

the University of Toronto and the National Research Council of Canada for financial support and Professor N. C. Payne for crystallographic information before publication.

**Registry No.** *cis*- $\alpha$ -[Co(*R,R,S,S*-tetars)Cl<sub>2</sub>]Cl, 50805-06-6; *cis*- $\beta$ -[Co(*R,R,S,S*-tetars)O<sub>2</sub>]ClO<sub>4</sub>, 52195-72-9; *cis*- $\beta$ -[Co(*R,R,S,S*-tetars)-(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 50804-65-4; *cis*- $\alpha$ -[Co(*R,R,S,S*-tetars)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 50804-67-6; H<sub>2</sub>O<sub>2</sub>, 7722-84-1;  $\Delta$ -*cis*- $\alpha$ -[Co(*R,R*-tetars)Cl<sub>2</sub>]Cl, 50805-13-5;  $\Delta$ -*cis*- $\beta$ -[Co(*R,R*-tetars)O<sub>2</sub>]ClO<sub>4</sub>, 52225-11-3;  $\Delta$ -*cis*- $\beta$ -[Co(*R,R*-tetars)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 50804-59-6; *cis*-[Co(diars)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-

(ClO<sub>4</sub>)<sub>3</sub>, 50804-95-0; *cis*-[Co(diars)<sub>2</sub>O<sub>2</sub>]ClO<sub>4</sub>, 52195-74-1; *trans,trans*-[CH<sub>3</sub>CN(*R,S*-tetars)CoOCo(*R,S*-tetars)CH<sub>3</sub>CN](ClO<sub>4</sub>)<sub>4</sub>, 52195-76-3; *trans,trans*-[CH<sub>3</sub>CN(diars)<sub>2</sub>CoOCo(diars)<sub>2</sub>CH<sub>3</sub>CN](ClO<sub>4</sub>)<sub>4</sub>, 52195-78-5; *cis*- $\alpha$ -[Co(*R,R,S,S*-tetars)SO<sub>4</sub>]ClO<sub>4</sub>, 52195-80-9; *cis*- $\beta$ -[Co(*R,R,S,S*-tetars)SO<sub>4</sub>]ClO<sub>4</sub>, 52225-13-5;  $\Lambda$ -*cis*- $\alpha$ -[Co(*R,R*-tetars)SO<sub>4</sub>]ClO<sub>4</sub>, 52225-15-7;  $\Delta$ -*cis*- $\beta$ -[Co(*R,R*-tetars)SO<sub>4</sub>]ClO<sub>4</sub>, 52225-17-9; *cis*- $\beta$ -[Co(*R,S*-tetars)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 50883-37-9; *cis*- $\beta$ -[Co(*R,S*-tetars)SO<sub>4</sub>]ClO<sub>4</sub>, 52225-19-1; *cis*-[Co(diars)<sub>2</sub>SO<sub>4</sub>]ClO<sub>4</sub>, 52195-82-1; *cis*- $\beta$ -[Co(*R,S*-tetars)O<sub>2</sub>]ClO<sub>4</sub>, 52304-81-8; *trans,trans*-[CH<sub>3</sub>CN(*R,R,S,S*-tetars)CoOCo(*R,R,S,S*-tetars)CH<sub>3</sub>CN](ClO<sub>4</sub>)<sub>4</sub>, 52248-64-3; *trans,trans*-[CH<sub>3</sub>CN(*R,R*-tetars)CoOCo(*R,R*-tetars)CH<sub>3</sub>CN](ClO<sub>4</sub>)<sub>4</sub>, 52247-98-0.

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## Synthesis and Stereochemistry of Cobalt(III) Complexes of 1,3-Diamino-2-propanol and Related Ligands

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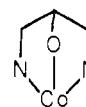
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*trans*-[Co(2-tmO)<sub>2</sub>]X (I) (2-tmOH is 1,3-diamino-2-propanol, X<sup>-</sup> is Cl<sup>-</sup>, Br<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) has been prepared. Its stereochemistry was determined by carbon-13 nmr. Earlier reports on the composition of this compound are in error. Complexes derived from I were *trans*-[Co(2-tmO)(2-tmOH)]Cl<sub>2</sub>, *trans*-[Co(2-tmOH)<sub>2</sub>]Cl<sub>3</sub>, *cis*-[Co(2-tmOH)(2-tmOH)Cl]Cl<sub>2</sub>, and *trans*-[Co(2-tmOH)<sub>2</sub>Cl<sub>2</sub>]Cl. The stereochemistry of each of these compounds was also determined by carbon-13 nmr. A convenient preparation of 2,3-diamino-1-propanol (1-tmOH) was developed and the complexes *trans*-[Co(1-tmOH)<sub>2</sub>]Br<sub>2</sub> and [Co(1-tmOH)<sub>3</sub>]Br<sub>3</sub> were prepared. Hydrolysis reactions of diacido complexes were studied. No complexes in which 1-tmOH served as a tridentate ligand were isolated. A previous assumption concerning the stereochemistry of [Co(tmNH<sub>2</sub>)<sub>2</sub>]<sup>3+</sup> (tmNH<sub>2</sub> is 1,2,3-triaminopropane) was confirmed by carbon-13 nmr measurements.

### Introduction

Our introduction to the chemistry reported in this paper came when we attempted to utilize Co<sup>3+</sup> as a blocking agent for the amino groups in 1,3-diamino-2-propanol.<sup>1</sup> For this purpose we needed the tris(diamine)cobalt(III) complex. All our attempts to prepare this complex were frustrated by formation of [Co(2-tmO)<sub>2</sub>]<sup>+</sup> (I) although several synthetic routes were utilized. In this complex the ligand is bound in tridentate fashion. A report on the preparation of the tris(diamine) complex of 2-tmOH is in error.<sup>2</sup> In fact there have been other, earlier reports on cobalt(III) complexes of this ligand.<sup>3</sup> In each case the complex obtained initially was incorrectly formulated.<sup>4</sup>

Very few studies have been made on complexes of potentially tridentate ligands of the 1,2,3-trisubstituted propane type.<sup>5</sup> The behavior of 2-tmOH as a tridentate ligand was surprising to us in view of the chelate ring strain which should exist in a structure of the type<sup>6</sup>



We were, however, aware of recent reports on complexes of hydroxyamines which show a number of novel compositions and a variety of equilibria involving the hydroxyl groups. Most of the work, up to this time, has been concerned with 2-aminoethanol<sup>7</sup> and 2-(2-aminoethylamino)ethanol (etolen),<sup>8</sup> which contain primary alcohol functions. When one considers the number of hydroxylic compounds that are present in natural systems, it is surprising how little research has been done on their metal complexes. Because of the paucity of data on complexes of 1,2,3-tridentate ligands and on potentially chelating alcohols we undertook a thorough investigation of the title complex. Acid-base equilibria which exist for this complex allow the formation of a large number of interesting species. Carbon-13 nmr was particularly useful for assignment of stereochemistry to these species. Complexes of the isomeric ligand 2,3-diamino-1-propanol (1-tmOH) are also reported. Alcohols are not normally considered to be good ligands but the work reported here, as well as that al-

(1) Hereafter 1,3-diamino-2-propanol is abbreviated 2-tmOH; its alkoxide form is 2-tmO. In metal-complexed form the alkoxide is always coordinated while 2-tmOH indicates coordination of the protonated form.

(2) W. C. Drinkard and H. F. Bauer, *J. Amer. Chem. Soc.*, **82**, 5031 (1960).

(3) (a) F. G. Mann, *J. Chem. Soc.*, 2904 (1927); (b) J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Chem.*, **17**, 331 (1939).

(4) As [Co(2-tmOH)<sub>2</sub>(OH)<sub>2</sub>]<sup>+</sup>. This complex was reported to lose 2 mol of water upon heating to give *trans*-[Co(2-tmO)<sub>2</sub>]<sup>+</sup>.

(5) The only complete study, which includes assignment of stereochemistry, is that on the Co<sup>III</sup>L<sub>2</sub><sup>+</sup> complexes of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>(NH<sub>2</sub>)CO<sub>2</sub><sup>-</sup>: W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

(6) An examination of molecular models indicates that meridional binding of a ligand of this type is impossible contrary to what is sometimes assumed. See H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Van Nostrand, New York, N. Y., 1960, p 155.

(7) (a) H. Yoneda and S. Kida, *J. Amer. Chem. Soc.*, **82**, 2139 (1960); V. V. Udovenko and A. N. Gerasenkova, *Russ. J. Inorg. Chem.*, **11**, 1105 (1966); V. V. Udovenko and L. G. Reiter, *ibid.*, **15**, 958 (1970); V. V. Udovenko, O. N. Stepanenko, and B. G. Eroshok, *Russ. J. Inorg. Chem.*, **17**, 1409 (1972); (b) K. Ohashi, J. Fujita, B. Shimoyama, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 2422 (1968); Y. Kuge and S. Yamada, *ibid.*, **42**, 2552 (1969); R. L. Dotson, *J. Inorg. Nucl. Chem.*, **34**, 3131 (1972).

(8) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **82**, 2992 (1960); B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *ibid.*, **90**, 1362 (1968); J. A. Broomhead, *ibid.*, **90**, 4480 (1968); B. Das Sarma, and J. C. Bailar, Jr., *ibid.*, **91**, 5958 (1969); J. Bassett, R. Grzeskowiak, and B. L. O'Leary, *J. Inorg. Nucl. Chem.*, **32**, 386 (1970).

Table I. Analytical Data

	% C		% H		% N		% X		% Co	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1-tmOH·2HCl	22.10	22.25	7.42	7.48	17.18	16.78	43.49	43.94		
1-tmOH·2HBr	14.30	14.34	4.80	4.80	11.12	11.25	63.43	63.24		
<i>trans</i> -[Co(2-tmO) <sub>2</sub> ]Cl·2H <sub>2</sub> O	23.3	23.74	7.1	7.11	18.1	18.34	11.4	11.30		
<i>trans</i> -[Co(2-tmO) <sub>2</sub> ]Cl	26.45	26.32	6.64	6.55	20.54	20.50	13.00	13.37		
<i>trans</i> -[Co(2-tmO)(2-tmOH)]Cl <sub>2</sub>	23.32	22.98	6.21	6.25			22.94	22.50		
<i>trans</i> -[Co(2-tmOH) <sub>2</sub> ]Cl <sub>3</sub>	20.87	21.07	5.85	5.76	16.21	15.51	30.79	30.86		
<i>cis</i> -[Co(2-tmOH)(2-tmOH)Cl]Cl	20.87	21.16	5.85	5.91	16.21	16.37	30.79	30.58		
<i>trans</i> -[Co(2-tmOH) <sub>2</sub> Cl <sub>2</sub> ]Cl	20.87	20.81	5.85	5.81	16.21	15.69	30.79		17.06	16.35
[Co(1-tmOH) <sub>3</sub> ]Br <sub>3</sub>	18.99	18.99	5.31	5.24	14.77	15.22				
<i>trans</i> -[Co(1-tmOH) <sub>2</sub> Br <sub>2</sub> ]Br	15.05	14.93	4.21	4.22	11.70	11.66	50.06	49.21	12.31	11.89
[Co(tmNH <sub>2</sub> ) <sub>2</sub> ]Cl <sub>3</sub>	20.98	21.37	6.46	6.48	24.44	24.26	30.96	30.93	17.14	17.34

ready cited, indicates that atypical hydroxyl group-metal interactions may occur when the hydroxyl group is in close enough proximity to a strong donor such as nitrogen so that chelation is a possibility. The stereochemistry of the cobalt(III) complex of 1,2,3-triaminopropane, which was prepared first by Mann,<sup>9</sup> was determined by carbon-13 nmr as a part of the study of this class of tridentate ligands.

### Experimental Section

**Materials.** 1,3-Diamino-2-propanol was purchased from Aldrich Chemical Co. and was used without additional purification. Trisodium tris(carbonato)cobaltate(III) trihydrate was prepared according to Drinkard's procedure.<sup>10</sup> 1,2,3-Triaminopropane (tmNH<sub>2</sub>) was prepared by Curtius' general procedure.<sup>11</sup> Co(tmNH<sub>2</sub>)<sub>2</sub>Cl<sub>3</sub> was prepared by Mann's procedure<sup>9</sup> [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 456 (71), 325 (60)]. Syntheses of 2,3-diamino-1-propanol developed during this work are described below. All other chemicals and solvents were reagent grade and were used as obtained. Analytical data for all compounds discussed are given in Table I.

*trans*-[Co(2-tmO)<sub>2</sub>]Cl (I). Air was passed through a solution of 12 g (50 mmol) of CoCl<sub>2</sub>·6H<sub>2</sub>O and 10 g (110 mmol) of 2-tmOH in 150 ml of H<sub>2</sub>O, which also contained 0.1 g of suspended charcoal, for 17 hr. The originally pink solution appeared dark purple after this time. The solution was heated to dissolve crystalline material and was filtered to remove the charcoal. After evaporation to ~40 ml, dull purple crystals formed. These were collected and recrystallized from hot water. After drying *in vacuo* over P<sub>4</sub>O<sub>10</sub> the composition varied from Co(2-tmO)<sub>2</sub>Cl·2H<sub>2</sub>O to Co(2-tmO)<sub>2</sub>Cl·1/2H<sub>2</sub>O. Anhydrous material was obtained by heating *in vacuo* at 80° for a few hours; yield 8.7 g, 64%. The same complex could be prepared in moderate yield by treating Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>]·3H<sub>2</sub>O with slightly greater than 2 equiv of 2-tmOH·2HCl followed by addition of more than 2 equiv of HCl. These reflect optimized synthetic preparations. In fact several preparations involving 6:2 molar ratios of amine to Co(II) or amine hydrochloride to Co(CO<sub>3</sub>)<sub>3</sub><sup>3-</sup> gave the same compound. It was also obtained by heating [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> with 2-tmOH as described by Mann.<sup>3a</sup> No evidence for tris(diamine)cobalt(III) was ever obtained from any reaction.

*trans*-[Co(2-tmO)(2-tmOH)]Cl<sub>2</sub> (II). A solution of 1 g (3.3 mmol) of [Co(2-tmO)<sub>2</sub>]Cl was dissolved in 50 ml of 0.1 M HCl. The resulting orange-brown solution was evaporated under a stream of air to about 20 ml. Fine red crystals formed. These were collected and the filtrate was evaporated to give a purple oil. This oil was dissolved in a small amount of water and a second crop of material was formed as a red powder upon addition of ethanol. Both fractions were combined and dried *in vacuo* at 80°; yield 0.85 g, 75%. Compound II could be prepared in better yield by a second method, but only on a scale of less than 1 g. Compound I (0.25 g) was dissolved in 25 ml of concentrated HCl. The solution was diluted with 15 ml of water and evaporated to dryness with a stream of air. A few drops of water were added to the dried material. After a few minutes a red solid crystallized. This solid was filtered, washed with ethanol, and dried *in vacuo* at 80°; yield 0.24 g, 85%.

A pK<sub>a</sub> value for the reaction Co(2-tmO)(2-tmOH)<sup>2+</sup> + H<sub>2</sub>O ⇌ Co(2-tmO)<sub>2</sub><sup>+</sup> + H<sub>3</sub>O<sup>+</sup> was obtained by (a) dissolving equivalent a-

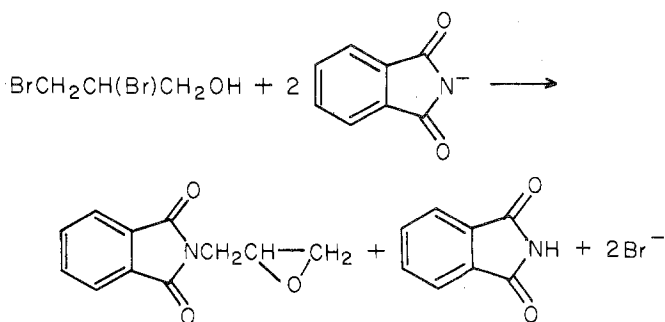
mounts of Co(2-tmO)<sub>2</sub><sup>+</sup> and Co(2-tmO)(2-tmOH)<sup>2+</sup> in water and (b) adding 0.5 equiv of HCl to a solution of Co(tmO)<sub>2</sub><sup>+</sup>. In both cases pH = pK<sub>a</sub> = 4. This value for the pK<sub>a</sub> was also consistent with the observed pH of aqueous solutions of II.

*trans*-[Co(2-tmOH)<sub>2</sub>]Cl<sub>3</sub> (III). This complex was prepared by dissolving either [Co(2-tmO)<sub>2</sub>]Cl or [Co(2-tmO)(2-tmOH)]Cl<sub>2</sub> in concentrated HCl (about 0.25 g in 25 ml) and slowly evaporating the solution with a stream of air. When the solution was reduced to a small volume, brown-red crystals formed. These were collected, washed with acetone, and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. For large-scale preparations or for cases where the air is especially damp the crystalline material may be contaminated with Co(2-tmO)(2-tmOH)Cl<sub>2</sub> and is very difficult to purify. In these cases it is advantageous to precipitate the compound as a fine brown powder from the concentrated HCl solution with dry acetone. The yield of crystalline material or powder is about 75%.

*cis*-[Co(2-tmOH)(2-tmOH)Cl]Cl<sub>2</sub> (V). A 1.6-g (5.9-mmol) portion of [Co(2-tmO)<sub>2</sub>]Cl was added to 25 ml of concentrated HCl and heated at ~80° for 4 hr. During this time the solution became homogeneous and changed to a deep purple color. Absolute ethanol (100 ml) and 25 ml acetone were added to the warm solution. A deep purple crystalline material formed. This solid was collected and washed with acetone. After the filtrate stood for 0.5 hr a second crop of the purple product precipitated. Both crops were dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The yields varied considerably but a typical yield was 1.18 g or 58%.

*trans*-[Co(2-tmOH)<sub>2</sub>Cl<sub>2</sub>]Cl (IV). The filtrate from the second crop of *cis*-[Co(2-tmOH)(2-tmOH)Cl]Cl<sub>2</sub> (see above) was heated gently after addition of 25–30 ml each of ethanol and acetone. After 15–20 min a green solid precipitated. This was collected and washed with acetone. The filtrate could be reheated to obtain further crops of green solid. The green compound was usually contaminated with purple solid but could be recrystallized by dissolving in a small amount of concentrated HCl and precipitating with ethanol. The complex was dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The yield again varied considerably. The maximum yield obtained was about 10% based on I.

**2,3-Diamino-1-propanol (Designated A in the Discussion Below).** Of the few published reports concerned with the preparation of A,<sup>12,13</sup> only one dealt with a practical synthesis. This preparation<sup>13</sup> involved the reaction of potassium phthalimide with 2,3-dibromo-1-propanol (B) in the absence of solvent followed by hydrolysis with 48% HBr and was reported to yield the dihydrobromide of A. We conducted this reaction several times, both according to the published recipe and in DMF solution, but the only products obtained after hydrolysis in any experiment were the isomeric 1,3-diamino-2-propanol (identified by melting point and nmr spectrum (D<sub>2</sub>O) of HBr salt) and phthalic acid. This isomerization can occur *via* neighboring-group participation of oxygen, probably with an epoxide forming as an intermediate, *i.e.*



(9) F. J. Mann and W. J. Pope, *Proc. Roy. Soc., Ser. A*, **107**, 80 (1925); F. J. Mann and W. J. Pope, *J. Chem. Soc.*, 2675 (1926).

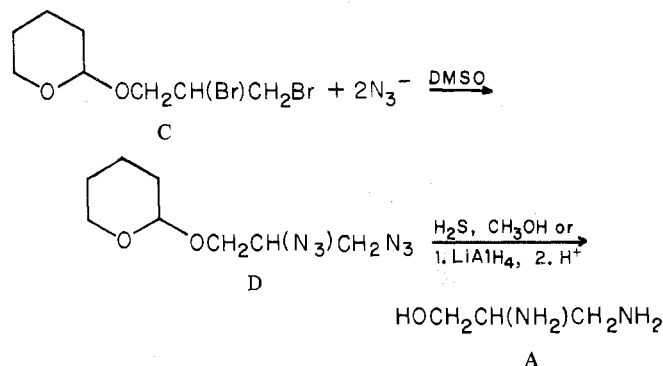
(10) W. C. Drinkard and H. F. Bauer, *Inorg. Syn.*, **8**, 202 (1966).

(11) T. Curtius and A. Hesse, *J. Prakt. Chem.*, **62**, 232 (1900).

Modifications of the procedures given here were made according to "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 819.

Anchimeric assistance by hydroxyl is well supported by existing data.<sup>14</sup>

Suitable syntheses of B involved the reaction of the tetrahydropyran derivative of B with sodium azide in DMSO followed by reduction with  $\text{LiAlH}_4$  in THF or with  $\text{H}_2\text{S}$  in methanol, *i.e.*



The derivative form of B was chosen for ease in isolating the diazide from the reaction mixture; however, it also ensures that the hydroxyl group will not participate in the reaction.

2,3-Dibromo-1-propanol was converted to the tetrahydropyran derivative C according to the procedure given by Woods and Kramer<sup>15</sup> (bp 84–86° (0.1 mm), nmr ( $\text{CDCl}_3$ -TMS)  $\tau$  5.32 (1 H), 5.5–6.5 (7 H), 8.33 (6 H); yield 75%).

**Preparation of D.** A mixture of 34.2 g (0.113 mol) of C, 22 g (0.23 mol) of sodium azide, and 200 ml of DMSO was heated at 65–70° for 20 hr. After cooling, 200 ml of water was added and the solution was extracted several times with 60–68° petroleum ether. These extracts were dried with sodium sulfate and the solvent was removed at ~2 mm and 35°. The yellow viscous oil, 23 g, 88%, had a strong 2090- $\text{cm}^{-1}$  absorption in the infrared spectrum; nmr ( $\text{CDCl}_3$ -TMS)  $\tau$  5.35 (1 H), 5.9–6.7 (7 H), 8.37 (6 H).

**Reduction of D to A with  $\text{H}_2\text{S}$ .**<sup>16</sup> The diazide (0.113 mol) was dissolved in 50 ml of absolute methanol and heated. When the solution began to reflux,  $\text{H}_2\text{S}$  was added by means of a gas dispersion tube. This reaction was conducted in a well-vented hood and the effluent gas was passed through concentrated NaOH. After a 15–30-min induction period during which time the solution color changed to a dark orange, the solution foamed vigorously and heating was discontinued. The reaction refluxed without application of heat for 3 hr. During this time large amounts of yellow solid appeared, but the reaction was not complete until it had ceased to evolve heat and the solution was again homogeneous. The progress of the reaction was followed by monitoring the azide stretching absorption in the infrared spectrum. The cooled dark solution was allowed to stand for several hours. Acidification with concentrated HBr caused copious gas evolution and precipitation of a yellow solid. The solid was removed by filtration and thoroughly washed with water. The water rinses were combined with the filtrate and evaporated to a small volume. Addition of ethanol precipitated an off-white solid. The dihydrobromide salt was recrystallized from ethanol and water in the presence of activated charcoal; yield 53%.

**Reduction of D to A with  $\text{LiAlH}_4$ .**<sup>17</sup> A solution of 22 g (0.1 mol) of D in 75 ml of THF (freshly opened, Fisher reagent grade) was added over ~1 hr to a suspension of 13 g of  $\text{LiAlH}_4$  in 250 ml of THF. After completion of the addition the mixture was refluxed for 12 hr. After hydrolysis with 15 ml water and 15 ml of 15% NaOH, the granular solids were removed by filtration and washed several times with THF. The filtrate and washes were combined and treated with sodium sulfate. THF was removed by rotary evaporation and the resulting oil was taken up in ethanol. Gaseous HCl bubbled beneath the surface of the ice bath cooled ethanol solution yielded a white solid. Ten grams of off-white solid was collected. Soxhlet ex-

traction of the granular solid obtained from hydrolysis of the reduction mixture with THF for 5 hr followed by work-up of the extractant as above yielded an additional 1.5 g of off-white solid. These fractions were combined, dissolved in hot water, and treated with Norit. Precipitation with ethanol yielded 10.5 g of the dihydrochloride of A; yield 64%; nmr ( $\text{D}_2\text{O}$ -DSS)  $\tau$  6–6.4 (3 H), 6.5–6.7 (2 H); mp 172–174°.

The dipicrate salt crystallized after addition of a concentrated aqueous solution of picric acid to a concentrated aqueous solution of the hydrochloride salt of the amine; mp 221.5–223°; lit.<sup>12</sup> mp 216–217°. Anal. Calcd: C, 32.86; H, 2.94; N, 20.44. Found: C, 32.85; H, 3.03; N, 20.70.

**[Co(1-tmOH)<sub>3</sub>]Br<sub>3</sub> (VI).** A suspension of 0.33 g (1 mmol) of  $\text{Na}_3\text{Co}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$  in 5 ml water was treated with 0.76 g (3 mmol) 1-tmOH·2HBr. This mixture was stirred for 2 hr during which time the color changed to orange. The solution was filtered and evaporated to dryness. The brown-orange residue was dissolved in a minimum amount of water and 5–6 ml of ethanol was added which caused an orange oil to separate. The cloudy ethanolic layer was decanted off and the oil was allowed to stand for ~1 hr. During this time an orange solid crystallized. The solid was collected by filtration and washed with ethanol. The compound was then dried *in vacuo* over  $\text{P}_2\text{O}_{10}$ ; yield 0.2 g, 35%. The tris(diamine) complex could also be prepared by aerial oxidation and it was the only complex isolated even with a 2:1 ligand to metal ratio. Infrared spectrum:  $\nu_{\text{O-H}}$  3472  $\text{cm}^{-1}$ ;  $\nu_{\text{N-H}}$  3195, 3160, 3080  $\text{cm}^{-1}$ .

**trans-[Co(1-tmOH)<sub>2</sub>Br<sub>2</sub>]Br (VII).** A 3.31-g (13.1-mmol) portion of 1-tmOH·2HBr and 2.16 g (6.55 mmol) of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  were added to 40 ml of  $\text{H}_2\text{O}$ . When the foaming subsided, 15 ml of 1 M HBr was slowly added. The mixture was stirred for 16 hr. The resultant dark reddish pink solution was filtered and the volume was reduced to about 5 ml under a stream of air. To the concentrate was added 25 ml of ethanol which precipitated a fine pink solid. This hygroscopic solid (this material has not been identified to be any stoichiometric species) was removed by filtration and the dark green filtrate evaporated to dryness. The dark brown residue was stirred with 1–2 ml of water and filtered. The bright yellow-green solid obtained in this manner was recrystallized from concentrated HBr and acetone; yield 1.25 g, 20%. Infrared spectrum:  $\nu_{\text{O-H}}$  3344  $\text{cm}^{-1}$ ;  $\nu_{\text{N-H}}$  3282, 3252, 3222, 3181, 3108  $\text{cm}^{-1}$ .

Reaction of VII with 2 equiv of NaOH produced an orange-pink solution. Addition of ethanol or acetone caused the separation of a pink oil, which was similar to material formed in reactions with excess hydroxide. An orange solution was decanted from the pink oil. Evaporation of this solution yielded an oil which could not be crystallized.

**Carbon-13 Nmr Studies of Base Hydrolysis.** A solution of 0.35 mmol of complex,  $[\text{Co}(2\text{-tmOH})_2\text{Cl}_2]\text{Cl}$  or  $[\text{Co}(1\text{-tmOH})_2\text{Br}_2]\text{Br}$ , in 0.2 ml of 6.7 M NaOH was prepared and stirred for 5 min. These solutions were neutralized with 38% DCl and diluted with  $\text{D}_2\text{O}$  to ca. 2 ml and DCl was added until  $[\text{H}^+] = 1 \text{ M}$ . Data collection was begun within 0.5 hr and completed within 3 hr.

In a second type of experiment 0.18 mmol of  $[\text{Co}(1\text{-tmOH})_2\text{Br}_2]\text{Br}$  was dissolved in 0.27 ml of 0.67 M NaOH. The solution was allowed to stand for 1 week. After diluting to ca. 2 ml the carbon-13 spectrum was taken.

**Physical Measurements.** All infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 457 grating infrared spectrophotometer and were calibrated vs. polystyrene film. Visible spectra were obtained with a Cary 14 spectrophotometer. pH measurements were carried out with a Corning Model 12 pH meter with calomel and glass electrodes. Ion-exchange measurements were carried out with Dowex AG 50W-X4 cation-exchange resin, 200–400 mesh, in the  $\text{H}^+$  or  $\text{Na}^+$  form as appropriate.

The carbon-13 nmr spectra were recorded at 25.2 MHz with complete proton decoupling on a Varian XL-100 nmr spectrometer in the Fourier transform mode. The pulse width was 8–20  $\mu\text{sec}$  with a pulse delay of 0.025 sec and acquisition time of 1.475 sec. The deuterium of the solvent ( $\text{D}_2\text{O}$  or DCl) was used for a lock signal. The samples were contained in 12-mm (o.d.) nmr tubes and the data were collected at 40°. For the neutral or basic solutions internal TSP was used as the reference. In acidic media the reference was internal acetic acid. All chemical shifts are given in ppm downfield from TSP. The methyl resonance in acetic acid was taken as 20.57 ppm with respect to TSP.

## Results and Discussion

**Characterization of Complexes.** Several methods which were used in an effort to prepare  $\text{Co}(2\text{-tmOH})_3^{3+}$  yielded only a red complex (I) which was shown to be  $[\text{Co}(2\text{-tmO})_2]^+$

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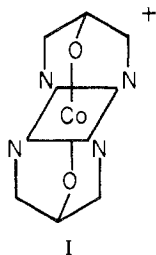
(15) G. F. Woods and D. N. Kramer, *J. Amer. Chem. Soc.*, 69, 2246 (1947).

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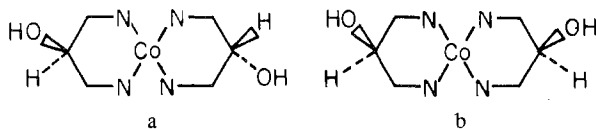
(17) E. G. Fleischer, A. E. Gebala, A. Levey, and P. A. Jasker, *J. Org. Chem.*, 36, 3042 (1971); M. S. Newman, D. H. Busch, G. E. Cheney, and C. R. Gustafson, *Inorg. Chem.*, 11, 2890 (1972).

as the appropriate salt on the basis of analysis, conductivity (1:1 electrolyte,  $\Lambda_M = 92$  at  $10^{-1} M$ ), and infrared spectrum (no -OH stretching absorption, Figure 1). 2-tmOH is thus acting as a tridentate ligand. The electronic absorption spectrum of this complex is shown in Figure 2. The splitting of the low-energy absorption ( $T_{1g} \leftarrow A_{1g}$  in  $O_h$  symmetry) suggests a trans configuration but the splitting of the  $T_{2g}$  absorption is surprising and is not generally observed for *trans*- $O_2N_4$  complexes of Co(III). The absorption spectrum of the dihydrate which is isolated initially is identical with that obtained for the anhydrous complex and the spectrum is unaffected by pH in the range 6-14. This indicates that the complex is not  $[Co(2-tmOH)_2(OH)_2]^+$  as suggested by Mann<sup>3a</sup> and by Breckenridge and Hodgins.<sup>3b</sup>

Pmr spectra were not useful in assigning the stereochemistry of this complex or derivatives because of small chemical shift differences in the second-order spectrum (here an  $(AB)_2C$  pattern). Carbon-13 nmr spectra, on the other hand, proved to be very useful. The proton-decoupled carbon-13 nmr spectrum consisted of two resonances at 77.90 and 44.08 ppm (in the partially decoupled spectrum the lower field line is a doublet and the upper field line a triplet). These data strongly support the symmetrical trans structure



It is not possible to say for sure that no other Co(III) complexes were formed in the various preparations; however, none have been detected. This is especially surprising since two 2-tmOH molecules can coordinate as bidentate ligands in two ways, *i.e.*



A recent study on Pt(II) complexes<sup>18</sup> led to the conclusion that both forms a and b were present. In b it is impossible for both hydroxyl groups to bind simultaneously to the metal ion in a trans fashion. In the formation of  $[Co(2-tmO)_2]^+$  there must be a kinetic process leading to form a alone or more likely, both forms are equilibrated leading to the more stable trans product, which may be derived from a.

Dissolution of  $[Co(2-tmO)_2]^+$  in acid leads to a number of different products depending upon the initial acid concentration and subsequent treatment. Some of these products are interconvertible. A summary of these reactions is shown in Scheme I.  $[Co(2-tmO)_2]Cl$  dissolved slowly in dilute HCl to form an orange-brown solution. After suitable treatment a complex of composition  $Co(2-tmO)(2-tmOH)Cl_2$  (II) (by elemental analysis) was obtained. This complex behaves approximately as a 2:1 electrolyte in aqueous solution ( $\Lambda_M = 226$ ,  $10^{-2} M$ ). The infrared spectrum of the compound (Figure 1) contains, in addition to absorptions assigned to -NH<sub>2</sub>, two sharp absorptions at 3479 and 3391  $cm^{-1}$  typical of ROH. The proton-decoupled carbon-13 nmr spectrum of

(18) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 11, 117 (1972).

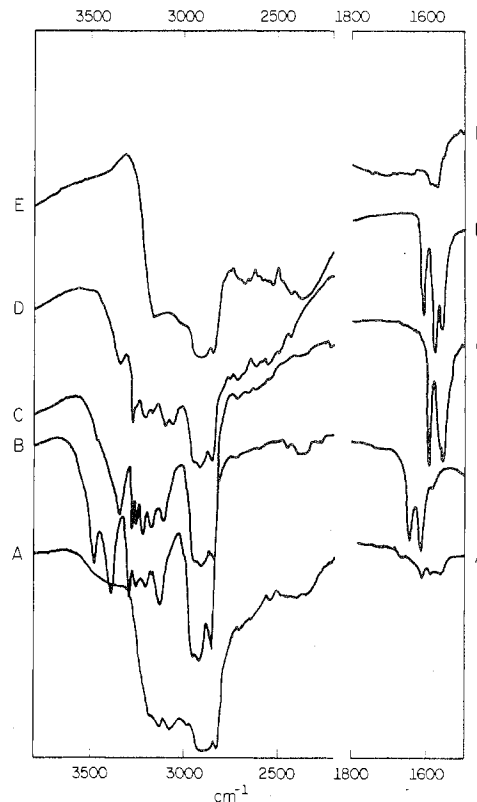


Figure 1. Infrared spectra (Nujol mulls): A, *trans*- $[Co(2-tmO)_2]Cl$ ; B, *trans*- $[Co(2-tmO)(2-tmOH)]Cl_2$ ; C, *trans*- $[Co(2-tmOH)_2]Cl_2$ ; D, *cis*- $[Co(2-tmOH)(2-tmOH)Cl]Cl_2$ ; E, *trans*- $[Co(2-tmOH)_2]Cl_3$ .

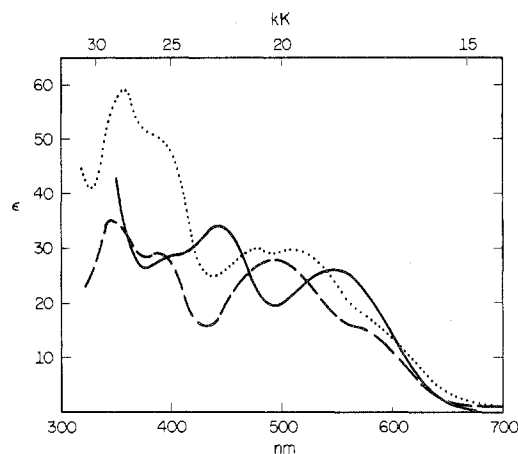
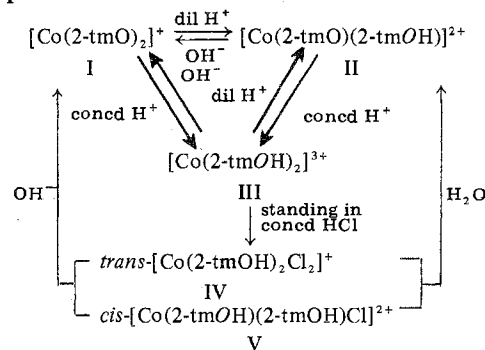


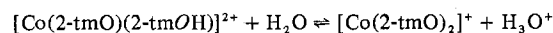
Figure 2. Electronic spectra (aqueous solutions unless otherwise noted): ---, *trans*- $[Co(2-tmO)_2]Cl$ ; ····, *trans*- $[Co(2-tmO)(2-tmOH)]Cl_2$ ; —, *trans*- $[Co(2-tmOH)_2]Cl_3$  (concentrated HCl).

#### Scheme I



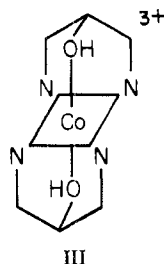
II consists of two resonances at 78.6 and 48.86 ppm, thus indicating a plane of symmetry for the complex. This spec-

trum is consistent with the apparent formula that was determined by analysis if one assumes that there is a rapid equilibrium of the type



for the complex in solution. A  $\text{p}K_a$  of 4 was determined for II.

The monoprotonated complex II is rapidly converted to I in base. Solutions of II prepared in water which stood for a few months contained predominantly I plus some  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and only a small amount of the monoprotonated complex. Dissolution of II (or I) in concentrated HCl on the other hand followed by evaporation of the solution to dryness yields a brown solid of stoichiometry  $\text{Co}(2\text{-tmOH})_2\text{Cl}_3$ , III. This complex was very unstable in basic solution, where it was converted immediately to I. In dilute acid or water III is converted rapidly to II. Its carbon-13 spectrum in concentrated HCl consists of two resonances at 79.08 and 43.38 ppm which suggests a structure for the complex which contains a plane of symmetry. A structure consistent with these data is



The infrared spectrum obtained on this brown product (Figure 1) did not contain an absorption which was identifiable as a simple  $-\text{OH}$  stretch (*i.e.*, in the region  $3300\text{--}3400\text{ cm}^{-1}$ , as found for II above). There is, however, a very broad absorption in the region  $2810\text{--}2370\text{ cm}^{-1}$ . We suggest that this is due to a very strong hydrogen bond from coordinated hydroxyl to chloride ion in the solid. This interpretation is supported by data obtained on a sample prepared in 38%  $\text{DCl-D}_2\text{O}$  which has a similar broad resonance in the region  $2000\text{--}1830\text{ cm}^{-1}$ .

Red-brown solutions of III became deep purple when they were allowed to stand for several days or if they were heated gently. Two products were isolated from these solutions. One of these, a green material, IV, was formulated as  $\text{trans-}[\text{Co}(2\text{-tmOH})_2\text{Cl}_2]\text{Cl}$  based on elemental analysis, the presence of an  $-\text{OH}$  stretching absorption in the infrared spectrum (Figure 1), and the absorption spectrum (Figure 3), which is typical of *trans*-dichlorotetraamine complexes. The other product obtained was a deep purple solid, V, which also analyzed for  $\text{Co}:2\text{-tmOH}:\text{Cl} = 1:2:3$ . Freshly dissolved solutions displayed 2:1 electrolyte behavior ( $\Lambda_M = 242, 10^{-2} M$ ). The infrared spectrum of V is shown in Figure 1. Two notable features are the absorption at  $3340\text{ cm}^{-1}$ , which is typical of an  $-\text{OH}$  stretch, and the broad absorption in the region  $2730\text{--}2430\text{ cm}^{-1}$ , which is similar to that for III (Figure 1) and which we believe is again due to strong hydrogen bonding of a coordinated hydroxyl proton to chloride ion. The carbon-13 spectrum for this complex in concentrated acid was more complicated than that of any of the compounds discussed earlier. There were six resonances—two intense resonances at 77.35 and 63.44 ppm and four approximately equal, less intense resonances at 45.12, 43.01, 41.35, and 40.61 ppm. The lowest field resonance can be confidently assigned to carbon attached to coordinated hydroxyl. Only slight chemical shift differences are observed between carbons

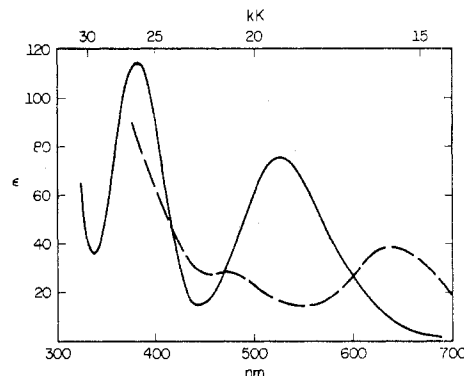
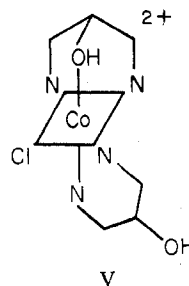


Figure 3. Electronic spectra: ---,  $\text{trans-}[\text{Co}(2\text{-tmOH})_2\text{Cl}_2]\text{Cl}$  (concentrated HCl); —,  $\text{cis-}[\text{Co}(2\text{-tmOH})(2\text{-tmOH})\text{Cl}]\text{Cl}_2$  ( $\text{H}_2\text{O}$ ).

attached to coordinated hydroxyl and coordinated alkoxide but since the medium is 38%  $\text{DCl}$  the coordinated oxygen must bear a deuteron. The resonance at 63.44 ppm is assigned to a carbon bonded to an uncoordinated hydroxyl group. This was determined by comparison with spectra of the free ligand obtained in acidic solution where the hydroxyl carbon resonance appears at 63.87 ppm. The electronic absorption spectrum of V is typical of *cis*-diacidotetraamine



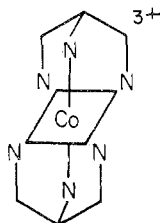
complexes (Figure 3). Compound V is the only *cis* product obtained in this system and the complexity of its carbon-13 nmr spectrum lends confidence to assignments of stereochemistry of the other complexes which are based heavily on their simple carbon-13 spectra.

In contrast to the 2-tmOH system, the isomeric 2,3-diamino-1-propanol readily forms the tris(diamine) complex  $[\text{Co}(1\text{-tmOH})_3]^{3+}$ , VI. Compound VI was the only species isolated from aerial oxidation of  $\text{Co}^{2+}$  in the presence of 1-tmOH $\cdot$ 2HBr, even with 2:1 stoichiometry. Compound VI could also be obtained from the reaction of  $\text{Co}(\text{CO}_3)_3^{3-}$  with 3 equiv of 1-tmOH $\cdot$ 2HX. The formulation of VI as the tris(diamine) complex is supported by the electronic spectrum [aqueous solution,  $\lambda_{\text{max}} (\epsilon, M^{-1} \text{ cm}^{-1})$  468 (93.7), 338 (128)], as well as by the infrared spectrum ( $\nu_{-\text{OH}}$   $3472\text{ cm}^{-1}$ ) and elemental analysis. No attempt was made to determine the stereochemistry of this product.

Reaction of  $\text{Co}(\text{CO}_3)_3^{3-}$  with 2 equiv of 1-tmOH $\cdot$ 2HBr and 2 equiv of HBr yielded a green complex, VII. This complex analyzed as  $\text{Co}(1\text{-tmOH})_2\text{Br}_3$ . Only one d-d absorption (656 nm) was observed in the electronic spectrum. Any others were obscured by a strong charge-transfer absorption which extended into the visible region. The 656-nm absorption is typical of *trans*-dihalotetraaminecobalt(III) species and we feel that this complex should be formulated as  $\text{trans-}[\text{Co}(1\text{-tmOH})_2\text{Br}_2]\text{Br}$ . Although there are four possible geometrical isomers for a *trans*-diacidobis(chelate) complex of this unsymmetrical ligand, only one species was evident in cation-exchange chromatography experiments. The stereochemistry of this species has not been established. The solubility of VII in bromide solutions was too low to permit carbon-13 nmr

analysis and aquation reactions complicated the carbon-13 nmr spectrum in  $D_2O$ .

Metal complexes of  $H_2NCH_2CH(NH_2)CH_2NH_2$  (tmNH<sub>2</sub>) were extensively studied by Mann over 40 years ago.<sup>9</sup> Both bi- and tridentate chelations of this ligand were observed. Only one Co(III) complex was prepared by Mann,  $Co(tmNH_2)_2^{3+}$ , and as only a single form was observed, he predicted it was the most symmetrical, *i.e.*



Examination of this complex by carbon-13 nmr indicated that only two kinds of carbon ( $\delta$  59.97, 48.01 ppm) were present in the complex ion. This then confirms Mann's assumption that the symmetrical cation is formed. Heating  $[Co(tmNH_2)_2]^{3+}$  in concentrated HCl for several hours produced no noticeable change. Thus any strain in the fused chelate ring system does not appear to affect the usual kinetic stability of the hexaammine complex.

**Hydrolysis Reactions of Acido Complexes.** Coordinated hydroxyl groups are clearly not easily displaced when they are part of a chelated ligand such as 2-tmOH. It was of particular interest to determine whether under hydrolysis reaction conditions a dangling hydroxyl rather than water would displace an acido group. At least three recent studies have dealt with this question for  $[Co(en)_2(X)H_2NCH_2CH_2OH]^{2+}$ .<sup>19</sup> Although this system is not so complex as those discussed here, some conflicting conclusions regarding the hydrolysis products have been reported. Chan and Leh<sup>19a</sup> studied the acid hydrolysis of this complex at 65° (0.1 M HClO<sub>4</sub>) and concluded that there was hydroxyl group assisted loss of halide followed by formation of an aquo complex. No products were isolated, however. Other workers<sup>19b,c</sup> concluded that an associative substitution process was important but that the product that resulted contained chelated ethanolamine. Base hydrolysis studies were conducted by three different groups and again conflicting results were obtained. Sargeson, *et al.*,<sup>19b</sup> reported that the chelated ethanolamine complex was formed in ~60% yield whereas others claimed that no chelated ethanolamine product was formed.<sup>19a,c</sup>

Because of the complexity of the systems which we are studying, only qualitative observations could be made concerning the participation of the two hydroxyl groups which are present in IV and VII in their hydrolysis reactions. Carbon-13 nmr spectra obtained on reaction mixtures could be used, in certain instances, to indicate bulk hydroxyl group binding although the sensitivity is too low to detect minor products.

Acid hydrolysis of IV (0.1 M HClO<sub>4</sub>, 25°) occurs with a half-life of *ca.* 1 min (green  $\rightarrow$  pink conversion). If one assumes the rate of loss of the second chloride to be about 100 times slower, as is the case for other *trans*-dihalotetraamminecobalt(III) systems, then IV should be converted to II within 1 or 2 days. In fact this conversion occurs, but only after a

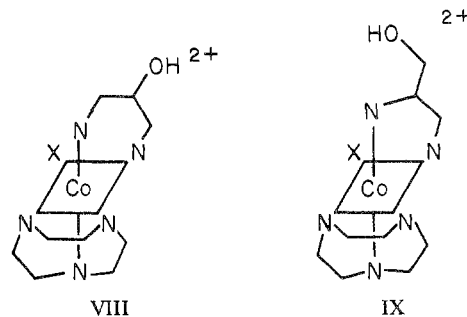
few weeks. During this time some net decomposition of Co(III) complex occurs and  $Co^{2+}(aq)$  is formed. Clearly, hydroxyl groups do not participate in both hydrolysis steps. It is unlikely that either hydroxyl group would be involved in an associative substitution process and not remain coordinated in the product since displacement of a hydroxyl group that is part of a chelate ring is very difficult.

Compound VII is converted to a purple species in 0.1 M HClO<sub>4</sub> (25°), with a half-life of about 3.5 hr. This is about the same as the half-life observed for the aquation of *trans*- $[Co(pn)_2Cl_2]^+$ .<sup>20</sup> As with the 2-tmOH system, the hydroxyl group does not seem to affect the rate of the reaction and the initial product is most likely the monoquo complex.

Base hydrolysis products of IV were examined by carbon-13 nmr and absorption spectroscopy. The carbon-13 nmr spectrum indicated that both dangling and coordinated hydroxyl groups were present in the products. The electronic absorption spectrum indicated that some *cis* product was present. The complexity of the carbon-13 nmr spectrum suggested at least three products were produced but they could not be clearly separated.

Base hydrolysis of VII for a short time did not yield products which contained coordinated hydroxyl groups. When VII was treated with 2 equiv of sodium hydroxide and allowed to stand for 1 week, coordinated hydroxyl groups were detected in the products by carbon-13 nmr spectroscopy. Again a mixture of products was formed and these were not separated. In fact no complex of 1-tmOH that had a coordinated hydroxyl could be isolated.

Participation of uncoordinated (dangling) potential donor groups in substitution reactions of metal complexes is an important aspect of coordination complex chemistry, but it has not received a great deal of attention. Unfortunately, little quantitative information could be obtained from studies of the bis(diamine) reactions of complexes of 1-tmOH and 2-tmOH. Structural differences between these potentially tridentate ligands are obviously important in determining the nature of the ligand-metal interaction. The fact that hydroxyl group coordination does not occur in 1-tmOH complexes is most likely a result of unfavorable reaction kinetics and not due to a lack of thermodynamic stability for the tridentate form. It is not possible, at this point, to determine what factors are most important in causing the difference in behavior of complexes of 1-tmOH and 2-tmOH. We are presently working with complexes VIII and IX and we plan



a rigorous study of hydroxyl group effects in both acid and base hydrolysis reactions.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Registry No. I, 50774-04-4; II, 52610-73-8; III, 52393-38-1; IV, 52393-39-2; V, 52393-40-5; VI, 52540-78-0; VII, 52483-66-6;

[Co(tmNH<sub>2</sub>)<sub>2</sub>]Cl<sub>3</sub>, 52393-41-6; C, 52393-58-5; D, 52438-81-0; A·2HCl, 52393-59-6; A·2HBr, 52393-60-9.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

## Synthesis of a Novel Pentacoordinate Glyoxime-Based Ligand and Preparation of Its Chlorocobalt(III) Complex<sup>1a</sup>

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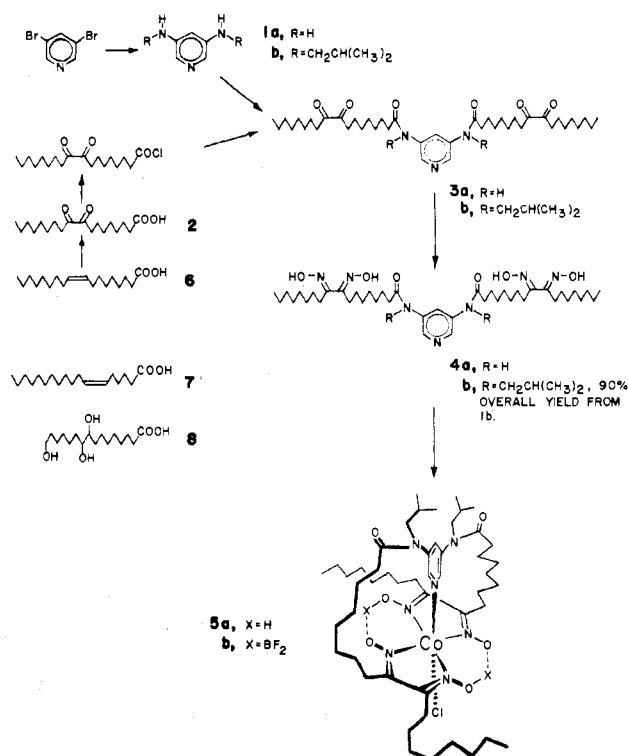
The synthesis and properties of the pentadentate, "basket-like" ligand *N,N'*-diisobutyl-*N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine (**4b**) are described, as well as the preparation and properties of its chlorocobalt(III) complex **5a**.

Cobaloximes have proved to be useful models for vitamin B<sub>12</sub>.<sup>2</sup> In vitamin B<sub>12</sub>, however, the fifth ligand, a 5,6-dimethylbenzimidazole, is covalently bound to the tetracoordinate planar corrin ligand. Several other important biological systems also consist of a metal atom with a square-planar, tetradentate N<sub>4</sub>-coordinating ring system and another nitrogen-coordinating heterocyclic base as the axial fifth ligand, notable examples being the cobalt in vitamin B<sub>12</sub><sup>3</sup> and the iron in cytochrome *c*, hemoglobin, and myoglobin.<sup>4</sup>

### Discussion and Results

Because of the dearth of synthetic pentacoordinate ligands and the interest<sup>5</sup> in the synthesis of these ligands as models for biological systems, we wish to report the simple, high-yield synthesis of the N<sub>5</sub>-pentacoordinate ligand **4b**. Ligand **4b** has three major advantages over simpler glyoxime ligands. First, the ligand is quite soluble in most organic solvents. Ligand **4a** was also synthesized, but it was found to be quite insoluble. Introduction of the isobutyl groups on the amide nitrogens in **4b** markedly improves the solubility. A second advantage of ligand **4b** over simpler glyoximes is that, in a complex with the glyoxime functionalities of **4b** coordinated to the metal, the pyridine part of the ligand is held in the proximity of one of the axial coordination sites. This feature was designed into the system to help counteract the tendency of some metal dimethyl-

Scheme I



(1) (a) Taken from the Ph.D. thesis of H. P. J., M.I.T., May 1974. (b) Camille and Henry Dreyfus Teacher-Scholar grant recipient; Alfred P. Sloan Fellow, 1973-1975. (c) National Science Foundation Predoctoral Fellow, 1970-1973; Goodyear Fellow 1973-1974.

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glyoxime complexes to be either four- or six-coordinate, but not five-coordinate. If a metal complex of **4b** is only tetracoordinate, the pyridine base would be uncoordinated; but, it would still be held very close to its prospective axial coordination site. Thus, when another ligand approaches the opposite axial coordination site, the pyridine base of **4b** would be favorably disposed to form the hexacoordinate species.<sup>5d,5f,6</sup>

The third advantage of a ligand like **4** is the extreme flexibility offered for the synthesis of other modified ligands. Other fatty acid fragments could easily be substituted for the oleic acid derivative **2** in the synthetic scheme. In fact, fatty acids were used in the synthesis in order to take advantage of the functionality already correctly positioned by

(6) The uv-visible spectra of the nickel(II) complex of ligand **4b** indicate that the pyridine is not coordinated. The nickel is tetracoordinate, as it is in most nickel(II) glyoxime complexes. The cobalt(III) complex **5a** of ligand **4b**, however, appears to involve coordination of the pyridine to the cobalt; *vide infra*.