$(ClO_4)_4 \cdot H_2O$, 37540-73-1; $[Co_2(NH_3)_9(H_2O)(C_2O_4)]Br_4 \cdot 2H_2O$, 37523-51-6; $[(NH_3)_5Co(C_2O_4H)](ClO_4)_2$, 15293-41-1; $[Co_2(NH_3)_4(NO_2)_4(C_2O_4)]$, 37548-99-5; $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3](NO_3)_4 \cdot 2H_2O$, 36593-60-9; $[(NH_3)_3Co\text{-}\mu(NH_2,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3$, 37549-00-1; $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3]Br_4$, 37523-52-7; $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$, 37540-75-3; $[Co(NH_3)_4CO_3]ClO_4$, 37549-01-2.

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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Synthesis of Peroxo- and Superoxodicobalt(III) Complexes of 2,2′,2″-Triaminotriethylamine

CHEN-HWA YANG and MERLAND W. GRIEB*

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Complex compounds $[NH_3(tren)CoOOCo(tren)NH_3]X_4 \cdot nH_2O$, where X = Cl with $n = 2$ and X = Br, I, NO_3, or ClO_4 with $n = 0$, were prepared by aeration of stoichiometric amounts of 2,2′,2″-triaminotriethylamine (tren), ammonia, and the corresponding cobalt(II) salt in aqueous solution. The pyridine (py) analog $[py(tren)CoOOCo(tren)(py)]I_4 \cdot H_2O$ was made similarly. The cations of these salts were somewhat unstable in aqueous solution and gradually transformed to stable $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ ion, the perchlorate salt of which also was prepared directly by aeration of solutions of tren and Co^{2+}. The rate of transformation was retarded by excess ammonia in the solution. The compounds $[(tren)Co(O_2,NH_2)Co(tren)]X_3 \cdot nH_2O$, where X = I with $n = 0$ and X = ClO_4 with $n = 1$, were obtained by ligand replacement. The corresponding superoxo complexes $[NH_3(tren)CoOOCo(tren)NH_3](ClO_4)_5 \cdot 2H_2O$, $[(tren)Co(O_2,NH_2)Co(tren)](ClO_4)_4 \cdot 2H_2O$, and (probably) $[H_2O(tren)CoOOCo(tren)H_2O](ClO_4)_5$ were prepared by oxidation of peroxo compounds. The electronic absorption spectra of these complexes were obtained and compared with the spectra of related binuclear species.

Introduction

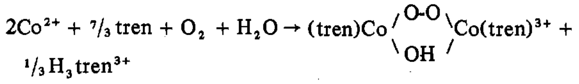
Binuclear, peroxo-bridged complexes of cobalt, which form upon reaction of cobalt(II)-amine complexes with molecular oxygen have evoked much recent interest.[1] Stoichiometric studies of solutions containing the linear ligand triethylenetetramine (trien) showed that the oxygen uptake reaction involved 2 mol of triethylenetetramine and cobalt(II) and 1 mol of oxygen.[2,3] Further investigations revealed that the ultimate product was doubly bridged $[(trien)Co(O_2,OH)Co(trien)]^{3+}$ [4] but that a singly bridged intermediate with nonbridging hydroxide ion ligand was consistent with kinetic observations.[5] A singly bridged peroxo compound, $[NH_3(trien)CoOOCo(trien)NH_3](ClO_4)_4 \cdot 2H_2O$ has been isolated,[6] as well as doubly bridged $[(trien)Co(O_2,NH_2)Co(trien)]^{4+}$, although details of the latter superoxo complex are not available.[7]

Doubly bridged peroxo complexes of cobalt in which the second bridge is the hydroxide ion have been recognized recently,[4,5,8] and two, with ethylenediamine[9] and *l*-propylenediamine[10] ligands, have been isolated.

We report herein the synthesis of singly and doubly bridged peroxo- and superoxocobalt(III) complexes containing 2,2′,2″-triaminotriethylamine corresponding to each type described above. Interest in this ligand derives from the fact that it affords fewer possibilities for isomerism in coordination complexes than does its linear isomer. While the methods employed in this study did not show isomerism in the binuclear ions, we have reported the two possible isomers of a mononuclear decomposition product of one of them.[11]

Results and Discussion

Addition of 2,2′,2″-triaminotriethylamine [tren, $N(CH_2CH_2NH_2)_3$] to an aerated solution of cobalt(II) ion results in a change of color from pink to brown. It was found spectrophotometrically that only one product, which had an absorption maximum at 350 nm, was formed at room temperature independent of the ratio of amine to cobalt. The reaction was very fast and quantitative, going to completion well within 10 min in a 10^{-4} *M* unbuffered solution. Oxygen uptake measurements taken at 30° (Figure 1) also showed a single reaction up to the ratio of 1.16 mol of 2,2′,2″-triaminotriethylamine to 1 mol of cobalt(II), at which point 0.5 molar equiv of O_2 was absorbed. Consistent with the known triprotic basicity of 2,2′,2″-triaminotriethylamine,[12] the reaction stoichiometry is best expressed by eq 1. When the experiment was repeated at ice tem-



$$2Co^{2+} + {}^{7}/_{3}\,tren + O_2 + H_2O \rightarrow (tren)Co\begin{matrix} / \overset{O\text{-}O}{} \backslash \\ \backslash \underset{OH}{} / \end{matrix}Co(tren)^{3+} + {}^{1}/_{3}\,H_3tren^{3+} \qquad (1)$$

perature, the break in the oxygen uptake curve corresponded to formation of $[H_2O(tren)CoOOCo(tren)H_2O]^{4+}$ without

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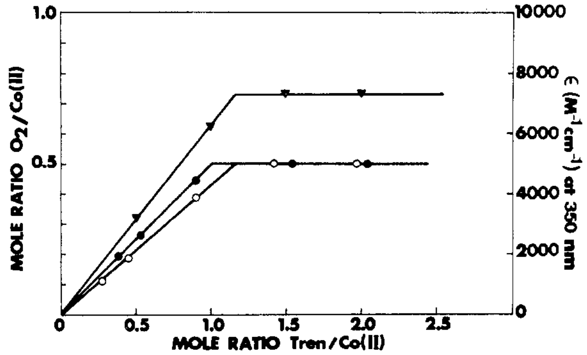
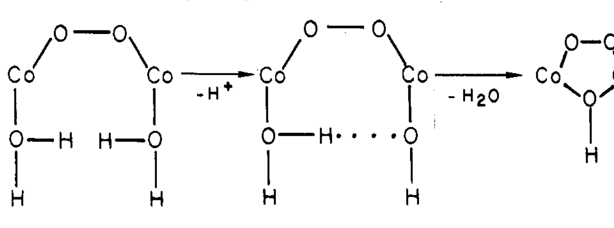


Figure 1. Stoichiometry of the Co(II)-tren reaction: ▼ , absorbance (350 nm) of Co^{2+}-tren solutions aerated at room temperature; ○, oxygen uptake at 30° of Co^{2+}-tren solutions; ●, oxygen uptake at 30° of Co^{2+}-tren-NH_3 solutions, [tren] = [NH_3]. Identical curve for Co^{2+}-tren at 0°.

evidence for a hydroxide bridge, even when the amine was in excess of the cobalt. These stoichiometries correspond exactly to those of the singly bridged intermediate ion first formed and the doubly bridged final product, which were detected in a kinetic study with the isomeric unbranched ligand triethylenetetramine.[5] It is expected that the mechanisms also are similar.

The doubly bridged ion has been isolated as [(tren)Co(O_2,OH)Co(tren)]$(ClO_4)_3$, a dark brown, diamagnetic, crystalline compound (Table I). It is stable in solution, and its electronic absorption spectrum is identical with that of the product of reaction 1. The conductance of a millimolar solution is indicative of a four-ion binuclear salt (Figure 3). Evidence for the hydroxide bridge is found in the infrared spectrum, where medium-intensity peaks at 3600 and 3545 cm^{-1} occur in a region usual for bridging hydroxide,[9,13] well separated from N-H stretching frequencies.

Failure to isolate the singly bridged diaquo ion stems apparently from its low stability relative to the doubly bridged final product. The structure of 2,2′,2″-triaminotriethylamine requires that two other groups coordinated to the same metal ion in a six-coordinate complex must occupy positions cis to each other. Thus, in the binuclear complex, not only are two water molecules positioned optimally for reaction but also it is likely that hydrogen bonding stabilizes the transition state and certain that formation of a five-membered ring imparts product stability[1] (eq 2).



(2)

Since the stability and ease of isolation of singly bridged peroxo complexes in which five amino groups are coordinated to each cobalt atom have become evident,[6,14,15] the oxygen uptake experiment was repeated at 30° with an equimolar mixture of ammonia and 2,2′,2″-triaminotriethylamine as ligand solution (Figure 1). One-half mole of oxygen was absorbed for each molar equivalent of the mixture at constant cobalt(II) concentration up to the amount indicative of formation of $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ ion, after which there was no further absorption.

Dark brown, diamagnetic salts of this complex were obtained from well-aerated, concentrated solutions of equimolar quantities of cobalt(II) salts, ammonia, and 2,2′,2″-triaminotriethylamine. These compounds were stable at room temperature but liberated gas when they dissolved in acid. From analyses (Table I) and conductivity measurements (Figure 3), they can be formulated as binuclear complexes $[NH_3(tren)CoOOCo(tren)NH_3]X_4 \cdot nH_2O$ where X = Cl with $n = 2$ and X = Br, I, NO_3, or ClO_4 with $n = 0$.

Attempts to incorporate monodentate amine ligands other than ammonia into complexes similar to those just described led to isolation of the pyridine complex [py(tren)CoOOCo(tren)(py)]$I_4 \cdot H_2O$, which was characterized by analyses (Table I) and conductivity measurements. Confirmation of the presence of coordinated pyridine is found in strong, sharp infrared absorptions at 1608, 1448, 1157, 1072, 769, and 701 cm^{-1}, which correlate well with strong absorptions in the spectrum of the free base. This is in agreement with the observation that bands of the pyridine spectrum are reproduced with only minor shifts or splitting in spectra of its complexes.[16] The attempt to prepare the perchlorate salt of this cation yielded [(tren)Co(O_2,OH)Co(tren)]$(ClO_4)_3$, as did attempts in which monoalkylamines (C_1 to C_3) were used. Because these attempts were made before the instability of the singly bridged ions was recognized fully and the products were recrystallized before analyses, the possibility of preparing these complexes cannot be precluded.

The doubly bridged peroxoamido complex was prepared by ligand replacement on μ-peroxo-μ-amido-octaamminedicobalt(III) nitrate followed by addition of a saturated solution of a soluble salt of the precipitating anion.[17] Thus were obtained [(tren)Co(O_2,NH_2)Co(tren)]I_4 and the corresponding perchlorate dihydrate. These salts were stable at room temperature and for several hours in neutral or ammoniacal solutions. The electronic absorption spectra of these complexes (Table II) are similar to those of other μ-peroxo-μ-amido complexes with amine ligands.[10]

The ion $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ is unstable in aqueous solution. A freshly prepared solution had an absorption maximum at 303 nm, which very rapidly decreased in intensity with a concomitant increase at 350 nm. At the end of the reaction the spectrum and molar absorbance were identical with those of $[(tren)Co(O_2,OH)Co(tren)]^{3+}$. Spectra of these two ions are shown in Figure 2. Similar spontaneous conversions have been observed for $[NH_3(L)CoOOCo(L)NH_3]^{4+}$ complexes, which at room temperature form $[(L)Co(O_2,OH)Co(L)]^{3+}$ in the times indicated: L = 2 ethylenediamine or 2 *l*-propylenediamine, 20 min; L = triethylenetetramine, 40 min.[10]

The formation and stability of the oxygenation product of equimolar (10^{-4} *M*) cobalt(II) and 2,2′,2″-triaminotriethylamine in various concentrations of aqueous ammonia were followed spectrophotometrically. In high concentrations of ammonia the spectrum of the reaction product is identical with that of $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ salts dissolved in 6 *M* ammonia (Figure 2), in which medium, for instance, the singly bridged complex is stable for about 25 min before the conversion to the stable, ultimate product [(tren)Co-

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Table I. Analytical Data for μ-Peroxo and μ-Superoxo Co(III) Complexes

Complex	% calcd					% found				
	C	H	N	O_2	Anion	C	H	N	O_2	Anion
$[NH_3(tren)CoO_2Co(tren)NH_3](ClO_4)_4$	16.49	4.84	16.02	3.66	45.50	16.21	4.93	16.10	3.70	45.70
$[NH_3(tren)CoO_2Co(tren)NH_3](NO_3)_4$	19.90	5.84	27.07		34.24	19.60	5.64	27.65		35.35
$[NH_3(tren)CoO_2Co(tren)NH_3]Cl_4 \cdot 2H_2O$	22.03	7.09	21.41	4.89	21.68	21.98	6.95	20.54	4.72	21.74
$[NH_3(tren)CoO_2Co(tren)NH_3]Br_4$	18.11	5.32	17.60	4.02	40.15	18.11	5.53	17.47	4.04	39.68
$[NH_3(tren)CoO_2Co(tren)NH_3]I_4$	14.65	4.30	14.23		51.59	14.80	4.15	13.00		50.13
$[py(tren)CoO_2Co(tren)py]I_4 \cdot H_2O$	23.46	4.30	12.44		45.07	22.65	4.16	12.41		45.64
$[(tren)Co(O_2,OH)Co(tren)](ClO_4)_3$	19.02	4.92	14.79	4.22	39.38	19.05	4.97	14.62	4.45	39.91
$[(tren)Co(O_2,NH_2)Co(tren)]I_3$	17.18	4.57	15.02		45.37	17.01	4.63	15.28		44.28
$[(tren)Co(O_2,NH_2)Co(tren)](ClO_4)_3 \cdot H_2O$	18.60	5.20	16.27		38.51	18.32	5.05	15.99		38.87
$[NH_3(tren)CoO_2Co(tren)NH_3](ClO_4)_5 \cdot 2H_2O$	14.27	4.59	13.87			14.35	4.50	13.90		
$[(tren)Co(O_2,NH_2)Co(tren)](ClO_4)_4 \cdot 2H_2O$	16.15	4.75	14.13			16.15	4.58	14.30		
$[H_2O(tren)CoO_2Co(tren)H_2O](ClO_4)_5$	14.77	4.13				15.40	4.14			

Table II. Absorption Spectral Data for μ-Peroxo- and μ-Superoxo Co(III) Complexes

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$[NH_3(tren)CoO_2Co(tren)NH_3]^{4+}$ [a]			500 sh	2.48	303	3.96
$[(tren)Co(O_2,OH)Co(tren)]^{3+}$ [b]			500 sh	2.66	350	3.86
$[(tren)Co(O_2,NH_2)Co(tren)]^{3+}$ [b]			484	2.76	325	3.70
$[NH_3(tren)CoO_2Co(tren)NH_3]^{5+}$ [d]	716	2.96	473	2.56	310	4.17
$[(tren)Co(O_2,NH_2)Co(tren)]^{4+}$ [d]	730	2.59	468	3.06	300	4.03
$[H_2O(tren)CoO_2Co(tren)H_2O]^{5+}$ [c]	710		490		310	

[a] In 6 M NH_3 solution. [b] In water. [c] In 0.1 M $HClO_4$. [d] In 0.3 M $HClO_4$.

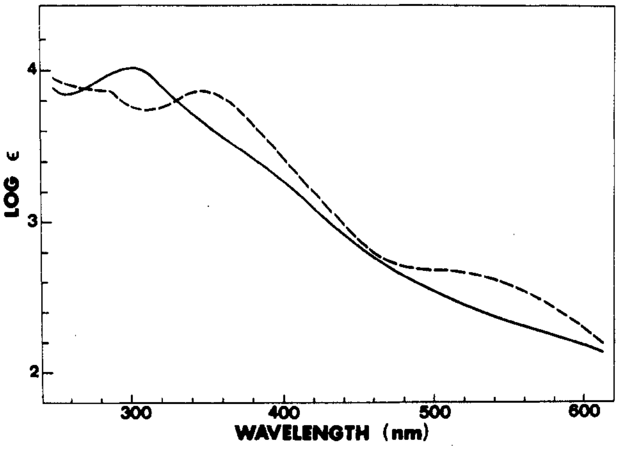
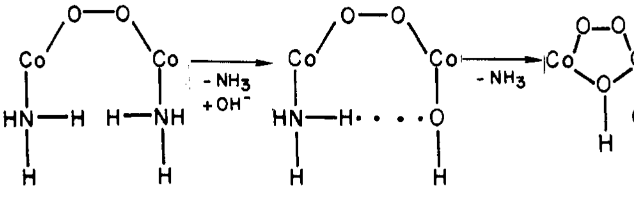


Figure 2. Absorption spectra: ———, $[NH_3(tren)CoO_2Co(tren)NH_3]^{4+}$ in 6 M NH_3 solution; – – –, $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ in water.

$(O_2,OH)Co(tren)]^{3+}$ becomes noticeable. In 0.6 M ammonia the conversion was half through before the spectrum could be recorded. Despite this instability, it was possible to prepare five salts of the singly bridged cation by use of high concentrations and low temperatures.

It is noteworthy that, despite the inclusion of ammonia molecules in the coordination sphere of $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ and the presence of high concentration of ammonia in solution, the stable product contains hydroxide rather than amide ion as the second bridge. While free ammonia in solution retards the rate of transformation, it does not prevent it, nor is a discernible equilibrium reached (eq 3).



(3)

Structure determinations have shown that the chelate rings of 2,2′,2″-triaminotriethylamine are severely strained in the six-coordinate complex $[Ni(NCS)_2(tren)]$.[18] This strain has been cited as the reason for a greater rate of hydrolysis for $[CoCl_2(tren)]^+$ than for *cis*-$[CoCl_2(trien)]^+$ and *cis*-$[CoCl_2(en)_2]^+$.[19] Similarly, the rate of ammonia elimination and ring closure is seen to be substantially faster for $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ than for $[NH_3(trien)CoOOCo(trien)NH_3]^{4+}$.

The brown μ-peroxo binuclear complexes $[NH_3(tren)CoOOCo(tren)NH_3]^{4+}$ and $[(tren)Co(O_2,NH_2)Co(tren)]^{3+}$ were readily oxidized by chlorine to the corresponding green μ-superoxo complexes of the same composition but having one additional positive charge. These were isolated as perchlorates (Table I). They are sensitive to light and heat but are relatively stable in cold acid solution. The electronic absorption spectra of these complexes closely resemble those of other μ-superoxo and μ-superoxo-μ-amido complexes.[10]

When $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ was oxidized by cerium(IV) in very dilute acid solution, a green salt was obtained. It also was sensitive to light and heat. Its color changed gradually from green to black, brown, and finally pink. It decomposed very rapidly in both water and acid solutions. From the elemental analysis (Table I) and spectrum pattern (strong absorption bands at about 710 and 490 nm, the first band being much stronger than the second), it was most likely a binuclear, singly bridged superoxo complex,[10] probably $[H_2O(tren)CoOOCo(tren)H_2O]^{5+}$. Its instability at room temperature precluded further study.

Conductance Measurements. Molar conductance values of millimolar solutions of four- and five-ion binuclear complexes failed to fall within ranges established with salts of hexaaquo cations and common mononuclear complex ions.[20] Comparison with values obtained with other binuclear salts (Figure 3) showed that the mobilities of larger binuclear cations are

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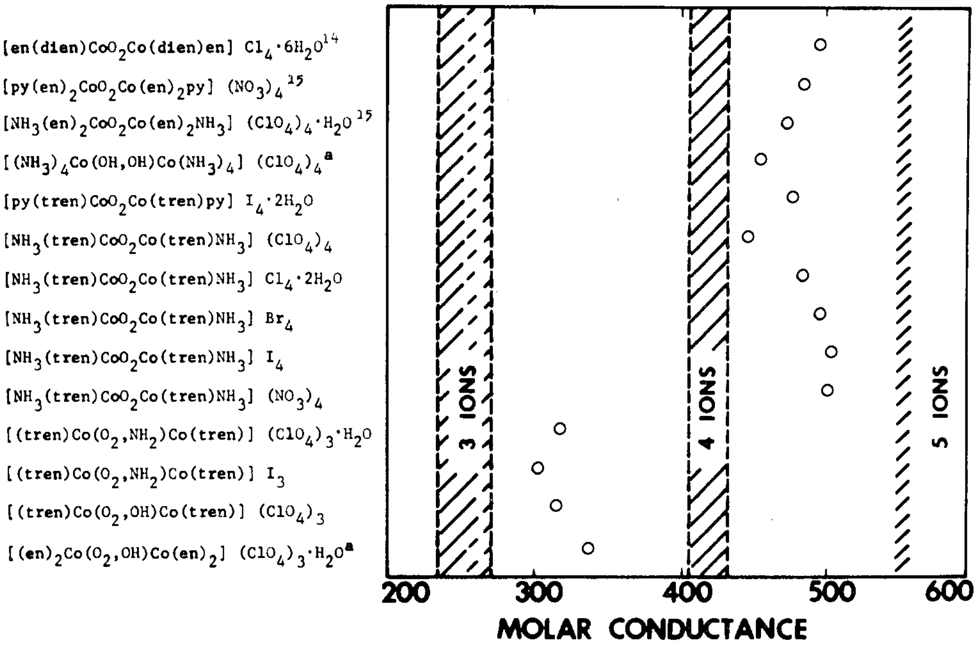

Figure 3. Comparison of molar conductance of 10^{-3} *M* solutions of binuclear complex salts (circles) with ranges for mononuclear complex salts (shaded areas), 25°. (^{a} From a Figure in ref 9.)

appreciably lower than those of smaller mononuclear ions and that the range 450-506 ohm^{-1} cm^2 mol^{-1} is reasonable for confirmation of five-ion salts containing a binuclear cation. Likewise, the range 308-340 ohm^{-1} cm^2 mol^{-1} seems reasonable, although somewhat narrow, for four-ion binuclear complexes.

Experimental Section

2,2′,2″-Triaminotriethylamine was obtained from Dow Chemical Co. It was purified by fractional distillation through a spinning-band column under *ca.* 2 Torr pressure. Reagent grade inorganic salts and organic chemicals for syntheses were used as supplied by various manufacturers. μ-Peroxo-μ-amido-octaamminedicobalt(III) nitrate was prepared by the method of Mori, *et al.*[17]

Electronic absorption spectra were obtained in matched 1-cm cells with Beckman DB and Perkin-Elmer 202 spectrophotometers. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer; samples were analyzed as KBr pellets and Nujol mulls between KBr plates. The molar conductance at 25.0° of 1.00 m*M* solutions was measured with an Industrial Instruments RC16B2 conductance bridge and a dipping conductance cell which had a cell constant 0.0961 cm^{-1}.

The stoichiometry of oxygen absorption was measured in a large Warburg apparatus constructed of glass, which was immersed in a constant-temperature bath. Peroxide oxygen was determined in the same apparatus by measurement of the volume of oxygen evolved upon heating a weighed sample of compound with excess saturated potassium hexacyanoferrate(III) solution.[14] Chloride, bromide, and iodide were determined gravimetrically as silver salts. Peroxo-bridged complexes, other than the iodide, were allowed to decompose first in dilute nitric acid. To avoid oxidation of iodide ion by hydrogen peroxide, which is liberated during decomposition of peroxo complexes, the iodides were dissolved directly into cold silver nitrate solution. Perchlorate ion was determined gravimetrically as nitron perchlorate and as tetraphenylarsonium perchlorate. Nitrate ion was determined gravimetrically as nitron nitrate. Carbon, hydrogen, and nitrogen analyses were made by B. Schecter and C. Sieland of this laboratory and by Galbraith Laboratories, Inc.

μ-Peroxo-bis[ammine(2,2′,2″-triaminotriethylamine)cobalt(III)] Salts. The singly bridged peroxo compounds $[\text{NH}_3\text{(tren)CoOOCo(tren)NH}_3]\text{X}_4\cdot n\text{H}_2\text{O}$ (X = Cl, $n = 2$; X = Br, I, NO_3, ClO_4, $n = 0$) were prepared by essentially the same method, with minor variations of concentrations, use of precipitating salts, and crystallization times. In a typical procedure, that for the preparation of the chloride, a solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (40 mmol in 15 ml of water) was aerated by a stream of air delivered through a fritted-glass gas dispersion tube while another solution of tren and NH_3 (40 mmol each in 15 ml) was added gradually (30 min). The solution was made nearly saturated with NH_4Cl (8 g), after which it was sealed and allowed to crystallize in the refrigerator for 2 days. The dark brown, crystalline product was collected on a sintered-glass filter, where it was washed with ethanol and ether before being dried in air and, ultimately, *in vacuo* over P_4O_{10}. The yield was poor because the salt is quite soluble.

The iodide salt was prepared in 63% yield by addition of KI (10 g in 20 ml of water) to a concentrated solution of the chloride. Both solutions must be kept well chilled to prevent oxidation reactions. The perchlorate, which is least soluble, was obtained in 67% yield without the use of a precipitating salt. *Caution*! The perchlorate salt exploded at 220°.

μ-Peroxo-bis[pyridine(2,2′,2″-triaminotriethylamine)cobalt(III)] Iodide Dihydrate. A solution of tren and pyridine (10 mmol of each in 40 ml) was added, as described above, to a solution of $\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (10 mmol in 10 ml). After further aeration in an ice bath, a cold, concentrated solution containing KI (5 g) was added. Orange-brown crystals formed within several minutes. These were washed with ethanol and ether and dried in the air. The yield was 60%.

μ-Peroxo-μ-hydroxo-bis[2,2′,2″-triaminotriethylaminecobalt(III)] Perchlorate. Method 1. A solution of tren (10 mmol in 20 ml) was added to an aerated solution of $\text{Co(ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (10 mmol in 20 ml). The mixture was aerated thoroughly and allowed to stand. Crystallization was induced by very slow addition of NaClO_4 (10 g) or ethanol (100 ml) during constant stirring. The yield was 65%.

Method 2. Ethanol was added to the filtrate from the preparation of $[\text{NH}_3\text{(tren)CoOOCo(tren)NH}_3](\text{ClO}_4)_4$ until turbidity was observed. Then the solution was cooled in an ice bath until fine brown crystals formed. This material was recrystallized from aqueous solution by addition of ethanol.

μ-Peroxo-μ-amido-bis[2,2′,2″-triaminotriethylaminecobalt(III)] Iodide and μ-Peroxo-μ-amido-bis[2,2′,2″-triaminotriethylamine-cobalt(III)] Perchlorate Dihydrate. μ-Peroxo-μ-amido-octaammine-dicobalt(III) nitrate (2 g) was dispersed into 10 ml of water, and tren (1.7 g in 5 ml of water) was added with stirring. The mixture was digested at 70° until evolution of ammonia was complete. The solution was cooled to ice temperature, and a saturated solution which contained KI (7 g) or NaClO_4 (5 g) as appropriate was added with stirring. Fine red-brown crystals formed within a few minutes. These were collected and washed once with a little cold water and several times with ethanol, after which they were dried over P_4O_{10}. The yield was 65% in both cases.

μ-Superoxo-bis[ammine(2,2′,2″-triaminotriethylamine)cobalt(III)] Perchlorate Dihydrate. One gram of the corresponding peroxo compound was added gradually with stirring to 15 ml of ice cold 0.3 *M* perchloric acid while chlorine gas was bubbled through. Dull green crystals formed in the bright green solution. The crystals were collected, washed, and dried as were the peroxo complexes.

μ-Superoxo-μ-amido-bis[2,2′,2″-triaminotriethylaminecobalt(III)] Perchlorate Hydrate. This doubly bridged green complex was synthesized from the analogous doubly bridged red-brown complex by chlorine oxidation as described above.

Registry No. $[NH_3(tren)CoO_2Co(tren)NH_3](ClO_4)_4$, 37480-75-4; $[NH_3(tren)CoO_2Co(tren)NH_3](NO_3)_4$, 37480-76-5; $[NH_3(tren)CoO_2Co(tren)NH_3]Cl_4\cdot 2H_2O$, 37475-77-7; $[NH_3(tren)CoO_2Co(tren)NH_3]Br_4$, 37480-77-6; $[NH_3(tren)CoO_2Co(tren)NH_3]I_4$, 37480-78-7; $[py(tren)CoO_2Co(tren)py]I_4\cdot H_2O$, 37475-78-8; $[(tren)Co(O_2,OH)Co(tren)](ClO_4)_3$, 37480-79-8; $[(tren)Co(O_2,NH_2)Co(tren)]I_3$, 37480-74-3; $[(tren)Co(O_2,NH_2)Co(tren)](ClO_4)_3\cdot H_2O$, 37475-76-6; $[NH_3(tren)CoO_2Co(tren)NH_3](ClO_4)_5\cdot 2H_2O$, 37189-79-0; $[tren\ Co(O_2,NH_2)Co(tren)](ClO_4)_4\cdot 2H_2O$, 37189-77-8; $[H_2O(tren)CoO_2Co(tren)H_2O](ClO_4)_5$, 37189-78-9.

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Contribution from the Department of Chemistry
and Geology, Clemson University, South Carolina 29631

Absolute Configuration of Coordination Compounds. I. Nickel(II) and Zinc(II) Complexes of PAPY[1]

V. A. FISHMAN and J. F. GELDARD*

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Exciton theory has been used to interpret the circular dichroism and visible spectra of the nickel(II) and zinc(II) complexes of PAPY. Excellent qualitative agreement between the observed and calculated spectra has enabled an assignment of absolute configuration for these complexes. The quantitative disagreement in line position is discussed in terms of the approximations involved in the theory.

Introduction

Recently, there has been considerable interest in the determination of the absolute configuration of coordination complexes by analysis of their circular dichroism (CD) spectra within the framework of the exciton theory.[2-10] The theory allows for coupling between free ligand transitions upon formation of a complex. The coupling arises from electrostatic interactions between the various transition dipole moments associated with the ligand transitions.

Transitions of the coordinated ligands can then be expressed as functions of those of the free ligands, and from a knowledge of these latter, one can deduce the signs of the CD bands for such transitions. Thus, the stereochemistry of a given optical isomer is determined by comparison of the observed and calculated CD spectra. This application of the theory gives qualitatively sound results although quantitative errors arise from the approximations inherent in the method.[11,12] The theory has been most commonly applied to tris-bidentate chelate complexes. In this paper, we apply the exciton method in bis-tridentate chelate complexes. Specifically, we assign the absolute configurations of the two complexes bis(1-(2′-pyridyl)-3-(6″-methyl-2″-pyridyl)-1,2-diaza-2-propenato)nickel(II) and bis(1-(2′-pyridyl)-3-(6″-methyl-2″-pyridyl)-1,2-diaza-2-propenato)zinc(II), complexes I and II, respectively.

Theory and Theoretical Results

The quantum mechanical formulation of optical activity by Rosenfeld[13] leads to analytical expressions for the rotational strength R_{ba} of a molecular electronic transition from state $|a\rangle$ to state $|b\rangle$ and for the rotatory parameter β_a appropriate to molecules in state $|a\rangle$

$$R_{ba} = \mathrm{Im}\{\langle a|\vec{\mu}_e|b\rangle\cdot\langle b|\vec{\mu}_m|a\rangle\}$$

$$\beta_a = \frac{c}{3\pi\hbar}\sum_b R_{ba}/(\nu_{ba}^2 - \nu^2)$$

where $\vec{\mu}_e$ and $\vec{\mu}_m$ are the electric and magnetic dipole moment operators, respectively, and ν_{ba} is the frequency of excitation from state $|a\rangle$ to $|b\rangle$.

The exciton formulation of Moffitt[14] and Frenkel[15] allows the expression of the ground-state wave function of a bis-tridentate chelate complex, $|C_0\rangle$, as a product of the individually antisymmetrized ground-state wave functions of the two ligands, $|X_0\rangle$ and $|Y_0\rangle$, and the metal, $|M_0\rangle$: $|C_0\rangle = |X_0Y_0M_0\rangle$. Furthermore, certain of the excited states of the complex may be approximated by product functions involving only excited states of the ligands, the metal ion being represented by its ground-state wave function. Typically, corresponding to the ith excited state of the ligand X is an excited state of the complex, say the jth; the two states are related by $|C_j\rangle = |X_iY_0M_0\rangle$. It is to be noted that this formulation precludes electron exchange between the ligands and the metal and assumes no change in ligand geometry upon complexation. In the complexes reported here, ligands X and Y are identical and exhibit a broad absorption

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