Melson and D. H. Busch, *ibid.*, **87**, 1706 (1965).

(7) E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

(8) E. B. Fleischer, University of Chicago, Chicago, Ill., unpublished results.

(9) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Amer. Chem. Soc.*, **88**, 3170 (1966).

(10) L. T. Taylor and D. H. Busch, *ibid.*, **89**, 5372 (1967).

Table I. Analytical Data for Isomers of $Co(TRI)_2X_3 \cdot nH_2O$

Isomer	Formulation	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % X^a or S	Found, % C	Found, % H	Found, % N	Found, % X^a or S
A	$Co(TRI)_2(NO_3)_3 \cdot 2H_2O$	56.10	3.82	14.00		56.30	3.55	14.31	
B^b		56.10	3.82	14.00		56.34	3.42	14.36	
A	$Co(TRI)_2I_3 \cdot 3H_2O$	45.35	3.27	7.56	34.22	45.40	3.11	7.63	33.95
B^b		45.35	3.27	7.56		45.50	2.80	7.49	34.22
A	$Co(TRI)_2Cl_3 \cdot H_2O$	62.89	4.03	10.48	13.26	62.40	4.00	10.02	13.71
B	$Co(TRI)_2Cl_3 \cdot 3H_2O$	60.18	4.34	10.03	12.69	59.60	4.07	9.90	12.57
A	$Co(TRI)_2Br_3 \cdot 2H_2O$	52.90	3.61	8.83	25.15	53.05	3.30	9.17	25.04
B	$Co(TRI)_2Br_3 \cdot 5H_2O$	50.06	4.01	8.34	23.79	50.03	4.54	8.34	24.06
A	$Co(TRI)_2(NCS)_3 \cdot 3H_2O$	59.65	4.01	13.92	10.62	60.12	3.67	13.79	10.43
B	$Co(TRI)_2(NCS)_3 \cdot 2H_2O$	60.80	3.87	14.20	10.82	60.50	4.07	13.54	10.32
A	$Co(TRI)_2(BF_4)_3 \cdot H_2O$	52.75	3.38	8.79	23.85	52.74	3.40	8.64	16.88
B	$Co(TRI)_2(BF_4)_3 \cdot 3H_2O$	50.84	3.66	8.47	22.98	51.00	3.24	8.24	18.79
A	$Co(TRI)_2(ClO_4)_3 \cdot 2H_2O$	49.80	3.39	8.30	10.50	50.11	3.18	8.25	10.75
B^b		49.80	3.39	8.30		49.76	3.02	8.26	10.15
B	$Co(TRI)_2(PF_6)_3 \cdot H_2O$	44.61	2.86	7.43	30.25	45.02	3.18	6.95	29.25

[a] Where X = a halogen atom. [b] Formulation same as for isomer A.

Experimental Section

Materials. *o*-Aminobenzaldehyde was prepared using the method of Smith and Opie.[11] The resolving agent, *d*-dibenzoyltartaric acid, was synthesized from *d*-tartaric acid and benzoyl chloride[12] and was recrystallized from benzene–hexane before use. All other chemicals were obtained commercially and were of reagent grade or equivalent.

Reaction of *o*-Aminobenzaldehyde with Cobalt(II) Nitrate. Freshly prepared *o*-aminobenzaldehyde (12.1 g, 0.1 mol) was dissolved in 40 ml of absolute ethanol and brought to reflux temperature. A solution of $Co(NO_3)_2 \cdot 6H_2O$ (7.28 g, 0.025 mol) in 40 ml of absolute ethanol containing 3–4 drops of concentrated HNO_3 was slowly added. The color of the solution changed from yellow to red-brown. After 30 min of refluxing, a gray-black solid precipitated. The mixture was stirred and refluxed for a total of 8 hr. After chilling, the mixture was filtered. The solid was washed with ethanol and ether and dried, *in vacuo*, at 100°, yield ~ 70%.

Isolation of Bis(tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine)cobalt(III) Nitrate Dihydrate. The dark gray material from above (5 g) was washed by stirring in 250 ml of hot methanol for 30 min, and the insoluble material was collected by vacuum filtration. The washing procedure was repeated until the solid remaining was maroon in color and the methanol filtrates were no longer green but brown, yield ~ 50%. The maroon solid was dissolved with stirring and heating in 250 ml of methanol which had been acidified with 10–15 ml of concentrated HNO_3. The resulting orange solution was concentrated and chilled. The yellow and orange platelets which formed were collected, washed with chilled methanol and ether, and dried, *in vacuo*, at room temperature, yield ~50%. *Anal.* Calcd for $CoC_{42}H_{34}N_9O_{11}$: C, 54.96; H, 3.96; N, 13.74. Found: C, 55.06; H, 4.24; N, 13.47.

Separation of Geometric Isomers of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$. The mixture of yellow and orange platelets described above was separated into a pure orange form, called isomer A, and a pure yellow form, called isomer B, by fractional recrystallization from acidic 1-propanol. For example, when 1.0 g of the mixture was stirred in 1 l. of hot 1-propanol containing 10 ml of concentrated HNO_3, approximately 0.25 g was recovered as isomer A, which is essentially insoluble in the alcohol. The remaining 0.75 g was recovered as isomer B by concentration of the propanol filtrates. Both isomers were washed with ether and dried, *in vacuo*, at 100°. Analytical results appear in Table I.

Preparation of Other Derivatives of Bis(tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine)cobalt(III), $Co(TRI)_2X_3 \cdot nH_2O$. General Procedure. A 1.0-g sample of either the A or B form of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$ was dissolved in 250 ml of methanol or water. To this was added a solution containing a fourfold molar excess of the required sodium salt. Several drops of the corresponding acid were also added, whenever available.

The I, NCS, BF_4, PF_6, and ClO_4 derivatives precipitated immediately. The corresponding Cl and Br complexes were obtained by concentrating and chilling their solutions.

All products were recrystallized several times from acidic methanol. The complexes were then collected and washed with chilled methanol and ether. The PF_6 and BF_4 derivatives were dried, *in vacuo*, at room temperature. All others were vacuum dried at 100°. These procedures gave yields of ~80%. Analytical data are reported in Table I.

Resolution of *dl*-$Co(TRI)_2(NO_3)_3 \cdot 2H_2O$. To a solution of 1.35 g of *dl*-$Co(TRI)_2(NO_3)_3 \cdot 2H_2O$, isomer B, which had been dissolved in 200 ml of hot water, was added 200 ml of a 1:1 methanol–water solution containing 1.59 g (0.0049 mol) of *d*-dibenzoyltartaric acid. A yellow powder precipitated immediately. The mixture was stirred for several hours and allowed to cool to room temperature. The (+)-*d*-dibenzoyltartrate diastereoisomer was collected, washed with chilled methanol, and dried, *in vacuo*, at room temperature, yield ~40%. *Anal.* Calcd for $CoC_{96}H_{85}N_6O_{26}$: C, 64.20; H, 4.78; N, 4.67. Found: C, 64.58; H, 4.52; N, 4.37.

The filtrate was concentrated on a rotary evaporator to a volume of 100 ml. The solid which precipitated (a mixture of enantiomers and excess resolving agent) was removed and discarded. Evaporation of the remaining filtrate produced the other antipode as the nitrate, (−)-$Co(TRI)_2(NO_3)_3 \cdot 2H_2O$. The product was recrystallized from methanol which had been acidified with a few drops of concentrated HNO_3, washed, and dried, *in vacuo*, at 100°, yield ~40%. *Anal.* Calcd for $CoC_{42}H_{34}N_9O_{11}$: C, 56.0; H, 3.82; N, 14.00. Found: C, 56.44; H, 3.67; N, 14.41.

Synthesis of (+)- and (−)-$Co(TRI)I_3 \cdot 3H_2O$. The *d*-dibenzoyltartrate diastereoisomer was recrystallized twice from methanol, $[\alpha]_{524}$ +1600. A 1.0-g sample was then ground in a mortar and pestle with 2.0 g of potassium iodide which had been dissolved in about 5 ml of methanol containing a few drops of hydriodic acid. During the grinding, the color of the paste changed from yellow to red-brown. The mixture was taken up in 300 ml of hot methanol. The resulting solution was filtered and concentrated to a volume of 5 ml. The brick-red crystals which formed, $(+)_{524}$-$Co(TRI)_2I_3 \cdot nH_2O$, were collected and washed with methanol. The crystals turned maroon during vacuum drying at 100°, yield ~90%. *Anal.* Calcd for $CoC_{42}H_{36}N_6I_3O_3$: C, 45.34; H, 3.27; N, 7.56; I, 34.22. Found: C, 45.50; H, 2.80; N, 7.36; I, 34.43. Two recrystallizations from acidic methanol with 50% product recovery were necessary to achieve constant rotation, $[\alpha]_{524}$ +4526.

A 0.52-g sample of $(-)_{524}$-$Co(TRI)_2(NO_3)_3 \cdot 2H_2O$ was dissolved in 50 ml of water and added to a solution of 2.0 g of potassium iodide in 20 ml of water containing a few drops of hydriodic acid. Brick red crystals, $(-)_{524}$-$Co(TRI)_2I_3 \cdot nH_2O$, formed immediately. The mixture was chilled and the crystals were collected and washed. Upon drying, *in vacuo*, at 100°, the crystals turned maroon, yield ~80%. *Anal.* Calcd for $CoC_{42}H_{36}N_6I_3O_3$: C, 45.34; H, 3.27; N, 7.56; I, 34.22. Found: C, 45.44; H, 2.93; N, 7.47; I, 34.47. Two recrystallizations from acidic methanol were necessary to achieved constant rotation, $[\alpha]_{524}$ −4515.

Partial resolution was achieved by a single passage of an aqueous solution of *dl*-$Co(TRI)_2(BF_4)_3 \cdot 3H_2O$ through a column packed with potato starch. This method was not pursued since the procedure using the resolving agent was more efficient.

Infrared Spectra. A Perkin-Elmer 337 recording infrared spectrophotometer was used to measure the infrared spectra of the

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[11] L. I. Smith and J. W. Opie, *Org. Syn.*, **28**, 11 (1948).

[12] D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **78**, 3061 (1956).

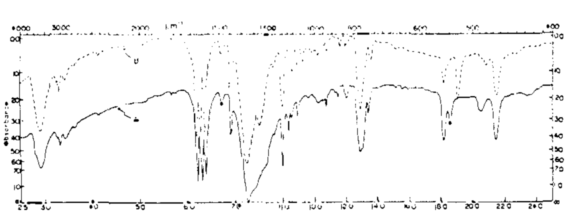

Figure 1. Infrared spectra (KBr disks) of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$: isomer A, ——; isomer B, - - - - -.

complexes. Both potassium bromide and Nujol mull techniques were utilized. Polystyrene was used for calibration.

Electronic Spectra. Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Solution spectra were run in 1-cm quartz cells. Spectra of solid samples were measured in Nujol mulls using the diffuse transmittance technique.[13]

Optical Rotatory Dispersion and Circular Dichroism. The ORD and CD spectra were determined using a Durrum-Jasco ORD/UV-5 recording spectrophotometer, Durrum Instrument Corp., Palo Alto, Calif. Measurements were conducted in 1-cm quartz cells using $\sim 10^{-4}$–10^{-5} *M* aqueous solutions.

Molar Conductivities. Electrical resistances of solutions were measured using an Industrial Instruments, Inc. Model RC 16B conductivity bridge. Distilled water was used as the solvent.

Magnetic Measurements. Magnetic susceptibilities were measured using both the Gouy and Faraday methods. Susceptibilities of ligands and anions were calculated from Pascal's constants.[14]

Analyses. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.[15]

Table II

Compound	Old results and formulation		New results and correct formulation		
	Calcd	Found	Calcd	Found (2 methods)	
meso-$Co(TRI)_2I_3 \cdot 3H_2O$	7.93	8.04	5.36	5.36	5.52
dl-$Co(TRI)_2I_3 \cdot 3H_2O$	7.93	7.80	5.36	5.41	5.46
meso-$Co(TRI)_2(NSC)_3 \cdot 3H_2O$	9.87	9.34	6.50	7.08	7.10
dl-$Co(TRI)_2(NCS)_3 \cdot 2H_2O$	9.87	9.32	6.64	7.10	6.94

Results and Discussion

Self-condensation of *o*-aminobenzaldehyde in the presence of cobalt(II) ions produces a mixture of products. Purification of the crude material by washing with methanol followed by oxidation of the product with concentrated nitric acid has led to the isolation of a yellow-orange material which can be formulated as $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$. Two crystalline forms, denoted A and B, have been separated by fractional recrystallization from acidic 1-propanol. Metathetical reactions have been used to synthesize two distinct series of complexes of the type $Co(TRI)_2X_3 \cdot nH_2O$, where X is Cl, Br, I, NCS, BF_4, PF_6, and ClO_4, and *n* is 1–5.

These compounds have been characterized as complexes containing the fully cyclized ligand, tribenzo-[*b,f,j*][1,5,9]triazacycloduodecine, TRI, structure II, on the basis of elemental analyses, infrared and mass spectra, and a single-crystal X-ray structure determination.[16] Analytical data are presented in Table I.[15]

The infrared spectra of all of the complexes, when taken in Nujol mulls, show traces of water, but the extent of hydration is uncertain. The formulations given in Table I are those which provided the best fits for the analytical data. Fluorine analyses of the BF_4 and PF_6 derivatives are usually lower than expected. This may be due to problems with the analytical technique used, or to partial hydrolysis of the fluorine containing anion to form BF_3OH^- and PF_5OH^- species. Sharp bands in the 3500–3300-cm^{-1} region of the infrared spectra of the BF_4 and PF_6 complexes, which are absent from the spectra of the other derivatives, suggest the latter possibility. Similar bands in the spectra of the BF_4 derivatives of $Ni(1,7\text{-}CT)^{2+}$, a macrocyclic complex prepared by condensation of $Ni(en)_3^{2+}$ with acetone,[17] have been attributed to hydrolysis of the BF_4 group.[18]

The presence of a fully cyclized ligand in both the A and B series of complexes is indicated by the infrared spectra. The absence of any bands which might be assigned to the $-NH_2$ or $>C=O$ stretching frequencies, and the appearance of a strong band at ~ 1568 cm^{-1}, which is attributed to the coordinated $>C=N$ stretching mode, suggests the formation of a cyclized structure containing Schiff base linkages. Strong peaks at ~ 1613 and ~ 1590 cm^{-1} and medium peaks at ~ 1492 and ~ 1452 cm^{-1} can be correlated with the usual modes of *ortho*-disubstituted benzene.

Spectra of the $Co(TRI)_2X_3$ complexes are similar to those of the corresponding $Ni(TRI)_2X_2$ compounds with one exception; the intensity of the $>C=N$ stretching mode in the nickel(II) case is weak for the TRI compounds and strong for the TAAB complexes. While this provided a convenient means of differentiating between the two types of nickel macrocycles,[5] it cannot be generally applied to the TRI and TAAB complexes of other metals.

The infrared spectra of the A and B forms of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$, which are illustrated in Figure 1, have been useful in differentiating between these two forms. Slight differences in band intensities occur in the region 1613–1570 cm^{-1}. A more noticeable difference occurs in the region 500–600 cm^{-1}; namely, the band at 538 cm^{-1} in compound A is replaced by a more intense band at 523 cm^{-1} in compound B. No explanation for these differences can be given; however, they persist for every derivative within a given series. The infrared spectrum of the parent mixture of A and B forms is a composite of the two spectra shown in Figure 1. A tabulation of the complete infrared spectra of both nitrate derivatives is reported in Table III.

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(13) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 3, 1279 (1964).

(14) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 403.

(15) Commercial cobalt analyses on more than 30 samples of these complexes, submitted over a period of 2.5 years, were consistently high by 40–50%. This suggested the presence of only two anions per cobalt ion, and led to an earlier but incorrect formulation of these compounds as cobalt(II) dimers containing the tetradentate ligand, $Co_2(TAAB)_2X_2 \cdot nH_2O$: S. C. Cummings, G. A. Melson, and D. H. Busch, *Inorg. Nucl. Chem. Lett.*, 1, 69 (1965); Abstracts, 155th National Meeting of the American Chemical Society, April 1968. The same commercial laboratory is now able to get reasonable values for cobalt analyses on these compounds by two methods. An illustration of the situation is found in Table II. Columns 2 and 3 give expected and found results consistent with the formulation $Co_2(TAAB)_2X_2 \cdot nH_2O$. The "found" data were all obtained at least 18 months ago. Columns 4, 5, and 6 report data consistent with the formulation $Co(TRI)_2X_3 \cdot mH_2O$. The "found" data are quite recent. In view of the problems encountered, cobalt analyses are not published in support of the conclusions contained herein. The two formulations are indistinguishable on the basis of analyses for other elements alone.

(16) R. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, 92, 1929 (1970).

(17) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(18) L. G. Warner, Ph.D. Thesis, The Ohio State University, 1968.

Table III. Infrared Spectra of Isomers of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$[a]

Isomer A[b]	Assignments[c]	Isomer B[b]
3420 (m)	H_2O	3455 (m)
3062 (vw)		3070 (vw)
3008 (w)	CH st	3008 (w)
2916 (vw)	CH st	2920 (vw)
1614 (vs)	C_6—ring I	1611 (vs)
1591 (vs)	C_6—ring II	1590 (vs)
1572 (s)	C═N st	1571 (vs)
1492 (w)	C_6—ring III	1493 (w)
1452 (m)	C_6—ring IV	1452 (m)
1388 (vs)	NO_3	1385 (vs)
1357 (vs, sh)	NO_3	1332 (s)
1322 (s, sh)	NO_3	1319 (s, sh)
1283 (w)		1285 (w)
1253 (m)		1252 (m)
1192 (w)		1192 (w)
1170 (vw)		1170 (vw)
1118 (vw)		1120 (vw)
1036 (vw)		1040 (vw)
975 (w)		978 (w)
930 (vw)		928 (w)
870 (w)		861 (w)
833 (w)		838 (w)
		828 (w)
775 (s)	CH def	774 (s)
767 (s, sh)	CH def	767 (s, sh)
746 (w)		741 (w)
549 (m)		548 (m)
538 (w)		
		523 (m)
488 (w)		481 (w)
466 (m)		464 (m)

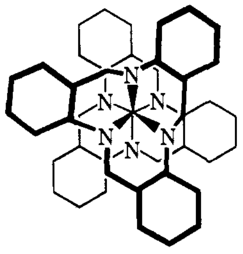
[a] KBr disks. [b] Values given in cm.$^{-1}$. [c] Abbreviations: m, medium; w, weak; vw, very weak; s, strong; vs, very strong; sh, shoulder.

Mass spectra provide convincing evidence for the presence of the TRI ligand in both series of complexes.[19] Although the cobalt compounds are not very volatile, mass spectra were obtained for the A and B bromide derivatives. The most striking feature of both spectra is an intense peak at 308. Peaks at 308 and 310 in the mass spectra of $Ni(TRI)Cl_2$ and $Ni(TRI)_2Br_2$, respectively, are characteristic of the TRI complexes and have been assigned as $(TRI\text{-}H)^+$ and $(TRI + H)^+$. On the basis of the similarities in the mass spectra of all of these compounds, it is almost certain that both the A and B series of cobalt complexes contain the TRI ligand. The existence of TRI in the B complexes has been established by the aforementioned X-ray crystal study.[16]

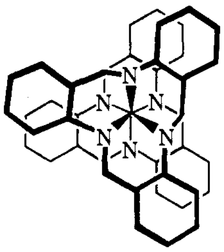
The presence of cobalt(III) in the compounds is consistent with the results of measurement of magnetic susceptibilities, conductivities, and electronic spectra. The derivatives in both series are essentially diamagnetic, exhibiting only small residual paramagnetisms of ~0.5 BM, typical of spin-paired cobalt(III). In 10^{-3} *M* aqueous solutions, Λ_M values calculated for the derivatives vary from 325 to 486 ohm^{-1}, indicating 3:1 electrolyte behavior.

Electronic reflectance (diffuse transmittance) spectra of all derivatives are broad but do show absorption bands attributable to the cation in the regions of ~21,800 and ~28,500 cm^{-1}. These have been assigned, as a first approximation, to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions characteristic of (pseudo) octahedral cobalt(III). The higher energy band can also be observed in the absorption spectra measured in aqueous solution; however, it exhibits much greater intensity than is expected for normal d–d transitions (ϵ_{350} ~35,000). The lower energy band is completely obscured. Both of these phenomena have been attributed to the presence of high-energy charge-transfer bands in the ultraviolet, which have a broad tail extending into the visible region.

Because the A and B forms have the same elemental compositions and contain the same ligand and the same numbers of anions, they have been characterized as geometric isomers. The existence of geometric isomers in this system can be explained by the relative progression of ring members in the two cyclic ligands. From structure II, it is evident that the TRI ligand contains a definite repeating unit, –C–N–benzene. When two TRI ligands are simultaneously bound to the cobalt(III) ion, the stereochemistry depends on the relative direction in which the repeating units progress in the two macrocycles. Structures IV and V are useful in clarifying this explanation.



IV



V

The above structures represent the direction in which the C–N–benzene repeating units progress in each cycle, when viewed from an external point along the threefold axis. A *meso* form results when the ring members of the two ligands progress in the same direction, structure IV. A racemic form is produced when the ring members of each cycle progress in opposite directions, structure V. These relationships are well illustrated by projecting down the threefold axis as shown in earlier discussions of the $Ni(TRI)_2{}^{2+}$ case.[10]

The existence of *dl*-$Co(TRI)_2{}^{2+}$ was first indicated by the resolution of $Co(TRI)_2(NO_3)_3 \cdot 2H_2O$, isomer B. When an excess of *d*-dibenzoyltartaric acid was added to an aqueous solution of the nitrate complex, the $(+)_{524}$ enantiomer was selectively precipitated as the highly insoluble diastereoisomer, $(+)_{524}$-$Co(TRI)_2$(*d*-DBT)$_3 \cdot 8H_2O$. After two recrystallizations from methanol, a constant rotation of +1600 was observed. The enantiomer was further purified by conversion to the corresponding iodide, $(+)_{524}$-$Co(TRI)_2I_3 \cdot 3H_2O$, which was recrystallized to constant rotation, $[\alpha]_{524}$ +4526. The $(-)_{524}$ enantiomer was initially obtained as the nitrate by concentration of the filtrate which remained after the (+)-*d*-dibenzoyltartrate salt had been removed. It too was purified by conversion to the iodide, $(-)_{524}$-$Co(TRI)_2I_3 \cdot 3H_2O$. After two recrystallizations, a constant rotation was observed, $[\alpha]_{524}$ −4515. Solutions of the resolved isomers are stable to racemization for periods of several months. Inertness toward ligand dissociation was also noted in the resolved complexes of $Ni(TRI)(H_2O)_3{}^{2+}$.[10]

An absolute handedness cannot be assigned to the asymmetry of $Co(TRI)_2{}^{3+}$ on the basis of the chirality

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(19) P. Thornton and D. H. Busch, unpublished results.

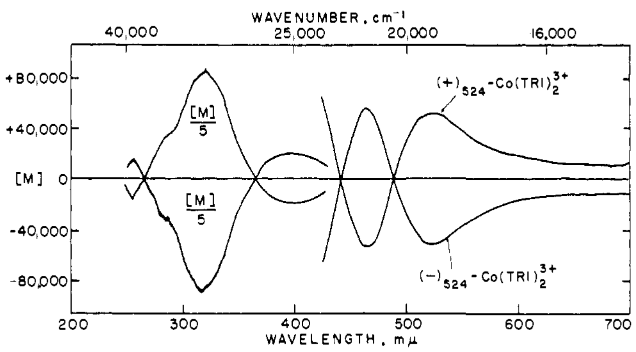

Figure 2. Optical rotatory dispersion of (+)$_{524}$- and (−)$_{524}$-Co(TRI)$_2$I$_3$ in 10^{-4} *M* solutions. Characteristic wavelengths, λ (mμ), and corresponding rotations for the (+)$_{524}$ and (−)$_{524}$ isomers, respectively, are as follows: 524, +4526, −4515; 491, 0, 0; 465, −4750, +4745; 442, 0, 0; 390, +8420, 8410; 365, 0, 0; 318, −36,700, +36,700; 285, −13,750, +13,750.

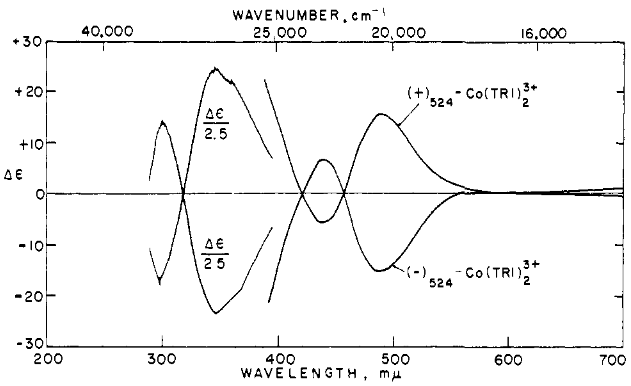

Figure 3. Circular dichroism of (+)$_{524}$- and (−)$_{524}$-Co(TRI)$_3$I$_3$ in 10^{-4} *M* aqeuous solutions. Characteristic wavelengths, λ (mμ), and corresponding Δε for the (+)$_{524}$ and (−)$_{524}$ isomers, respectively, are as follows: 491, +15.5, −15.5; 442, −6.0, +6.0; 364, +52.3, −51.2; 346, −60.3, −60.3; 300, −40.8, +34.1.

rules derived for octahedral chelates.[20] However, a definite chirality is imparted to the complex due to the helical nature of the TRI ligands. Each TRI ligand resembles a three-bladed propeller due to the tilt of the benzene rings. Consequently, the chirality of Co(TRI)$_2$$^{3+}$ may be either right-handed or left-handed and the corresponding isomers would be designated Δ or Λ using Piper's notation.[21] Wing and Eiss have properly resolved the question of absolute configuration for this compound.[16]

Optical rotatory dispersion and circular dichroism of aqueous solutions of (+)$_{524}$- and (−)$_{524}$-Co(TRI)$_2$I$_3$ are illustrated in Figures 2 and 3. Data obtained from the ORD and CD curves are presented along with the figures.

It will be recalled that the absorption spectra of Co(TRI)$_2$$^{3+}$ in the visible region exhibit two broad bands, at ~21,800 cm^{-1} (460 mμ) and at ~28,500 cm^{-1} (350 mμ). These could be interpreted on the basis of (pseudo) octahedral symmetry about the cobalt(III) ion. The CD spectra of the resolved isomers clearly identify at least two components for each band, at 491, 442 and 364, 346 mμ, as is expected since the effective molecular symmetry is of lower degree. From models and the results of the crystal study, it is evident that the local symmetry of Co(TRI)$_2$$^{3+}$ is D$_3$ and that the CD spectrum should be more correctly interpreted using this point group. The electronic states of this substance are discussed in greater detail by Wing and Eiss.[16]

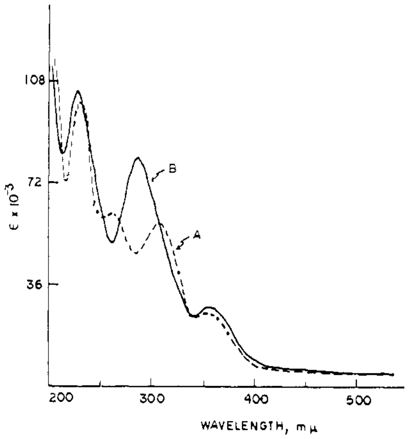

Figure 4. Ultraviolet spectra of isomers of Co(TRI)$_2$$^{3+}$ in aqueous solutions: isomer A, - - - - - -; isomer B, ———.

Attempts to resolve the A isomer using the same methods which were employed in isomer B proved unsuccessful. Similarly, attempts to interconvert the A and B isomers in neutral and acidic solutions failed. This suggests that isomer A may be *meso*-Co(TRI)$_2$$^{3+}$, structure V, in which the relative progression of ring members in the two TRI ligands is in the same direction. The noninterconvertibility of the geometric isomers, just as the nonracemization of the optical isomers, requires the complexes to be inert toward dissociation of the ligand. All evidence suggests this to be true, as indeed it should be, in view of the general inertness of cobalt(III).

Dreiding stereomodels, as well as stereographic projections of Co(TRI)$_2$$^{3+}$ obtained from the X-ray crystal study, show that there is considerable overlap of the benzene rings in the two TRI ligands. The distance between nonbonded benzene rings in the racemic form has been shown to be ~3.0 Å. That expected for the *meso* isomer is somewhat longer, ~3.5 Å. It is known from studies of the paracyclophanes[22] that π systems of overlapping benzene rings can interact, causing splitting of the $\pi \rightarrow \pi^*$ bands observed in the ultraviolet region of the spectrum. Similar interactions might be anticipated for the benzene rings of racemic Co(TRI)$_2$$^{3+}$. The benzene rings of the *meso* isomer are expected to interact less strongly.

The ultraviolet spectra of *dl*-Co(TRI)$_2$$^{3+}$ and unresolved isomer A are shown in Figure 4. The band at 345 mμ in the spectrum of each isomer has already been assigned to the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. It is probable that the remaining bands are due to parity-allowed transitions within the ligand. The spectrum of *dl*-Co(TRI)$_2$$^{3+}$ exhibits bands at 228 and 286 mμ. The spectrum of unresolved isomer A contains the band at 230 mμ, while that at 286 mμ appears to have split into two bands at 260 and 308 mμ. The spectrum of Ni(TRI)(H$_2$O)$_3$$^{2+}$ provides a useful comparison. Since only one TRI ligand is present in this nickel complex, there is no opportunity for interaction between nonbonded

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(20) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).

(21) T. S. Piper, *ibid.*, **83**, 3908 (1961).

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benzene rings, and the ultraviolet spectrum should be that of unperturbed TRI. Bands are observed at 325 and 275 mμ, and the spectrum is similar to that illustrated for isomer A. This suggests little if any interaction between benzene rings in isomer A and is consistent with its formulation as *meso*-Co(TRI)$_2{}^{3+}$. It is probable that the different absorption pattern observed in the spectrum of isomer B, *dl*-Co(TRI)$_2{}^{3+}$, results from the interactions of overlapping benzene rings, as predicted.

Acknowledgment. This investigation was supported in part by U. S. Public Health Service Grant No. GM-10040 from the Institute of General Medical Sciences. We are indebted to Dr. Keith Farmery for repeating many of these experiments.

Evidence for Piper's Model of Optical Activity. The Structure and Absolute Configuration of $(+)_{5461}$-Bis(tribenzo[*b,f,j*]-[1,5,9]triazacycloduodecine)cobalt(III) Iodide[1]

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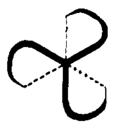
Abstract: The absolute configuration of $(+)_{5461}$-bis(tribenzo[*b,f,j*][1,5,9]triazacycloduodecine)cobalt(III) iodide has been determined from an X-ray diffraction study. The symmetry of the complex ion is D_3, and like most other known trigonal (pseudo-octahedral) transition-metal complexes it possesses a small (8°) twist distortion about the threefold axis. This distortion is in the counterclockwise direction as is the case for Λ-(+)-Co(en)$_3$, which has a remarkably similar circular dichroism spectrum in the region of the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{1g} \leftarrow {}^1A_{1g}$ optical transitions of d^6 octahedral cobalt(III). We suggest that this correspondence constitutes experimental support for Piper's model of optical rotation in trigonal complexes. The crystals studied belong to space group $P2_12_12_1$ with a_0 = 19.592 (3), b_0 = 14.609 (3), and c_0 = 14.508 (3) Å. The observed density was 1.79 g/cm^3, with 1.74 g/cm^3 calculated for four formula units in the cell. The structure was solved using 3297 statistically significant unique reflections collected by a counter method, and refined to a final *R* factor of 0.043. The mean Co–N bond is 1.923 (5) Å, and the mean distance between adjacent phenyl rings is 3.2 Å.



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Trigonal cobalt(III) has been an important testing ground for theories,[3–7] and models[8,9] of optical rotation, with the goal being the determination of absolute configurations[10–13] from the optical data. The pivotal point in the use of the optical data has been the assignment of the low-energy doublet generally observed at *ca.* 4800 Å in the circular dichroism (CD) spectra. Progress has been somewhat hampered, however, due to the need to rest heavily on studies of ions of the type Co(AA)$_3{}^{n+}$, **1**, for which Saito, *et al.*,[14] have provided the basis of discussion through their determination of the absolute configuration of the (+)-Co(en)$_3{}^{3+}$ ion. The major difficulty with the above system is the stereochemical flexibility of the chelate rings.[15] Although the single crystal CD study of (+)-Co(en)$_3{}^{3+}$ by Ballard, McCaffery, and Mason[16] has resolved some of the uncertainties in the assignment of the doublet, *vide supra*, the ambiguities persist for solution spectra. Workers have, therefore, sought other criteria for judging assignments, the most widely used being the ion-pair effect.[17–19] In brief, it has been proposed[19] that the primary effect on the CD spectrum of adding an ion such as PO$_4{}^{3-}$ to a solution of **1** is an increase in the intensity of the ${}^1A_2 \leftarrow {}^1A_1$ component of the trigonally split ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition while the ${}^1E_a \leftarrow {}^1A_1$ com-

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(1) $(+)_{5461}$-Co(TRI)$_2$I$_3\cdot$3H$_2$O, where TRI is tribenzo[*b,f,j*][1,5,9]triacycloduodecine.

(2) (a) Riverside; (b) Portland.

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