

## Cobalt(III) Complexes of the Cyclic Triamine 1,4,7-Triazacyclononane and Aminoalcohol Ligands

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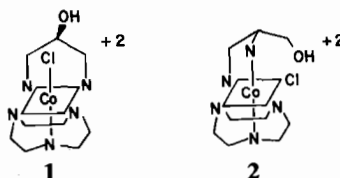
*New Co(III) complexes of 1,4,7-triazacyclononane (TACN) have been prepared. These include [Co(TACN)(NO<sub>2</sub>)<sub>3</sub>], [Co(TACN)Cl<sub>3</sub>] and [Co(TACN)Br<sub>3</sub>] which were precursors to aminoalcohol complexes of the type [Co(TACN)tmOH]<sup>3+</sup> (tmOH = 2,3-diamino-1-propanol and 1,3-diamino-2-propanol bonded in tridentate fashion) and [Co(TACN)tmOH(X)]<sup>2+</sup> (tmOH same as above bonded in bidentate fashion and X = Cl and Br). Base hydrolysis reactions of the latter complexes were studied. No chelation of the dangling hydroxyl group was observed in any hydrolysis reaction. Complexes containing chelated hydroxyl groups were very resistant to substitution.*

### Introduction

Recently we reported a study on the Co(III) complexes of two isomeric diaminoalcohol ligands, 1,3-diamino-2-propanol (2-tmOH) and 2,3-diamino-1-propanol (1-tmOH).<sup>1</sup> Complexes of these two ligands were quite different in their chemical behavior. The alcohol group in the 2-tmOH case showed a strong propensity for coordination to the metal ion. Only the bis complex *trans*-[Co(2-tmO)<sub>2</sub>]<sup>+</sup>, in which the ligand is bonded in a tridentate fashion, could be isolated from reactions of 2-tmOH with Co(II) or Co(III) starting materials. The alcohol group in 1-tmOH does not act as a good ligand and no complex that contained a coordinated hydroxyl group was isolated. Basic solutions of *trans* diacidobisdiamine complexes of each of the isomeric ligands undergo color changes that are typical of hydrolysis reactions. In fact, analyses of the solutions of products from such reactions by <sup>13</sup>C nmr showed that there was some chelation of the hydroxyl group in the 2-tmOH system but not (initially) in the 1-tmOH case. Because of the complexity of the product mixtures, as evidenced by the <sup>13</sup>C nmr spectra, it was not possible to fully characterize the products of such hydrolysis reactions.

Because of the substantial difference in the behavior of the complexes of these two ligands we have

prepared complexes **1** and **2** which contain one hydroxylamine ligand for further study of reactions of complexes of these isomeric ligands. Some of this work is reported here. These complexes contain the symmetrical tridentate ligand 1,4,7-triazacyclononane (TACN), which is highly symmetrical and can only bind to facial positions of an octahedral complex. To our knowledge only the complex [Co(TACN)<sub>2</sub>]<sup>+3 2</sup> has been previously reported with this ligand although such a ligand could have considerable utility for a variety of studies. Included in this report are the preparations of useful starting materials of the type [Co(TACN)X<sub>3</sub>].



### Experimental

#### Materials

1,3-Diamino-2-propanol, 2,3-dibromo-1-propanol and 2,3-dihydropyran were purchased from Aldrich Chemical Company. 1,3-Dibromo-2-propanol was from Eastman Chemicals and ethylenediamine from Mallinkrodt. All were the best grade available from the supplier and they were used without further purification. 2,3-Diamino-1-propanol was prepared as previously described [1] and the trihydrobromide salt of 1,4,9-triazacyclononane (TACN) was prepared in 60% yield by the procedure described by Richman and Atkins.<sup>3</sup>

Analytical data for the compounds discussed are given in Table I.



A 0.29 g (1 mmol) sample of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and a 0.31 g (4.4 mmol) sample of NaNO<sub>2</sub> were added

TABLE I. Analytical Data.

Compound	Calculated				Found			
	C	H	N	X	C	H	N	X
[Co(TACN)(NO <sub>2</sub> ) <sub>3</sub> ]	22.09	4.63	25.76		21.76	4.57	25.54	
[Co(TACN)Cl <sub>3</sub> ]	24.47	5.13	14.27	36.12	24.78	5.36	13.62	35.74
[Co(TACN)Br <sub>3</sub> ]·H <sub>2</sub> O	16.10	3.84	9.40	53.80	16.12	3.88	9.22	53.88
[Co(TACN)(1-tmOH)](ClO <sub>4</sub> ) <sub>3</sub>	18.75	4.37	12.15		18.27	4.44	11.90	
[Co(TACN)(2-tmOH)](ClO <sub>4</sub> ) <sub>3</sub>	18.75	4.37	12.15		18.47	4.14	11.92	
[Co(TACN)(1-tmOH)Cl]Cl <sub>2</sub> ·2H <sub>2</sub> O	25.73	6.95	16.60		25.54	6.76	16.10	
[Co(TACN)(1-tmOH)Cl]Cl <sub>2</sub> ·2H <sub>2</sub> O	25.73	6.95	16.60		25.94	6.40	16.85	
[Co(TACN)(2-tmOH)Cl]Cl <sub>2</sub> ·2H <sub>2</sub> O	25.73	6.95	16.60		25.49	6.98	16.08	
[Co(TACN)(dienOH)]Cl <sub>3</sub>	32.65	7.30	19.03		32.11	7.91	19.18	

to 2 ml of a buffer solution made of 0.8 g (20 mmol) NaOH and 2.3 ml (2.4 g, 40 mmol) acetic acid in 20 ml water. Aeration was then begun. A solution of 0.28 g (0.75 mmol) TACN·3HBr and 0.09 g (2.25 mmol) NaOH in 2 ml water was added dropwise to the buffered solution. This resulted in the immediate precipitation of a yellow-green solid. Aeration was continued for one hour after which time the solid was collected, washed well with water, rinsed with acetone, and dried *in vacuo*. Yield 0.19 g, 78%. Infrared spectrum:  $\nu_{\text{N-H}}$  3216  $\text{cm}^{-1}$ .

#### [Co(TACN)Cl<sub>3</sub>]

A 0.15 g (0.46 mmol) sample of [Co(TACN)(NO<sub>2</sub>)<sub>3</sub>] was added to 6–10 ml 1 M HCl and heated on a steam bath for a few hours until the solution was homogeneous and a dark violet color. It was then evaporated to dryness. The blue-green residue was broken up in a few drops of water, in which it was almost totally insoluble, and collected by filtration. The blue-green trichloro complex was washed with water and acetone and dried *in vacuo*. Yield 75 mg, 55%. Occasionally the blue-green residue was contaminated with a small amount of yellow crystalline material. This was quite soluble in water and thus easily removed. The addition of concentrated HCl to the filtrate reprecipitated the yellow species which analyzed as a hydrochloride salt of [Co(TACN)<sub>2</sub>]Cl<sub>3</sub>. [Co(TACN)Cl<sub>3</sub>] could be prepared more quickly using concentrated HCl, but the yield was somewhat lower. Infrared spectrum:  $\nu_{\text{N-H}}$  3220  $\text{cm}^{-1}$ .

#### [Co(TACN)(1-tmOH)](ClO<sub>4</sub>)<sub>3</sub>

A 0.1 g (0.34 mmol) sample of [Co(TACN)Cl<sub>3</sub>], 0.06 g (0.37 mmol) 1-tmOH·2HCl, and 3 ml 0.2 M NaOH were added to enough water to make a total volume of 10 ml. This was heated on a steam bath for four hours. The resulting orange solution was filtered, acidified with concentrated HCl and evaporated to near dryness. A few milliliters of concentrated HClO<sub>4</sub> was added and the solution left to stand for several

hours. The orange needles which crystallized were then collected by filtration, washed with ethanol, and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. Yield 0.11 g, 56%. Infrared spectrum:  $\nu_{\text{O-H}}$  3420  $\text{cm}^{-1}$ ;  $\nu_{\text{N-H}}$  3240  $\text{cm}^{-1}$ .

#### [Co(TACN)(2-tmOH)](ClO<sub>4</sub>)<sub>3</sub>

A 0.20 g (0.68 mmol) sample of [Co(TACN)Cl<sub>3</sub>] was added to a solution of 0.07 g (about 0.8 mmol) 2-tmOH in 5 ml water. This was gently warmed on a steam bath for two hours during which time the solution became homogeneous and a red-orange color. The volume was then reduced to 1–2 ml and a few ml of concentrated HClO<sub>4</sub> added. After several hours orange needles crystallized. These were collected, washed with ethanol, and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. Yield 0.21 g, 53%. Infrared spectrum:  $\nu_{\text{O-H}}$  3330  $\text{cm}^{-1}$ ;  $\nu_{\text{N-H}}$  3285, 3250  $\text{cm}^{-1}$ .

#### Attempts to Displace the Coordinated Hydroxyl Group in [Co(TACN)(1-tmOH)](ClO<sub>4</sub>)<sub>3</sub> and [Co(TACN)(2-tmOH)](ClO<sub>4</sub>)<sub>3</sub>

When [Co(TACN)(1-tmOH)](ClO<sub>4</sub>)<sub>3</sub> was heated in concentrated H<sub>2</sub>SO<sub>4</sub> or HCl at 100° C for several hours the initially orange solutions turned pink. During evaporation of the HCl solution the color changed to orange and only starting material could be crystallized. The addition of ether to the H<sub>2</sub>SO<sub>4</sub> solution caused a pink oil to separate. This was taken up in a small amount of concentrated HCl, but again this solution became orange and only starting material could be crystallized. [Co(TACN)(2-tmOH)](ClO<sub>4</sub>)<sub>3</sub> could be recovered unchanged after refluxing in concentrated HCl for several days. The 2-tmOH complex was heated 150° C in concentrated H<sub>2</sub>SO<sub>4</sub> for a few hours. An oil was obtained by the addition of ether and this was dissolved in a small amount of concentrated HCl. Only Co(II) species were isolated. When heated at 100–120° C in concentrated H<sub>2</sub>SO<sub>4</sub> for 24 hours only starting material was obtained.

On the assumption that the oils resulting from the H<sub>2</sub>SO<sub>4</sub> reactions contained some of the complex with

a dangling hydroxyl group, attempts were made to form the pyran derivative of the alcohol to prevent subsequent chelation. The oil was dissolved in a 50–50 mixture of 2,3-dihydroxypropan and DMSO and left at room temperature for 24 hours. Treatment with ether precipitated an orange oil which was taken up in a concentrated solution of tetraethylammonium chloride in ethanol. This was warmed gently for a few hours and left to stand for two days. The solution gradually turned a dark brown color and no solid was ever obtained.

*Pyran Derivatives of 1-tmOH and 2-tmOH (1-tmOpy and 2-tmOpy)*

The pyran derivatives of the amines were prepared from the corresponding dibromo alcohols as described in the synthesis of 1-tmOH<sup>1</sup> using LiAlH<sub>4</sub> to carry out the reduction of the diazide. Hydrolysis of the reaction mixture was done with 12% NaOH and solids formed were removed by filtration. After removal of solvent by rotary evaporation, benzene was added to the oil that remained and the oil was dried by distillation of benzene–water azeotrope.

After removal of the benzene the products were distilled. 1-tmOpy: b.p. = 78°C (0.2 torr); nmr (CDCl<sub>3</sub>–TMS), τ5.4–5.5 (1H), 6–7 (5H), 7–7.5 (2H), 8.25 (6H), 8.6 (4H). 2-tmOpy: b.p. = 73°C (0.1 torr); nmr (CDCl<sub>3</sub>–TMS), τ5.4 (1H), 5.9–6.8 (3H), 7.1–7.35 (4H), 8.4 (6H), 8.52 (4H). Care must be taken to insure adequate stirring during the reduction to effect complete reaction. Any unreacted azide will distill with the diamine.

*[Co(TACN)(1-tmOH)Cl]Cl<sub>2</sub>·2H<sub>2</sub>O*

A 0.23 g (1.27 mmol) sample of 1-tmOpy was dissolved in 1 ml absolute methanol and 0.25 g (0.85 mmol) [Co(TACN)Cl<sub>3</sub>] was added. The mixture was heated on a steam bath for 2 hours during which time it became homogeneous and a reddish orange color. The solution was evaporated to dryness with a stream of air and the residue dissolved in 1 ml of 3 M HCl. After stirring for 5 minutes the solution was placed on an ion exchange column in the H<sup>+</sup> form and eluted with 3 M HCl. Two bands developed immediately – a leading rose-colored band and a much smaller orange band. Each of these subsequently split into two bands. The two rose bands were collected separately and the solvent removed by rotary evaporation at 28°C. The resulting solids were then dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The first fraction was identified as the isomer which cannot chelate. The yield was 60 mg, 17%. The second fraction was identified as the isomer which can chelate. The yield was 100 mg, 28%.

*[Co(TACN)(2-tmOH)Cl]Cl<sub>2</sub>·2H<sub>2</sub>O*

A 0.1 g (0.57 mmol) sample of 2-tmOpy was dissolved in 1 ml methanol and 0.15 g (0.51 mmol) [Co

(TACN)Cl<sub>3</sub>] added. The mixture was heated on a steam bath for an hour. The methanol was evaporated to about one-half to one-third the volume and then filtered to yield a pink violet solid. The solid was contaminated with some unreacted [Co(TACN)Cl<sub>3</sub>], but the analytical data showed that it was predominantly [Co(TACN)(2-tmOpy)Cl]Cl<sub>2</sub>. This solid was dissolved in one ml of 3 M HCl and stirred for five minutes. It was then placed on an ion exchange column in the H<sup>+</sup> form and eluted with 3 M HCl. In some attempts a faint purple band separated immediately, moving more rapidly than the rest of the material on the column. This fraction could be [Co(TACN)(H<sub>2</sub>O)Cl<sub>2</sub>]Cl, but it was not isolated. About 90% of the sample was contained in the second band which was rose-colored. The last band was orange. A very small rose-colored band split off from the main band about half-way through the elution. Other than this, no separation was observed in the rose band. It was collected and the solvent removed by rotary evaporation at 28°C. The residual solid was fairly hygroscopic and difficult to work with. Analytical results suggested a dihydrate composition. No yield was determined but it did not exceed 30%.

*[Co(TACN)(2-tmOH)Br]Br<sub>2</sub>*

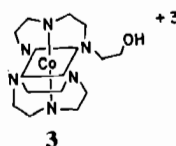
A 0.20 g (1.15 mmol) sample of 2-tmOpy was dissolved in 2 ml of absolute methanol and 0.43 g (1.0 mmol) [Co(TACN)Br<sub>3</sub>] was added. This was heated on a steam bath for two hours. After filtering to remove any unreacted tribromide, washing the solid well with methanol, the filtrate was evaporated to dryness with a stream of air. The residue was dissolved in 2 ml of 3 M HBr and stirred for five minutes. The solution was then placed on an ion exchange column and eluted with 3 M HBr. Six bands developed. The leading band was gray–violet, the second band reddish, the third and fourth bands purple–violet, the fifth band yellow, and the sixth band orange. The two purple–violet bands were collected separately and the solvent removed by rotary evaporation at 28°C. The yield was estimated at 30% for the first fraction of purple material (band 3) which was identified as the isomer which can chelate. The yield of the second purple band, the isomer which cannot chelate (band 4), was about 15%.

The <sup>13</sup>C 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 μsec with a pulse delay of 0.25 sec and acquisition time of 1.475 sec. The deuterium of the solvent was used for a lock signal. The samples were contained in 12 mm (O.D.) nmr tubes and the data collected at about 40°C. 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

The ligand 1,4,7-triazacyclononane (TACN) is unique in that it is one of a very small number of tridentate ligands that can only bind to three facial positions of a six-coordinate complex. Others include *cis*, *cis*-1,3,5-triaminocyclohexane<sup>4</sup> and 1,1,1-tri(amino-methyl)ethane.<sup>4</sup> These ligands also have 3-fold symmetry when bound in this fashion. TACN was chosen for our work because it is comparatively easy to prepare and it would provide the smallest number of magnetically non-equivalent carbon atoms under most circumstances when present in a metal complex. The latter factor was an important consideration since <sup>13</sup>C nmr spectroscopy was to be used for characterizing reaction products from base hydrolysis reactions of acido complexes. Prior to development of the high-yielding, general synthesis of cyclic amines by Richman and Atkins<sup>3</sup> TACN was available only by very low yielding routes. Koyama and Yoshino prepared the only metal complex of TACN, [Co(TACN)<sub>2</sub>]Cl<sub>3</sub>, that we are aware of.<sup>2</sup> Oxidation of a 1:1 mixture of Co<sup>+2</sup> and TACN · 3HBr in buffered NaNO<sub>2</sub> medium proved to be a satisfactory way of obtaining [Co(TACN)(NO<sub>2</sub>)<sub>3</sub>]. Although this complex is very insoluble it is a useful starting material for the preparation of other mono-TACN species via the trihalo complexes<sup>5</sup> which were easily prepared by acid hydrolysis of the nitro-complex with the appropriate acid.

In addition to the hydroxydiamine complexes described below, a number of other Co(III) complexes were prepared from [Co(TACN)X<sub>3</sub>] (X = Cl, Br). These included complex 3 in which the hydroxytriamine was coordinated through the three nitrogen donors.



Preparation of 1- and 2-tmOH complexes from [Co(TACN)Cl<sub>3</sub>] proved to be straightforward and these were readily isolated as tris perchlorate salts.<sup>7</sup> It came as somewhat of a surprise, however, to find that both complexes contained the diaminoalcohol as a tridentate ligand since we were not able to isolate a complex that contained 1-tmOH in tridentate form during our earlier studies.<sup>1</sup> That the hydroxyl groups in these complexes were coordinated to the metal ion was readily established by <sup>13</sup>C nmr. Both the 1- and 2-tmOH complexes exhibited low-field resonances with chemical shifts that were typical of a carbon atom bonded to a coordinated hydroxyl group (Table II). The sensitivity of <sup>13</sup>C nmr spectroscopy to symmetry and its usefulness as a tool for stereochemical studies in Co(III) systems<sup>1,8</sup> is further demonstrated by these examples. The <sup>13</sup>C nmr spectrum of [Co(TACN)(2-tmOH)]<sup>+3</sup>, 4, contained four resonances in addition to the resonance for the carbon bonded to oxygen (Table II). This simply demonstrates the presence of the plane of symmetry that is expected to be present in this ion:

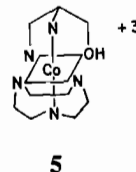
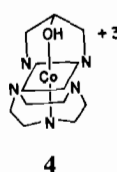


TABLE II. Spectroscopic Data for [Co(TACN)(tmOH)]<sup>+3</sup> and [Co(TACN)(tmOH)Cl]<sup>+2</sup>.

Compound	<sup>13</sup> C NMR <sup>a</sup>				Absorption <sup>b</sup>		
	C-OH	C-NH <sub>2</sub> (sec)	C-NH <sub>2</sub> (pri)	TACN	Band I	Band II	
[Co(TACN)(1-tmOH)] <sup>+3</sup>	67.47	56.57	45.46	54.02	50.66	476(63) <sup>d</sup>	340(59)
				51.44	50.06		
				51.60	48.40		
				53.08	50.46		
[Co(TACN)(1-tmOH)Cl] <sup>+2 c</sup>	59.62	58.45	45.06	52.97	50.14	520(87) <sup>e</sup>	360(85)
				52.54	49.83		
					52.37		
					51.48		
[Co(TACN)(2-tmOH)] <sup>+3</sup>	77.00		48.58	50.06		466(59) <sup>d</sup>	338(62)
					50.6		
[Co(TACN)(2-tmOH)Cl] <sup>+2 f</sup>	64.27		43.41	50.6-51.5	532 <sup>e</sup>	369 <sup>g</sup>	
	63.62		42.12				

<sup>a</sup> DCl solutions. <sup>b</sup> λ in nm, ε in parenthesis. <sup>c</sup> Isomer in which the hydroxyl group can coordinate. <sup>d</sup> 1 M HCl. <sup>e</sup> H<sub>2</sub>O.

<sup>f</sup> Mixture of isomers.

The  $^{13}\text{C}$  nmr spectrum of  $[\text{Co}(\text{TACN})(1\text{-tmOH})]^{+2}$ , **5**, contained eight resonances in addition to the resonance attributed to the hydroxyl carbon (Table II). This clearly indicates the lack of symmetry that this ion must have.

Although the TACN-aminoalcohol complexes were readily prepared we were unable to prepare acido complexes of either of these by substitution of the hydroxyl group (see Experimental). This somewhat surprising inertness of a chelated hydroxyl ligand to substitution has been previously noted by Sargeson, *et al.*<sup>9</sup> for  $[\text{Co}(\text{en})_2\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}]^{+3}$ . The hydroxyl group in this complex was not substituted in 6 *M* HBr at 100°C. Since acido complexes were required for base hydrolysis reactions another route was sought. They were ultimately prepared by substitution in  $[\text{Co}(\text{TACN})\text{Cl}_3]$  using the pyran derivatives of the diaminoalcohols (1-tmOpy and 2-tmOpy). These derivatives were prepared and handled in basic solution to avoid hydrolysis of the acetal; the ease of hydrolysis of this function under acidic conditions made it easy to generate the hydroxyl form of the complex. Chelation of either 1-tmOpy or 2-tmOpy can occur in two ways to yield stereoisomers. After hydrolysis of such a pair of stereoisomers only one of these isomers forms a complex that contains a hydroxyl group that can coordinate in a hydrolysis reaction. We were unable to achieve a separation of these stereoisomers in the pyran form. Instead the pyran derivatives were hydrolyzed in the appropriate acid and chromatographed on an ion exchange column. Several species were detected upon development of the columns. The acido complexes were identified by their behavior on the column and by comparison of their absorption spectra with those of the corresponding  $[\text{Co}(\text{en})_2(\text{H}_2\text{NCH}_2\text{CH}_2\text{OH})\text{X}]^{+2}$  complexes.<sup>10</sup> Separation of the stereoisomers was achieved with  $[\text{Co}(\text{TACN})(1\text{-tmOH})\text{Cl}]^{+2}$  and  $[\text{Co}(\text{TACN})(2\text{-tmOH})\text{Br}]^{+2}$  and these were isolated as chloride and bromide salts, respectively.  $[\text{Co}(\text{TACN})(2\text{-tmOH})\text{Cl}]^{+2}$  was not successfully separated into its stereoisomers although it was possible to show that both isomers were present by  $^{13}\text{C}$  nmr (Table II). The  $^{13}\text{C}$  nmr spectrum contained two downfield resonances characteristic of carbon bonded to a free hydroxyl group. In the case of  $[\text{Co}(\text{TACN})(1\text{-tmOH})\text{Cl}]^{+2}$  and  $[\text{Co}(\text{TACN})(2\text{-tmOH})\text{Br}]^{+2}$  the stereoisomers of each were differentiated initially on the basis of their relative rates of acid hydrolysis. One fraction of both of these complexes showed a slightly greater rate of hydrolysis (loss of acido complex by absorption spectroscopy). The fraction showing the highest rate of hydrolysis was chosen as the isomer that could chelate the hydroxyl group. This choice was based on the idea that in the absence of any involvement of the hydroxyl group in the hydrolysis reaction the two isomers should hydrolyze at nearly the same rate and that involvement of the hydroxyl group which can occur in only one

isomer of each compound, should increase the rate of hydrolysis. These choices were shown to be correct by isolation of complexes containing the amino alcohol ligands in tridentate form from perchloric acid solutions of these fractions (as  $\text{ClO}_4^-$  salts) after these solutions stood for a few days.

As demonstrated earlier for the bis tmOH complexes there is a substantial chemical shift difference between carbon atoms bonded to coordinated and free hydroxyl groups (see Table II). This insured that a hydrolysis product that contained a coordinated hydroxyl group would be readily detected.

Hydrolysis reactions of the TACN-tmOH complexes were conducted in 0.5 *M* NaOH and by pH-stat titration at pH 9.5. Analyses of the product solutions, after suitable work-up, by  $^{13}\text{C}$  nmr showed that no products that contained a coordinated hydroxyl group were formed in the base hydrolysis reaction of either the 1-tmOH or 2-tmOH Cl and Br derivatives (within the limits of detection). The product solutions, which were initially orange, turned rose-red during  $^{13}\text{C}$  data collection (DCl solution). These color changes suggest that the primary hydrolysis product is the aquo species and that anation occurred in the acid solution during analysis. More than one product was indicated to be present by the  $^{13}\text{C}$  nmr data.

The results of these experiments serve to further illustrate the complexity of reactions that involve hydroxyl ligands. Several useful pieces of information have been obtained. The mode of binding of an aminoalcohol ligand is dependent upon the other ligands in the system – compare  $[\text{Co}(1\text{-tmOH})_3]^{+3}$  and  $[\text{Co}(1\text{-tmOH})_2\text{Cl}_2]^{+}$  with  $[\text{Co}(\text{TACN})(1\text{-tmOH})]^{+3}$ . Kinetic effects are the controlling feature in base hydrolysis reactions and these may not result in appreciable amounts of hydroxyl group (or other dangling donor) binding, depending upon the system involved. Alexander and Spillert<sup>11</sup> prepared  $[\text{Co}(\text{en})_2\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_3]\text{Cl}]^{+3}$  and studied its base hydrolysis reactions. Only a small amount of  $[\text{Co}(\text{en})_3]^{+3}$  was formed (< 5%). Buckingham and co-workers have studied a variety of systems that involve bidentate ligands in which there is a dangling donor group.<sup>12</sup> The amount of chelation can vary tremendously. The factors that determine the competition of the dangling donor with water for the vacant coordination site in the intermediate are probably several-fold but must include the degree of solvation of the dangling donor and conformation effects in the ligand containing the dangling donor group.

This work has several other important features. Useful starting materials containing a single TACN molecule as a tridentate ligand have been prepared in reasonable yield. The ease of preparation of this cyclic triamine should make it a useful ligand for a variety of applications. The pyran derivative of an alcohol has been successfully utilized as a blocking group during complex formation. Earlier work involv-

ing alcoholamine ligands could have benefitted from this approach.

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