tonation helping cleavage of the O atom being transferred from $ClO_4^-$ to the Mo reactant in reaction 1 and/or 2.

Although we have no way at present of proceeding to a fuller interpretation with precise identification of the Mo ions involved as intermediates, distinctive features of the reactions have been indicated in this work.

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**Registry No.** $ClO_4^-$, 14797-73-0; $Mo(H_2O)_6^{3+}$, 34054-31-4; $Mo_2O_4(H_2O)_6^{2+}$, 40804-49-7; $[(9\text{-aneN}_3)(H_2O)Mo(OH)_2Mo(H_2O)(9\text{-aneN}_3)]^{4+}$, 92542-35-3.

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Contribution from the Department of Chemistry,
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# Alkaline Hydrolysis of *t*-$[Co(tren)(NH_3)SCN]^{2+}$ and Other *t*- and *p*-$[Co(tren)(NH_3)X]^{2+}$ Complexes

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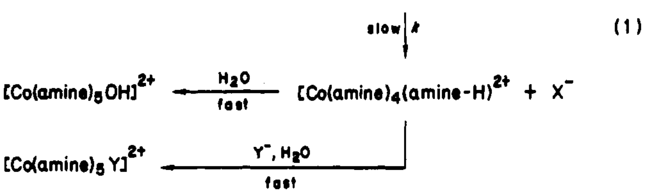
The synthesis of *t*- and *p*-$[Co(tren)(NH_3)NCS]^{2+}$ and *t*- and *p*-$[Co(tren)(NH_3)SCN]^{2+}$ is reported. Alkaline hydrolysis of *p*-$[Co(tren)(NH_3)SCN]^{2+}$ ($k_{OH} = 1.1 \times 10^4$ mol$^{-1}$ dm$^3$ s$^{-1}$) results in only *p*-$[Co(tren)(NH_3)(OH)]^{2+}$, but hydrolysis of *t*-$[Co(tren)(NH_3)SCN]^{2+}$ ($k_{OH} = 3.1 \times 10^{-2}$ mol$^{-1}$ dm$^3$ s$^{-1}$) results in *t(SCN)*-$[Co(tren)(OH)SCN]^+$ (35%), *t*-$[Co(tren)(NH_3)NCS]^{2+}$ (5%) as well as *p*-$[Co(tren)(NH_3)(OH)]^{2+}$ (50%) and *t*-$[Co(tren)(NH_3)(OH)]^{2+}$ (10%). In alkaline solution *t(SCN)*-$[Co(tren)(OH)SCN]^+$ isomerizes to *t(NCS)*-$[Co(tren)(OH)NCS]^+$ ($k = 3 \times 10^{-5}$ s$^{-1}$) while in aqueous acid isomerization of *t(SCN)*-$[Co(tren)(OH_2)SCN]^{2+}$ is slower ($k = 1.3 \times 10^{-6}$ s$^{-1}$). The alkaline hydrolysis of *t*-$[Co(tren)(NH_3)X]^{2+}$ ($X = NCS^-$, $N_3^-$) gives only *t(X)*-$[Co(tren)(OH)X]^+$ products ($k_{OH}^{NCS} = 2.5 \times 10^{-3}$ mol$^{-1}$ dm$^3$ cm$^{-1}$, $k_{OH}^{N_3} = 1.2 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$). All data are at $I = 1.0$ mol dm$^{-3}$ ($NaClO_4$) and 25.0 °C.

A major remaining question to be answered in the base hydrolysis of cobalt(III)–acido complexes concerns the lifetime of the five-coordinate intermediate formed following the loss of $X^-$ (eq 1).[1] Is any molecular event possible within this intermediate

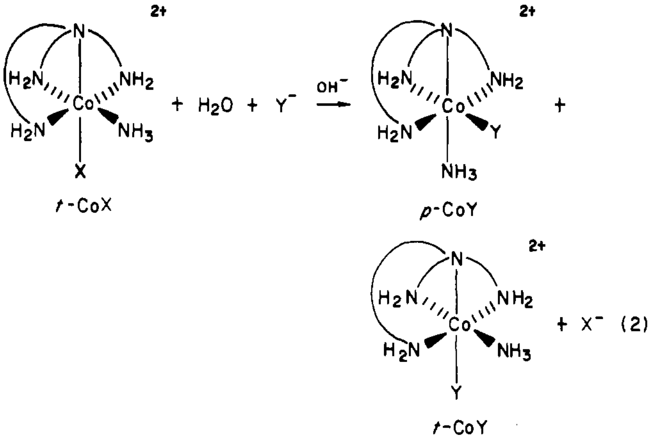


(1)

prior to the coordination of a $H_2O$ molecule or other entering group $Y^-$? It appears that capture from the immediate environment of the solvent cage occurs,[2] but it is unclear whether the intermediate moves toward equilibration with its solvent cage or whether it is more reactive than that. Possibly the best evidence concerning lifetimes comes from the mutarotation of deprotonated amine centers during the base hydrolysis of (*R*)- and (*S*)-$\alpha,\beta$-$[Co(tetren)(NO_3)]^{2+}$ [3] and $\beta_2$-(*RR,SS*)-$[Co(trien)(glyOR)Cl]^{2+}$,[4] which cannot be accounted for by mutarotation in the deprotonated reactant or in the hydroxo product. Mutarotation of deprotonated amine centers in Co(III) complexes occurs at a rate of $10^4$–$10^5$ s$^{-1}$,[5] which implies some stability for the intermediate. However, in base hydrolysis reactions coordination by $H_2O$ and reprotonation may be concerted, forcing more rapid inversion in these cases.

Another possibility is to look for stereochemical change about the metal that cannot arise from preconditioned solvation or ion-pairing effects. Clear evidence of this is not easy to find, but a few years ago we reported a small amount (~0.5%) of isomerization and geometrical change of *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$ to *cis*-$[Co(en)_2(NH_3)NCS]^{2+}$ during the base hydrolysis of the former that could not be accounted for by exchange of coordinated $SCN^-$ with solvent-labeled $S^{14}CN^-$.[6] This suggests a definite lifetime for the intermediate within the solvent cage sufficient to allow stereochemical reorganization within a tight $[Co(en)(en\text{-}H)(NH_3)]^{2+}SCN^-$ ion pair.

A significant feature of the base hydrolysis of *t*-$[Co(tren)(NH_3)X]^{2+}$ complexes is the large amount of stereochemical change to the *p* configuration (eq 2).[7] Such stereochemical change



*t*-CoX

*p*-CoY

*t*-CoY

(2)

$Y = OH^-, N_3^-$

can be regarded as mutarotation about the metal, and it must occur in the five-coordinate intermediate or as part of the rate-determining loss of $X^-$, since it does not occur in the reactant, its conjugate base, or the *t*-CoY products. For different X the amount of mutarotation varies, and for particular X it is dependent on the electrolyte and its concentration.[7] However, the difficulty here is that the entering group Y is, or can be considered as, part of the solvent cage and its geometrical origin remains obscure. A more precisely located internal competitor in the reactant is required to test for mutarotation about the metal.

We therefore decided to investigate the base hydrolysis of *t*-$[Co(tren)(NH_3)SCN]^{2+}$ to see if mutarotation included *p*-$[Co(tren)(NH_3)NCS]^{2+}$ as a product and if so study its isomerization within the solvent cage as a function of added external competitors. A positive answer would imply an intermediate with

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(1) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1.
(2) Buckingham, D. A.; Edwards, J. D.; McLaughlin, G. M. *Inorg. Chem.* **1982**, *21*, 2770.
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0020-1669/86/1325-2569$01.50/0

a lifetime sufficient to allow mutarotation and redistribution of entering groups within the solvent cage. It would also provide confirmation for the previous result with *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$.[6]

This paper reports the results of this investigation, as well as other results that add to our understanding of the base hydrolysis of the Co(III)–tren system.

## Experimental Section

**Preparations. *t*- and *p*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$.** The preparation of these two complexes has been reported previously, but the following procedure has resulted from refinement to avoid bis(azido) products. *t*-$[Co(tren)(NH_3)(OH_2)](ClO_4)(NO_3)_2$ (1.5 g) was dissolved in water (6 cm$^3$) containing 1.0 g of $LiN_3$. The pH was adjusted to 5 (HOAc), and the temperature was quickly raised to 70 °C. After 9 min, 2 cm$^3$ of water was added, followed by $NaClO_4$. On cooling, the product crystallized. The purple-crimson crystals of *t*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$ were recrystallized from warm water by adding $NaClO_4$ and $LiNO_3$ and were stored in the dark. *p*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$ was prepared in a similar manner but with a pH of 4.5 (HOAc) and by heating for 12 min. Anal. Calcd for $CoC_6H_{21}N_9O_7Cl$: C, 16.93; H, 4.97; N, 29.62. Found for the *t* isomer: C, 16.9; H, 5.0; N, 29.8 ($\epsilon_{508}$ 400 mol$^{-1}$ dm$^3$ cm$^{-1}$).[8] Found for the *p* isomer: C, 16.7; H, 5.1; N, 30.2. ($\epsilon_{503}$ 370 mol$^{-1}$ dm$^3$ cm$^{-1}$).[8]

***t*-$[Co(tren)(NH_3)NCS]Cl_2 \cdot 0.5H_2O$ and *t*-$[Co(tren)(NH_3)SCN]Br_2 \cdot H_2O$.** *t*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$ (5.2 g) dissolved in NaSCN (104 cm$^3$, 10 mol dm$^{-3}$) at 40 °C was treated alternately with small portions of $NaNO_2$ (1.686 g, 100% excess) and $HClO_4$ (6 mol dm$^{-3}$) dropwise, until all the azido complex had reacted (~5 min). The yellow species, $H_2C_2N_2S_3$, that precipitated was filtered off and the solution diluted with water (10 dm$^3$, 0.01 mol dm$^{-3}$). The products were sorbed on cation-exchange resin (Dowex 50W-X2, 100–200 mesh, H$^+$ form) using a large column mounted in an ISCO cabinet kept at 2 °C. On elution with HCl (1–2 mol dm$^{-3}$) the dark purple band (S bound) eluted first closely followed by the larger orange band (N bound). The two products were separately collected and rotary evaporated to dryness by a good vacuum and minimum heating. A small volume of warm water and LiCl was added to each fraction, and the solutions were cooled. The orange N-bound isomer is sparingly soluble as the chloride salt and was filtered from each fraction. To the combined filtrates was added LiBr, and the violet S-bound bromide salt crystallized. Both the N- and S-bound isomers were recrystallized from warm water by adding LiCl or LiBr, respectively. Their isomeric purity was checked by RP-HPIPC. Anal. Calcd for $[CoC_7H_{21}N_6S]Cl_2 \cdot 0.5H_2O$ (*t*-NCS): C, 23.34; H, 6.16; N, 23.33; S, 8.90. Found: C, 23.6; H, 6.4; N, 23.4; S, 8.9 ($\epsilon_{492}$ 328 mol$^{-1}$ dm$^3$ cm$^{-1}$; $\epsilon_{300}$ 2070 mol$^{-1}$ dm$^3$ cm$^{-1}$). Calcd for $[CoC_7H_{21}N_6S]Br_2 \cdot H_2O$ (*t*-SCN): C, 18.35; H, 5.06; N, 18.35; S, 6.99. Found: C, 18.3; H, 5.1; N, 18.5; S, 6.7 ($\epsilon_{507}$ 160 mol$^{-1}$ dm$^3$ cm$^{-1}$; $\epsilon_{296}$ 17 700 mol$^{-1}$ dm$^3$ cm$^{-1}$).

***p*-$[Co(tren)(NH_3)NCS]Br_2$ and *p*-$[Co(tren)(NH_3)SCN]Br_2 \cdot 0.5H_2O$.** To *p*-$[Co(tren)(NH_3)N_3](ClO_4)_2$ (5.0 g) dissolved in NaSCN (5 cm$^3$, ~20 mol dm$^{-3}$) small portions of $NaNO_2$ (1.62 g) and $HClO_4$ (6 mol dm$^{-3}$) were added alternately at room temperature until all the azido complex had reacted (10–15 min). The solution was then diluted with cold water and sorbed onto Dowex 50W-X2 cation-exchange resin kept at 2 °C in a refrigerated cabinet. Elution with HCl (1 mol dm$^{-3}$) separated the yellow N-bound isomer from the slower moving orange-red S-bound product. Both complexes were recovered by rotary evaporation of the separately collected fractions with particular care being taken during recovery of the readily isomerized S-bound isomer. The solid residues were dissolved in a small volume of warm water, and the complexes were recovered as the bromide salts. The solution containing the S-bound isomer was treated first with LiCl to remove small small amounts of the N-bound isomerization product and then with LiBr. The product was dissolved in the minimum volume of water and slowly rotary evaporated at room temperature to give three fractions. The third fraction contained chromatographically (RP-HPIPC) pure *p*-$[Co(tren)(NH_3)SCN]Br_2 \cdot 0.5H_2O$. Anal. Calcd for $[CoC_7H_{21}N_6S]Br_2$ (*p*-NCS): C, 19.10; H, 4.81; N, 19.10; S, 7.29. Found: C, 19.4; H, 4.7; N, 19.1; S, 7.6 ($\epsilon_{482}$ 257 mol$^{-1}$ dm$^3$ cm$^{-1}$; $\epsilon_{303}$ 1760 mol$^{-1}$ dm$^3$ cm$^{-1}$). Calcd for $[CoC_7H_{21}N_6S]Br_2 \cdot 0.5H_2O$ (*p*-SCN): C, 18.72; H, 4.94; N, 18.72; S, 7.14. Found: C, 18.9; H, 5.1; N, 18.8; S, 6.7 ($\epsilon_{495}$ 150 mol$^{-1}$ dm$^3$ cm$^{-1}$; $\epsilon_{292}$ 12 600 mol$^{-1}$ dm$^3$ cm$^{-1}$).

***t*-$[Co(tren)(NH_3)Br]Br_2 \cdot 0.5H_2O$.** To *t*-$[Co(tren)(NH_3)OH_2](ClO_4)(NO_3)_2$ (0.5 g) dissolved in water (1.0 cm$^3$) was added 48% hydrobromic acid (2.0 cm$^3$). As the mixture was heated in a water bath to ca 80 °C, the red-orange color of the solution deepened, and violet crystals deposited. These were collected, and the complex was crystallized as the dibromide salt by dissolving in water, passing through an anion-exchange column (Br$^-$ form), reducing the eluate to a small volume, and adding LiBr. The light purple crystals that quickly formed were filtered, washed with methanol, and air-dried. Anal. Calcd for $[CoC_6N_5H_{21}Br]Br_2 \cdot 0.5H_2O$: C, 15.30; H, 4.51; N, 14.87; Br, 50.90. Found: C, 15.7; H, 4.8; N, 14.3; Br, 50.9, ($\epsilon_{542}$ 154 mol$^{-1}$ dm$^3$ cm$^{-1}$).

***t*(*NCS*),*p*(*Cl*)-$[Co(tren)Cl(NCS)]Cl \cdot H_2O$.** *t*-$[Co(tren)(NH_3)NCS]Cl_2$ (70 mg) was dissolved in water (2.0 cm$^3$) and NaOH (2.0 cm$^3$, 1 mol dm$^{-3}$) added. After being allowed to stand for 30 min at room temperature (~$6t_{1/2}$ for hydrolysis) the reaction was quenched by adding a small volume of concentrated HCl. Dark orange crystals of *t*(*NCS*),*p*($OH_2$)-$[Co(tren)(OH_2)NCS]Cl_2$ separated almost immediately. These were filtered off, washed with MeOH, and heated (80 °C) under vacuum (1 mmHg) for 1 h. During this time the color changed from orange to bright red. Anal. Calcd. for $[CoC_7H_{18}N_5ClS]Cl \cdot H_2O$: C, 23.87; H, 5.73; N, 19.89; Cl, 20.12. Found: C, 23.7; H, 6.0; N, 20.3; Cl, 20.2.

**Rate Studies.** Rate data were obtained with a Cary 219 or a Durrum stopped-flow spectrophotometer. Reactions were followed in aqueous NaOH or Hepes or *N*-ethylmorpholine buffers, at 25.0 °C and $I$ = 1.0 mol dm$^{-3}$ ($NaClO_4$). Linear plots of log ($A_t - A_\infty$) vs. time were obtained for at least $3t_{1/2}$ in each case.

For *t*-$[Co(tren)(NH_3)SCN]Cl_2$, *t*-$[Co(tren)(NH_3)NCS]Cl_2$, and *p*-$[Co(tren)(NH_3)NCS]Br_2$ 40-µL samples (0.03 mol dm$^{-3}$ in water) were injected into thermostated NaOH solutions (2.6 cm$^3$, [OH$^-$] = 1.0, 0.5, 0.25, 0.1, 0.025 mol dm$^{-3}$) contained in a 1-cm cuvette. With an absorbance range of 0.1, the decrease in absorbance was followed at 518 nm for *t*-$[Co(tren)(NH_3)SCN]Cl_2$, at 495 nm for *t*-$[Co(tren)(NH_3)NCS]Cl_2$, and at 482 nm for *p*-$[Co(tren)(NH_3)NCS]Br_2$. The reaction of *p*-$[Co(tren)(NH_3)SCN]Br_2$ was followed in Hepes buffers (0.1 mol dm$^{-3}$). Forty-microliter samples (0.03 mol dm$^{-3}$ in water) were injected into thermostated solutions (pH 6.8, 7.7, 7.8) in a 1-cm cuvette. The absorbance decrease was followed at 410 nm. Rates were similarly obtained for *t*-$[Co(tren)(NH_3)N_3]^{2+}$ in NaOH (1.0, 0.67, 0.5 mol dm$^{-3}$) at 508 nm. The stopped-flow apparatus was used to follow the hydrolysis of *p*-$[Co(tren)(NH_3)N_3]^{2+}$ at 503 nm. A stock solution of *p*-$[Co(tren)(NH_3)N_3](NO_3)(ClO_4)$ ($6.7 \times 10^{-4}$ mol dm$^{-3}$, 30 cm$^3$, $I$ = 1 mol dm$^{-3}$ ($NaClO_4$)) was mixed with NaOH solutions ([OH$^-$] = 0.5, 0.4, 0.3, 0.2, 0.1 mol dm$^{-3}$). The reaction of *t*-$[Co(tren)(NH_3)Br]Br_2$ in NaOH (0.091, 0.057, 0.048 mol dm$^{-3}$, $I$ = 1.0 mol dm$^{-3}$ ($NaClO_4$)) was followed by monitoring the decrease in absorbance at 542 nm.

*t*-$[Co(tren)(OH_2)SCN]^{2+}$ was eluted from the SP-C25 column (described below) with $NaClO_4$ (0.2 mol dm$^{-3}$). The ionic strength was increased to 1.0 mol dm$^{-3}$ (solid $NaClO_4$), and samples were rapidly mixed with NaOH (1.0 mol dm$^{-3}$) or *N*-ethylmorpholine to give [OH$^-$] = 0.5, 0.33, or 0.1 mol dm$^{-3}$ or measured pHs of 11.76 or 8.27. The absorbance increase at 505 nm ($\lambda_{max}$ of *t*-$[Co(tren)(OH)SCN]^+$) was followed (3-cm$^3$ solution, 1-cm cuvette). In all cases, small amounts of the product *t*-$[Co(tren)(OH)NCS]^+$ were present in the initial solutions.

**Reaction Products.** RP-HPIPC ( reversed-phase–high-performance ion-pair chromatography) analyses[9] were carried out on Radial-Pak $C_{18}$ cartridges (10 µm, 100 × 5 mm) using a RCM-100 radial compression module (Waters Associates), a Varian 5000 pump, a Waters U6K injector assembly, a thermostated Varian UV-50 variable wavelength detector, and a HP 3390 A integrator in conjunction with a Varian 9176 recorder. For hydrolysis of *t*-$[Co(tren)(NH_3)SCN]Br_2$ products were determined in the following three ways.

**Method 1.** To *t*-$[Co(tren)(NH_3)SCN]Br_2$ (3.12 mg) in water (0.2 cm$^3$) was added 0.5 mol dm$^{-3}$ NaOH (0.2 cm$^3$). After $t_{1/4}$ (45 s), $2t_{1/2}$ (3 min), $5t_{1/2}$ (7.5 min), $10t_{1/2}$ (15 min) and 24 h, 50-µL aliquots of the reaction mixture were quenched into 30 µL of 0.5 mol dm$^{-3}$ HCl ($HClO_4$ and HOAc also tested as quenching solutions). Forty-microliters samples were injected into the HPLC analyzer.

**Method 2.** *t*-$[Co(tren)(NH_3)SCN]Br_2$ (60 mg) was base-hydrolyzed in 1.00 mol dm$^{-3}$ NaOH (10 cm$^3$) at 25 °C for $5t_{1/2}$ (112 s) before quenching with 1 mol dm$^{-3}$ HCl (10 cm$^3$). The reaction mixture was then diluted with water (100 cm$^3$), sorbed onto cation-exchange resin (Dowex 50W-X2, 100–200 mesh, H$^+$ form) and eluted with HCl (1–2 mol dm$^{-3}$). A very faint (<1%) purple 1+ band was followed by a large purple 2+ band, leaving an orange 3+ band at the top of the column. The 2+ band was collected, rotary evaporated to dryness, redissolved in water, reloaded onto Dowex 50W-X2 ion-exchange resin, and eluted with 1 M HCl. Three bands then separated: a thin purple 1+ band that quickly eluted, followed by purple and then red-orange 2+ bands (*t*-$[Co(tren)(OH_2)X]^{2+}$ (X = NCS$^-$, SCN$^-$) and *t*-$[Co(tren)(NH_3)$-

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[8] The previously reported[7] λ values for maximum extinction were (incorrectly) reversed, as was their elution behavior on Dowex 50W-X2 (Na$^+$) cation-exchange resin; the *t*-$N_3$ isomer elutes more rapidly than the *p*-$N_3$ isomer.

[9] Buckingham, D. A. *J. Chromatogr.* **1984**, *313*, 93–127.

**Table I.** Molar Absorptivities ($mol^{-1}\ dm^3\ cm^{-1}$) for a Number of *t*- and *p*-$[Co(tren)(NH_3)X]^{2+}$ Ions in Aqueous Solution

| complex | λ | ε | λ | ε | ref |
|---|---|---|---|---|---|
| *t*-$[Co(tren)(NH_3)Cl]Cl\cdot ClO_4$ | 530 | 123 | 362 | 115 | 7 |
| *t*-$[Co(tren)(NH_3)OH_2](ClO_4)(NO_3)_2$ | 498 | 102 | 343 | 93 | 7 |
| *t*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$ | 508 | 400 | | | this work |
| *t*-$[Co(tren)(NH_3)NCS]Cl_2$ | 492 | 328 | 300 | 2070 | this work |
| *t*-$[Co(tren)(NH_3)SCN]Br_2$ | 507 | 160 | 296 | 17700 | this work |
| *t*-$[Co(tren)(NH_3)Br]Br_2$ | 542 | 154 | | | this work |
| *t*-$[Co(tren)(NH_3)CH_3SO_3](ClO_4)_2$ | 514 | 122 | 350 | 91 | 7 |
| *t*-$[Co(tren)(NH_3)NO_3](NO_3)_2$ | 503 | 134 | 346 | 112 | 7 |
| *t*-$[Co(tren)(NH_3)((CH_3)_2SO)](ClO_4)(NO_3)_2$ | 514 | 139 | 352 | 126 | 7 |
| *p*-$[Co(tren)(NH_3)Cl]Cl\cdot ClO_4$ | 509 | 94 | 365 | 96 | 7 |
| *p*-$[Co(tren)(NH_3)OH_2](ClO_4)(NO_3)_2$ | 482 | 100 | | | 7 |
| *p*-$[Co(tren)(NH_3)N_3](ClO_4)(NO_3)$ | 503 | 370 | | | this work |
| *p*-$[Co(tren)(NH_3)NCS]Cl_2$ | 482 | 257 | 303 | 1760 | this work |
| *p*-$[Co(tren)(NH_3)SCN]Br_2$ | 495 | 150 | 292 | 12600 | this work |

$NCS]^{2+}$). The original 3+ band (*t*- and *p*-$[Co(tren)(NH_3)OH_2]^{3+}$) was anated by evaporating to dryness on a steam bath, redissolving in Analar concentrated HCl, and again taking to dryness. This was chromatographed in the same way as for the 2+ band, giving purple and red 2+ products (*t*- and *p*-$[Co(tren)(NH_3)Cl]^{2+}$). Visible spectra were recorded and Co was estimated from known extinction coefficients.[16] In most cases analyses were also carried out by RP-HPIPC. Samples before and after anation were analyzed for Co by atomic absorption.

**Method 3.** To *t*-$[Co(tren)(NH_3)SCN]Br_2$ (50 mg) in water (3.50 $cm^3$) was added 0.5 mol $dm^{-3}$ NaOH (3.50 $cm^3$), and after $5t_{1/2}$ (7.5 min) the reaction was quenched with 0.5 mol $dm^{-3}$ $HClO_4$ (1.80 $cm^3$). Two drops of acetic acid were added to the reaction mixture (pH 3.5–4), which was diluted with water (100 $cm^3$) and loaded onto Sephadex-C25 cation-exchange resin (length 4–5 cm, $Na^+$ form). A drop of *N*-ethylmorpholine was added directly above the loaded band and 0.1 $cm^3$ (2 drops) to 0.2 mol $dm^{-3}$ $NaClO_4$ so that the eluent was basic (pH 7.5–8) during elution of the first 1+ purple band. This band remained on the column for ~6 min; it was quenched into HOAc (1 drop) when eluted. The eluent was then changed to 0.3 mol $dm^{-3}$ $NaClO_4$ (pH ~4–5 (HOAc)) whereupon red *t*-$[Co(tren)(NH_3)NCS]^{2+}$ separated from the orange $[Co(tren)(NH_3)OH_2]^{3+}$ species.

All fractions were analyzed by RP-HPIPC and by atomic absorption. The 1+ band when acidified eluted as a 2+ ion. Visible spectra were recorded for the aqua and *t*-$[Co(tren)(NH_3)NCS]^{2+}$ fractions.

Reaction products for the alkaline hydrolysis of other *t*- and *p*-$[Co(tren)(NH_3)X]^{2+}$ complexes ($X = NCS^-, SCN^-, N_3^-$) were analyzed by chromatographic methods (IEC, RP-HPIPC). To 0.1 g of the complex was added NaOH (25 $cm^3$, 1 mol $dm^{-3}$). After being allowed to stand in a water bath at 25.0 °C for $6t_{1/2}$, the solution was quenched with HCl (25 $cm^3$, 1 mol $dm^{-3}$), diluted (~4x), sorbed onto Dowex resin ($H^+$ form), and eluted with 1.0 M NaCl (or HCl). After the collected fractions were reduced to dryness on a steam bath, the products were dissolved in a small volume of concentrated HCl, the solution was filtered to remove excess NaCl, and the filtrate was taken to dryness. Analysis was by RP-HPIPC.

## Results

**Synthesis.** The S-bound thiocyanate isomers *p*- and *t*-$[Co(tren)(NH_3)SCN]^{2+}$ have been prepared in admixture with the corresponding N-bound isothiocyanate isomers by treating *p*- or *t*-$[Co(tren)(NH_3)N_3](NO_3)(ClO_4)$ with $NO_{aq}^+$ in the presence of excess $NCS^-$ (eq 3). This method has previously been used

$$\begin{aligned} &t\text{- or } p\text{-}[Co(tren)(NH_3)N_3]^{2+} + NO_2^- + H^+ \xrightarrow{NCS^-} \\ &\quad t\text{- or } p\text{-}[Co(tren)(NH_3)NCS]^{2+} + \\ &\quad t\text{- or } p\text{-}[Co(tren)(NH_3)SCN]^{2+} + \\ &\quad\quad t\text{- or } p\text{-}[Co(tren)(NH_3)OH_2]^{3+} \qquad (3) \end{aligned}$$

to prepare $[Co(NH_3)_5SCN]^{2+}$ [10] and *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$.[6] For the *p* complex an aqueous solution containing 20 mol $dm^{-3}$ NaNCS resulted in almost no aqua product, but for the *t* complex the same concentration gave excessive crystallization of *t*-$[Co(tren)(NH_3)N_3](NCS)_2$ and 10 mol $dm^{-3}$ NaNCS was found to be more appropriate. Less aqua complex was formed, and therefore better yields were obtained, if $NaNO_2$ and $HClO_4$ were added alternately in small amounts to the reaction mixture. The *p*-$CoN_3^{2+}$ isomer required a longer time to react (10–15 min) than the *t*-$CoN_3^{2+}$ isomer (5 min), and possibly some loss of *p*-$[Co(tren)(NH_3)SCN]^{2+}$ through isomerization to the N-bound isomer resulted from this (see below). No indication of *p* to *t*, or *t* to *p*, isomerization was found in these preparations. The larger amount[11] of $CoNCS^{2+}$ could be separated from $CoSCN^{2+}$ by ion-exchange chromatography (IEC), and a temperature of 2 °C was used to limit isomerization. This was particularly important for *p*-$CoSCN^{2+}$. Alternatively, the preferred method involved rotary evaporation of the combined $CoNCS^{2+}$ + $CoSCN^{2+}$ band from a short IE column (2 M HCl), followed by crystallization of poorly soluble $[Co(tren)(NH_3)NCS]Cl_2$ from the minimum volume of water and IEC on a longer column of the enriched $CoSCN^{2+}$ solute. *p*-$CoNCS^{2+}$ elutes more rapidly than *p*-$CoSCN^{2+}$, whereas the reverse holds for *t*-$CoNCS^{2+}$ and *t*-$CoSCN^{2+}$. Careful addition of NaBr to a not too concentrated solution of $[Co(tren)(NH_3)SCN]X_2$ ($X = OAc^-, Cl^-$) results in complete removal of Co–$NCS^{2+}$ as its $Br^-$ salt.

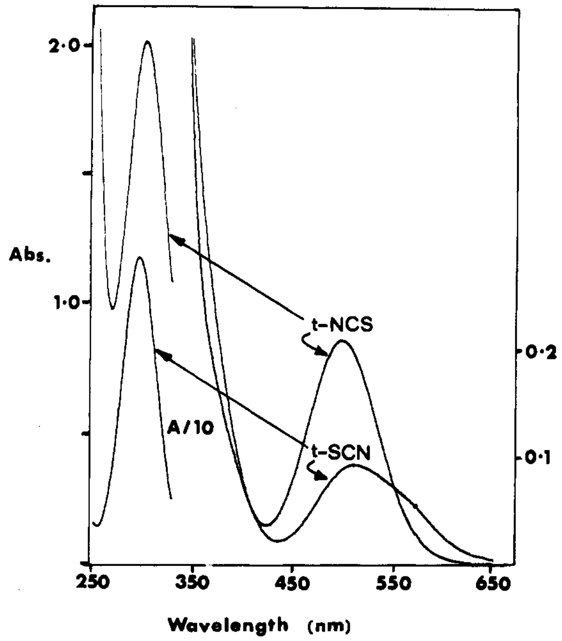

**Figure 1.** Absorption spectra for *t*-$[Co(tren)(NH_3)NCS]Cl_2\cdot 0.5H_2O$ ($6.4 \times 10^{-4}$ mol $dm^{-3}$) and *t*-$[Co(tren)(NH_3)SCN]Br_2\cdot H_2O$ ($5.9 \times 10^{-4}$ mol $dm^{-3}$) in water (25.0 °C).

Absorption spectra are given in Figures 1 and 2. Table I compares extinction coefficients with those of other acido *t* and *p* complexes. The intense near-UV absorption for the $CoSCN^{2+}$ isomers is typical of coordinated thiocynate,[6,12] as is the asymmetry of the ligand field absorption. The red shift in the latter compared to the case of the $CoNCS^{2+}$ isomers is in agreement with the lower

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(10) Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668–673.

(11) No quantitative experiments on product ratios were carried out, but $[CoNCS^{2+}]/[CoSCN^{2+}] > 2$ for both isomers.

(12) Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655–661.

**Table II.** Rate Data for the $OH^-$-Induced Reactions of *t*- and *p*-$[Co(tren)(NH_3)X]^{2+}$ ($X = SCN^-, NCS^-, N_3^-, Br^-$) at 25.0 °C and $I = 1.0$ mol dm$^{-3}$ ($NaClO_4$)

| | | [NaOH], mol dm$^{-3}$ | $10^2k_{obsd}$, s$^{-1}$ | $10^2k_{OH}$,[a] mol$^{-1}$ dm$^3$ s$^{-1}$ |
|---|---|---|---|---|
| *t*-$[Co(tren)(NH_3)SCN]^{2+}$ (λ = 518 nm) | | 1.0 | 3.01 | 3.0 |
| | | 0.5 | 1.55 | 3.1 |
| | | 0.25 | 0.79 | 3.2 |
| | | 0.025 | 0.078 | 3.1 |
| | pH | $10^7[OH^-]$,[b] mol dm$^{-3}$ | $10^3k_{obsd}$, s$^{-1}$ | $10^3k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *p*-$[Co(tren)(NH_3)SCN]^{2+}$ (λ = 410 nm) | 6.8 | 1.38 | 1.88 | 13.7 |
| | 7.7 | 9.12 | 8.77 | 9.7 |
| | 7.8 | 66 | 70.7 | 10.7 |
| | | [NaOH], mol dm$^{-3}$ | $10^3k_{obsd}$, s$^{-1}$ | $10^3k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *t*-$[Co(tren)(NH_3)NCS]^{2+}$ (λ = 495 nm) | | 1.0 | 2.52 | 2.52 |
| | | 0.5 | 1.27 | 2.54 |
| | | 0.25 | 0.65 | 2.58 |
| | | [NaOH], mol dm$^{-3}$ | $10^2k_{obsd}$, s$^{-1}$ | $10^2k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *p*-$[Co(tren)(NH_3)NCS]^{2+}$ (λ = 482 nm) | | 1.0 | 3.08 | 3.1 |
| | | 0.5 | 1.73 | 3.5 |
| | | 0.25 | 0.85 | 3.4 |
| | | 0.1 | 0.34 | 3.4 |
| | | [NaOH], mol dm$^{-3}$ | $10^3k_{obsd}$, s$^{-1}$ | $10^3k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *t*-$[Co(tren)(NH_3)N_3]^{2+}$ (λ = 508 nm) | | 1.0 | 1.1 | 1.1 |
| | | 0.67 | 0.81 | 1.2 |
| | | 0.5 | 0.66 | 1.3 |
| | | [NaOH], mol dm$^{-3}$ | $k_{obsd}$, s$^{-1}$ | $k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *p*-$[Co(tren)(NH_3)N_3]^{2+}$ (λ = 503 nm) | | 0.5 | 0.21 | 0.42 |
| | | 0.4 | 0.175 | 0.44 |
| | | 0.3 | 0.13 | 0.48 |
| | | 0.2 | 0.095 | 0.47 |
| | | 0.1 | 0.047 | 0.47 |
| | | [NaOH], mol dm$^{-3}$ | $10^3k_{obsd}$, s$^{-1}$ | $k_{OH}$, mol$^{-1}$ dm$^3$ s$^{-1}$ |
| *t*-$[Co(tren)(NH_3)Br]^{2+}$ (λ = 542 nm) | | 0.091 | 21.66 | 0.24 |
| | | 0.057 | 13.86 | 0.24 |
| | | 0.048 | 11.18 | 0.24 |

[a] $k_{obsd}/[OH^-]$. [b] Derived by using $pK_w = 13.80$ ($I = 1.0$ mol dm$^{-3}$ ($NaClO_4$)).[15]

ligand field strength of S vs. N coordinated to Co(III).[13] The $\nu_{SCN}$ stretch in the IR spectrum is at a slightly higher frequency (2125 cm$^{-1}$ for *t*-$CoSCN^{2+}$, 2105 cm$^{-1}$ for *p*-$CoSCN^{2+}$) than the $\nu_{NCS}$ stretch (2095 cm$^{-1}$ for both isomers), and the absorption is possibly a little sharper. This is also in agreement with previous observations.[12]

The $[Co(tren)(NH_3)NCS]Cl_2$ isomers are stable as solids and in neutral or acidic solutions for long periods of time. However, the $[Co(tren)(NH_3)SCN]Cl_2$ isomers are less stable and isomerize to $[Co(tren)(NH_3)NCS]Cl_2$ both in solution and as solids.[14] This is very significant for *p*-$[Co(tren)(NH_3)SCN]Br_2$, and after 4 months at 5 °C >50% isomerization had occurred in the solid. For the experiments reported here this complex was used shortly after its preparation.

Reverse-phase HPIPC elution profiles for the isolated complexes are given in Figure 3 and for mixtures in Figure 4a. The rapidity and resolution achieved by this method of analysis[9] is obvious.

Alkaline hydrolysis of *t*-$[Co(tren)(NH_3)NCS]^{2+}$ results in the loss of the *p*-$NH_3$ ligand and the formation of *t*(*NCS*),*p*(*OH*)-$[Co(tren)(OH)NCS]^+$. Anation of this ion with aqueous HCl gives *t*(*NCS*),*p*(*Cl*)-$[Co(tren)Cl(NCS)]^+$ (eq 4), which has been isolated as its chloride salt.

$$t\text{-}[Co(tren)(NH_3)NCS]^{2+} + OH^- \rightarrow \underset{\text{dark orange}}{t(NCS),p(OH)\text{-}[Co(tren)(OH)NCS]^+} \xrightarrow{\text{concd HCl}} \underset{\text{red}}{t(NCS),p(Cl)\text{-}[Co(tren)Cl(NCS)]^+} \quad (4)$$

**Table III.** Second-Order Rate Constants (mol$^{-1}$ dm$^3$ s$^{-1}$) for Loss of $X^-$ or $NH_3$ in the Alkaline Hydrolysis of *t*- and *p*-$[Co(tren)(NH_3)X]^{2+}$ Ions at 25.0 °C and $I = 1.0$ mol dm$^{-3}$ ($NaClO_4$)

| | leaving group | | | |
|---|---|---|---|---|
| X | *t*-X | *p*-$NH_3$ | *p*-X | ref |
| $NH_3$ | | $5.4 \times 10^{-2}$ | | 15 |
| $SCN^-$ | $2.1 \times 10^{-2}$ | $1.0 \times 10^{-2}$ | $1.1 \times 10^4$ | this work |
| $NCS^-$ | | $2.5 \times 10^{-3}$ | $3.4 \times 10^{-2}$ | this work |
| $N_3^-$ | | $1.2 \times 10^{-3}$ | $4.4 \times 10^{-1}$ | this work |
| $Cl^-$ | $2 \times 10^{-2}$ | | $4 \times 10^2$ | 7, 16 |
| $Br^-$ | $2.4 \times 10^{-1}$ | | | this work |
| $NO_3^-$ | 2.7 | | | 7 |
| $Me_2SO$ | 3.7 | | | 7 |
| $MeSO_3^-$ | 10.0 | | | 7 |

**Table IV.** Rate Data for the Isomerization of *t*-$[Co(tren)(OH)SCN]^+$ in Alkaline Solution at 25.0 °C, λ = 505 nm, and $I = 1.0$ mol dm$^{-3}$ ($NaClO_4$)

| pH | $[OH^-]$, mol dm$^{-3}$ | $10^4k_{obsd}$, s$^{-1}$ |
|---|---|---|
| | 0.5 | 7.70 |
| | 0.33 | 5.50 |
| | 0.1 | 5.25 |
| 11.76[a] | $9.12 \times 10^{-3}$[b] | 5.78 |
| 8.27[a] | $2.95 \times 10^{-6}$[b] | 5.78 |

[a] In *N*-ethylmorpholine. [b] Using $pK_w = 13.80$.

**Alkaline Hydrolysis.** Table II lists rate data for the hydrolysis of the *t*-$[Co(tren)(NH_3)X]^{2+}$ ($X = SCN^-, NCS^-, N_3^-, Br^-$) and *p*-$[Co(tren)(NH_3)X]^{2+}$ ($X = SCN^-, NCS^-, N_3^-$) ions. The rate law

$$-d[CoX]/dt = k_{OH}{}^X[CoX][OH^-] \quad (5)$$

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(13) Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60–64.

(14) Details of these experiments will be reported elsewhere.

(15) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041–2043.

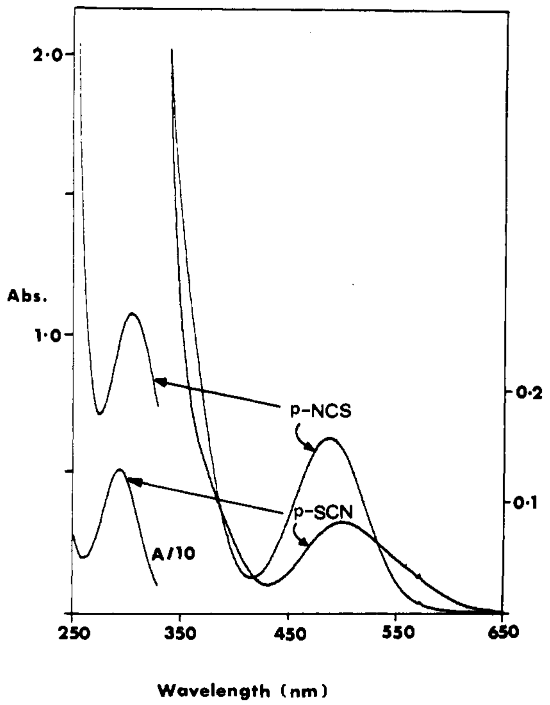

**Figure 2.** Absorption spectra for $p$-[Co(tren)(NH$_3$)NCS]Br$_2$ ($6.7 \times 10^{-4}$ mol dm$^{-3}$) and $p$-[Co(tren)(NH$_3$)SCN]Br$_2$·0.5H$_2$O ($5.9 \times 10^{-4}$ mol dm$^{-3}$) in water (25.0 °C).

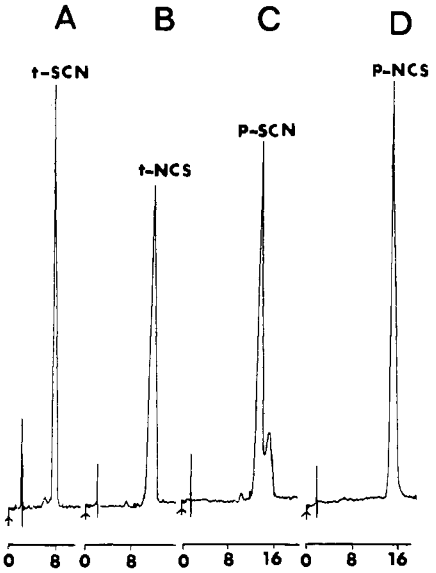

**Figure 3.** Elution profiles showing purity: (A) $t$-[Co(tren)(NH$_3$)SCN]$^{2+}$; (B) $t$-[Co(tren)(NH$_3$)NCS]$^{2+}$; (C) $p$-[Co(tren)(NH$_3$)SCN]$^{2+}$; (D) $p$-[Co(tren)(NH$_3$)NCS]$^{2+}$ (20% MeOH isocratic, 25 mM $p$-toluenesulfonate, pH 3.5, flow rate 2.0 cm$^3$ min$^{-1}$, AUFS 0.02, chart speed 0.25 cm min$^{-1}$, $\lambda$ = 500 nm).

holds in each case. Table III lists second-order rate constants, $k_{OH}^X$, and the not too different reactivities of $t$- and $p$-CoNCS$^{2+}$ (within a factor of 10) and the 10$^6$-fold difference between $t$- and $p$-CoSCN$^{2+}$ are noteworthy. It will be shown below that this is due to the change of leaving group in the two situations.

Table IV gives rate data for the reaction of $t(SCN),p(OH)$-[Co(tren)(SCN)OH]$^+$ under alkaline conditions. Clearly, the rate of this reaction is independent of [OH$^-$] over a wide range.

Reaction products depend on the reactant. With $t$-[Co(tren)(NH$_3$)SCN]$^{2+}$ some 60% of the immediate product is [Co(tren)(NH$_3$)OH]$^{2+}$, of which 83% of $p$-CoOH$^{2+}$ and 17% $t$-CoOH$^{2+}$. This was shown by recovering the quenched 3+ aqua product and anating it with HCl$_{aq}$ to give the corresponding $p$- and $t$-[Co(tren)(NH$_3$)Cl]$^{2+}$ ions. This process is known to occur with retention.[16] Analysis was then carried out by RP-HPIPC (Figure 4B). The remaining 40% is a mixture of $t$-[Co(tren)(NH$_3$)NCS]$^{2+}$ (5%) and $t(SCN)$-[Co(tren)(OH)SCN]$^+$ (35%), the latter resulting from hydrolysis of the $p$-NH$_3$ ligand. RP-HPIPC was invaluable in sorting out these products and their subsequent reactions. Figure 5 gives results of an experiment carried out with 3.12 mg of $t$-[Co(tren)(NH$_3$)SCN]Br$_2$ in 0.4 cm$^3$ of 0.25 mol dm$^{-3}$ NaOH (25 °C) as a function of time with quenching using HCl$_{aq}$ (40-$\mu$L samples).[17] The decay of the

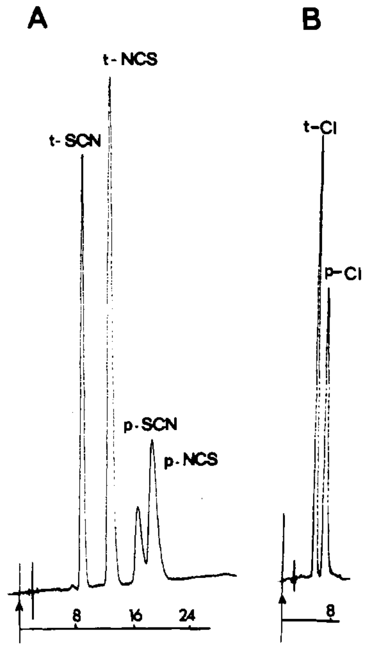

**Figure 4.** Elution profiles of (A) $t$- and $p$-[Co(tren)(NH$_3$)X]$^{2+}$ (X = NCS$^-$, SCN$^-$) isomers (20% MeOH isocratic, 25 mM $p$-tolyl phosphate, pH 2.75) and (B) $t$- and $p$-[Co(tren)(NH$_3$)Cl]$^{2+}$ isomers (15% MeOH isocratic, 25 mM $p$-toluenesulfonate, pH 3.5) (flow rate 2.0 cm$^3$ min$^{-1}$, AUFS 0.02, chart speed 0.25 cm min$^{-1}$, $\lambda$ = 500 nm).

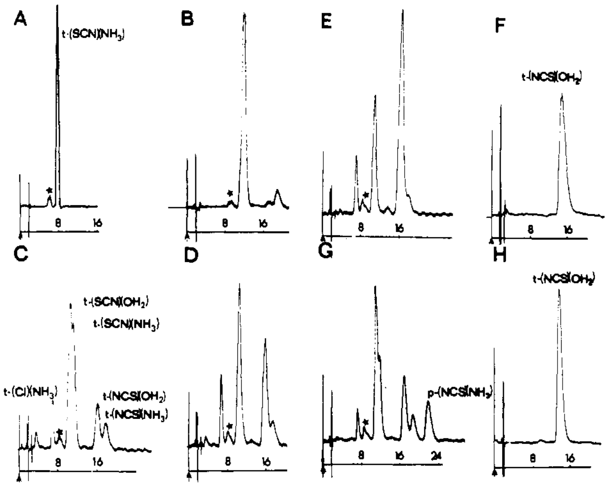

**Figure 5.** Elution profiles for samples (40 $\mu$L) following hydrolysis of 3.12 mg of $t$-[Co(tren)(NH$_3$)SCN]Br$_2$ in 0.4 cm$^3$ of 0.25 M sodium hydroxide at 25.0 °C for (A) immediate HCl$_{aq}$ quench, (B) $t_{1/4}$ (45 s), (C) $2t_{1/2}$ (3 min), (D) $5t_{1/2}$ (7.5 min), (E) $10t_{1/2}$ (15 min), (F) 1 day, and (G) $2t_{1/2}$ (spiked with $p$-[Co(tren)(NH$_3$)NCS](NO$_3$)$_2$). (H) represents the product of $t$-[Co(tren)(SCN)OH$_2$]$^{2+}$ reacted with OH$^-$ ion. Aliquots were quenched into 0.5 M hydrochloric acid (20% methanol, 25 mM toluenesulfonate (pH 3.5)) (flow rate 2.0 cm$^3$ min$^{-1}$, AUFS 0.2, chart speed 0.25 cm min$^{-1}$, $\lambda$ = 500 nm). Peaks denoted with an asterisk denote impurity (unreactive) present in the reactant.

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(16) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485–1490.

(17) The appearance of some $t$-[Co(tren)(NH$_3$)Cl]$^{2+}$ in chromatograms in Figure 5C–G is due to quenching with HCl$_{aq}$. This amount could be reduced by immediately analyzing the reaction mixture or eliminated entirely by quenching with HClO$_4$ or HO$_3$SCF$_3$.

reactant (Figure 5A) is accompanied by the appearance of *t*-$CoNCS^{2+}$ and *t*(*SCN*)-$CoSCN(OH_2)^{2+}$ (Figure 5B–D), the latter being difficult to distinguish from the reactant by this technique but being easily separated by conventional IEC at pH 9 when it elutes as a purple 1+ band. Subsequently, *t*(*SCN*)-$[Co(tren)(OH)SCN]^+$ isomerizes, and more slowly the *t*-$[Co(tren)(NH_3)(NCS)]^{2+}$ ion hydrolyzes to give the same *t*(*NCS*)-$[Co(tren)(OH)NCS]^+$ product which is eluted as a 2+ ion under the conditions of HPLC separation (Figures 5D–F). Both of the latter reactions were studied independently and occurred without the formation of other products (eq 6 and 7, Figure 5H). No detectable (<0.5%) isomerization to *p*-$[Co(tren)(NH_3)NCS]^{2+}$ occurs during base hydrolysis of *t*-$[Co(tren)(NH_3)SCN]^{2+}$; such an amount would be clearly observable (Figure 5G).

$$t(SCN)\text{-}[Co(tren)(OH)SCN]^+ \rightarrow t(NCS)\text{-}[Co(tren)(OH)NCS]^+ \quad (6)$$

$$t\text{-}[Co(tren)(NH_3)NCS]^{2+} + OH^- \rightarrow t(NCS)\text{-}[Co(tren)(OH)NCS]^+ + NH_3 \quad (7)$$

Similar RP-HPIPC analysis of the products of alkaline hydrolysis of *p*-$[Co(tren)(NH_3)SCN]^{2+}$ showed only *p*-$[Co(tren)(NH_3)OH]^{2+}$ and no isomerization, although this result (eq 8) is not as certain as the other due to the small amount of *p*-$CoNCS^{2+}$ impurity in the reactant (Figure 3C).

$$p\text{-}[Co(tren)(NH_3)SCN]^{2+} + OH^- \rightarrow p\text{-}[Co(tren)(NH_3)OH]^{2+} + NCS^- \quad (8)$$

Similar RP-HPIPC and IEC analysis demonstrated the products given by reactions 9 and 10 and by reaction 11. The last reaction showed no evidence for hydrolysis of coordinated $N_3^-$, and the violet product was isolated following anation as *t*($N_3$)-$[Co(tren)(Cl)N_3]Cl$.[18]

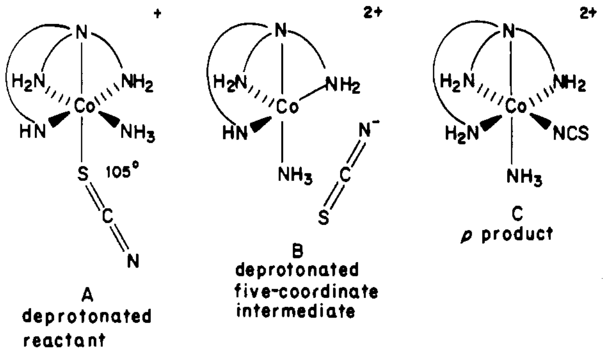
$$p\text{-}[Co(tren)(NH_3)NCS]^{2+} + OH^- \rightarrow p\text{-}[Co(tren)(NH_3)OH]^{2+} + NCS^- \quad (9)$$

$$p\text{-}[Co(tren)(NH_3)N_3]^{2+} + OH^- \rightarrow p\text{-}[Co(tren)(NH_3)OH]^{2+} + N_3^- \quad (10)$$

$$t\text{-}[Co(tren)(NH_3)N_3]^{2+} + OH^- \rightarrow t(N_3)\text{-}[Co(tren)(OH)N_3]^+ + NH_3 \quad (11)$$

## Discussion

The expected outcome of this investigation was not realized in that no detectable *p*-$[Co(tren)(NH_3)NCS]^{2+}$ is formed during the alkaline hydrolysis of *t*-$[Co(tren)(NH_3)SCN]^{2+}$. This is so even though considerable isomerization to *p*-$[Co(tren)(NH_3)OH]^{2+}$ occurs, with the *p*-$CoOH^{2+}$:*t*-$CoOH^{2+}$ ratio of 83:17 agreeing with that found previously for other leaving groups (X = $NH_3$,[15] $Me_2SO$,[7] $Cl^-$,[16,17] $NO_3^-$,[7] $MeSO_3^-$[7]). The results suggest that the 2+ intermediate formed on loss of $SCN^-$ (eq 1) does not have sufficient time to mutarotate about the metal before it is trapped by adjacent entering groups. Liberated $NCS^-$ gives only *t*-$CoNCS^{2+}$ since the entering group derives from this position, whereas $H_2O$ can penetrate both *p* and *t* sites from adjacent positions in the solvent cage. This is in agreement with experiments carried out with the *syn*-, *anti*-, and *sym*-*p*-$[Co(Me(tren))(NH_3)Cl]^{2+}$ isomers,[2] where considerable retention of the starting geometry occurs in the hydroxo product and certainly no common equilibrated geometry is achieved in the intermediates. It had been hoped in the present case that the combination of the driving force toward the trigonal-bipyramidal structure B (known to be favored by the tren ligand),[19] the presence of released $SCN^-$ with the N end of the dipole oriented toward the equatorial plane of the reactant A, and the known preference of Co(III) for the N end of thiocyanate might allow mutarotation about the metal in competition with $H_2O$ entry from the solvent cage.



A deprotonated reactant

B deprotonated five-coordinate intermediate

C *p* product

(12)

The negative result seriously questions the origins of the 1% *cis*-$[Co(en)_2(NH_3)NCS]^{2+}$ ion found in the alkaline hydrolysis of *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$.[6] It had been argued from tracer data that about half the cis product arose from competition within the ion pair of the intermediate, with Co–SCN bond breaking being intimately tied to mutarotation. We now plan to repeat these experiments using RP-HPIPC analysis of the products and will report our results shortly.

Internal competition within the intermediate for released $SCN^-$ does occur since 8–9% *t*-$[Co(tren)(NH_3)NCS]^{2+}$ is found for the path involving hydrolysis of coordinated thiocyanate. This is to be compared with 27% $[Co(NH_3)_5NCS]^{2+}$ formed in the alkaline hydrolysis of $[Co(NH_3)_5SCN]^{2+}$[12] and ~8% $[Co(en)_2(NH_3)NCS]^{2+}$ (~7% trans, 1% cis) formed from *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$.[6] However, in the absence of mutarotation about the metal it is not yet certain whether this internal competition involves complete Co–SCN bond rupture and rotation within the ion pair or whether bond rotation within coordinated thiocyanate is involved. We are currently investigating this aspect of the problem.

The amount of internal competiton differs from that found in the spontaneous and induced reactions. Complete isomerization to *t*-$[Co(tren)(NH_3)NCS]^{2+}$ is involved in the former process, and 54% ($Hg^{2+}$) and 67% ($Ag^+$) in the latter.[22] This might suggest, but does not require, a more stable intermediate for the amide base conjugate, which allows substantially more diffusion of released $SCN^-$ away from the metal before it reacts.

The second aspect of this study involves the $OH^-$-catalyzed hydrolysis of coordinated $NH_3$. This is a new result for acido 2+ ions $[Co(amine)_5X]^{2+}$ although it has been observed previously for $[Co(tren)(NH_3)_2]^{3+}$[15] and some planar $N_4$ macrocycles *trans*-$[Co([14]amine)(NH_3)_2]^{3+}$.[23] Here this occurs for *t*-$[Co(tren)(NH_3)X]^{2+}$ with X = $N_3^-$, $NCS^-$, and $SCN^-$. For $N_3^-$ and $NCS^-$ it is an exclusive process with *t*(*X*)-$[Co(tren)(OH)X]^+$ being

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(18) Details of the chemistry of these complexes will be reported shortly.

(19) There is much evidence to indicate that coordinated tren favors the trigonal-bipyramidal structure. Most divalent metal ions form $[M(tren)X]X$ complexes of this structure,[20,21] and when equilibrated over charcoal, *t*-$[Co(tren)(NH_3)Cl]^{2+}$ is converted entirely into *p*-$[Co(tren)(NH_3)Cl]^{2+}$, presumably via a Co(II) intermediate. In addition, under equilibrium conditions both $[Co(tren)(NH_3)OH_2]^{3+}$ and $[Co(tren)(NH_3)Cl]^{2+}$ adopt the *p* configuration. Thus, when allowed to stand in 1 mol $dm^{-3}$ DCl for 2 years, *t*-$[Co(tren)(NH_3)Cl]^{2+}$ is converted entirely into *p*-$[Co(tren)(NH_3)Cl]^{2+}$, and in 0.01 mol $dm^{-3}$ $HClO_4$ *t*-$[Co(tren)(NH_3)OH_2]^{3+}$ slowly forms *p*-$[Co(tren)(NH_3)OH_2]^{3+}$. Ligand exchange or ligand substitution occurs most easily in the *p* position with aquation of $[Co(tren)Cl_2]^+$ resulting largely in *t*(*Cl*)-$[Co(tren)(H_2O)Cl]^{2+}$ and anation of $[Co(tren)(OH_2)_2]^{3+}$ with $Cl^-$ appearing to initially form *p*(Cl)-$[Co(tren)(H_2O)Cl]^{2+}$. Aquation of *p*-$[Co(tren)(NH_3)X]^{2+}$ isomers are invariably faster processes than for the corresponding *t* isomers.

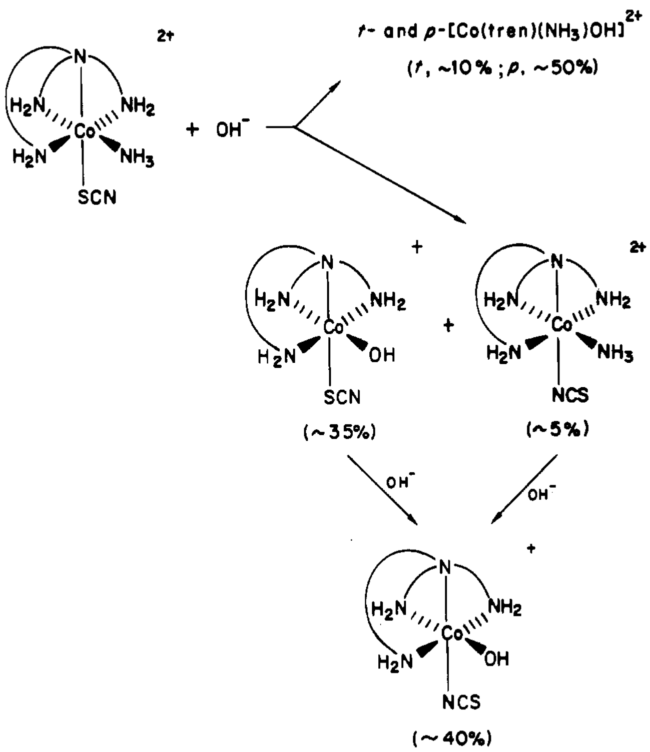
(20) Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 724.

(21) Di Vaira, M.; Orioli, P. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 595; *Inorg. Chem.* **1967**, *6*, 490–495.

(22) Gaudin, M.; Clark, C. R.; Buckingham, D. A., to be submitted for publication.

(23) Rillema, D. P.; Endicott, J. F.; Barber, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6987–6992.

**Scheme I**



the only product, but for X = SCN$^-$ this part accounts for only ~35% of the reaction path (Scheme I).

The first-order dependence on [OH$^-$] in the rate up to 1.0 mol dm$^{-3}$ implies a p$K_a$ >14 for the amine residue responsible for hydrolysis, and the release of NH$_3$ suggests deprotonation of either the cis or trans amine sites of tren (eq 13) rather than of coordinated NH$_3$.

$$t\text{-[Co(tren)(NH}_3\text{)X]}^{2+} + \text{OH}^- \underset{\text{fast}}{\overset{K_a/K_w}{\rightleftharpoons}} t\text{-[Co(tren-H)(NH}_3\text{)X]}^{+} + \text{H}_2\text{O} \xrightarrow[\text{slow}]{k_1} \text{products} \quad (13)$$

From Table III we have $k_{OH}{}^{NH_3} = k_1K_a[\text{OH}^-]/(K_w + K_a[\text{OH}^-])$. For [Co(tren)(NH$_3$)$_2$]$^{3+}$ a leveling off in rate occurs in the vicinity of 1.0 mol dm$^{-3}$ OH$^-$, giving $K_a$ = 3.0 mol$^{-1}$ dm$^{-3}$ for this higher charged 3+ ion. We expect the same amine residue to be involved for the 2+ ions with a p$K$, not much greater than 14. Table III compares $k_{OH}$ values for loss of X$^-$ ($k_{OH}{}^X$) and loss of NH$_3$ ($k_{OH}{}^{NH_3}$). Variations in $k_{OH}{}^{NH_3}$ are small, (1.2–10) × 10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ for the 2+ ions and 54 × 10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ for the 3+ ion (X = NH$_3$). This can in part be accounted for by the increased acidity of the latter ($K_a$ = 3.0 mol$^{-1}$ dm$^3$, $k_1$ = 1.8 × 10$^{-2}$ s$^{-1}$), and the absence of observed deprotonation in 1.0 mol dm$^{-3}$ OH$^-$ for the 2+ ions require $k_1$ < 1.8 × 10$^{-2}$ s$^{-1}$ for these deprotonated reactants (eq 13). Clearly, N$_3^-$, NCS$^-$, and SCN$^-$ are poorer leaving groups from the $t$ position than is NH$_3$ from the $p$ position.

Variations in $k_{OH}{}^X$ are substantial, with a factor of almost 10$^6$ between $p$-CoSCN$^{2+}$ and $p$-CoNCS$^{2+}$. $k_{OH}{}^X$ for $p$-CoNCS$^{2+}$ is 10 times smaller than for $p$-CoN$_3{}^{2+}$, but it is not possible in the absence of proton-exchange studies to determine whether these effects reside in $K_a$ or $k_1$. It is unlikely that $K_a$ differs much for the 2+ ions,[25] and the larger variations probably arise in $k_1$. The result for $t$-CoSCN$^{2+}$ allows the $p$-NH$_3$ group to be placed on a relative scale with other $p$-X leaving groups. NH$_3$ is similar to NCS$^-$ but some 10$^4$ poorer than Cl$^-$. Endicott has obtained a similar distinction using planar N$_4$ macrocycles.[23,24]

Finally, isomerization of $t$(*SCN*)-[Co(tren)(OH)SCN]$^+$ to $t$(*NCS*)-[Co(tren)(OH)NCS]$^+$ occurs without significant OH$^-$ catalysis and without detectable dihydroxo product being formed. Protonation causes the reaction to slow down with $k_{isom}$ for $t$-(*SCN*)-[Co(tren)(OH$_2$)SCN]$^{2+}$ being ~3 × 10$^{-5}$ s$^{-1}$ compared to 5–6 × 10$^{-4}$ s$^{-1}$ for the hydroxo complex. There is some suggestion of a term in [OH$^-$] in 0.5 mol dm$^{-3}$ NaOH (Table IV). These rates are to be compared with 1.3 × 10$^{-6}$ s$^{-1}$ for isomerization in $t$-[Co(tren)(NH$_3$)SCN]$^{2+}$.[22] Coordinated OH$_2$ and OH$^-$ obviously speed up isomerization when compared to NH$_3$, possibly by weakening the Co–SCN bond, but more examples of this type of reaction need to be investigated before firm mechanistic conclusions can be made.

**Registry No.** $t$-[Co(tren)(NH$_3$)N$_3$](ClO$_4$)(NO$_3$), 74006-52-3; $p$-[Co(tren)(NH$_3$)N$_3$](ClO$_4$)(NO$_3$), 101980-25-0; $t$-[Co(tren)(NH$_3$)(OH$_2$)](ClO$_4$)(NO$_3$)$_2$, 73949-30-1; $t$-[Co(tren)(NH$_3$)NCS]Cl$_2$, 101980-26-1; $t$-[Co(tren)(NH$_3$)SCN]Br$_2$, 101980-27-2; $p$-[Co(tren)(NH$_3$)NCS]Br$_2$, 102045-57-8; $p$-[Co(tren)(NH$_3$)SCN]Br$_2$, 102045-58-9; $t$-[Co(tren)(NH$_3$)Br]Br$_2$, 101980-28-3; $t$(*NCS*),$p$(*Cl*)-[Co(tren)Cl(NCS)]Cl, 102045-59-0; $p$-[Co(tren)(NH$_3$)NCS]Cl$_2$, 102045-60-3; $t$-(*SCN*)-[Co(tren)(OH)SCN]$^+$, 101980-29-4; $t$(*NCS*),$p$(*OH*)-[Co(tren)(OH)NCS]$^+$, 101980-30-7; $t$(*NCS*),$p$(*Cl*)-[Co(tren)Cl(NCS)]$^+$, 48145-43-3; $p$-[Co(tren)(NH$_3$)OH]$^{2+}$, 74006-53-4; $t$-[Co(tren)(NH$_3$)OH]$^{2+}$, 73949-33-4; $t$(*N*$_3$)-[Co(tren)(OH)N$_3$]$^+$, 101980-31-8; $t$(*SCN*)-[Co(tren)(OH$_2$)SCN]$^{2+}$, 101980-32-9.

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