Synthesis, Characterization and Acid Hydrolysis of [*N,N*-Bis(2-Aminoethyl)-1,2-ethanediamine]bis(solvent)cobalt(III) Complexes

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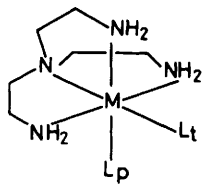
Synthesis of the precursor [*N,N*-bis(2-aminoethyl)-1,2-ethanediamine]bis(trifluoromethanesulphonato-*O*)cobalt(III) trifluoromethanesulphonate allowed facile synthesis of the bis(dimethyl sulphoxide), bis(dimethylformamide), bis(trimethyl phosphate), and bis(acetonitrile) complexes by solvolysis of the trifluoromethanesulphonato-complex in dry solvents. The new bis(solvent) complexes were characterized by spectroscopic methods and by microanalysis. In aqueous acid, they hydrolyse in two consecutive steps which differ in rate by a factor of less than ten. While the complexes are stereochemically rigid as a consequence of co-ordination of the *N,N*-bis(2-aminoethyl)-1,2-ethanediamine tripodal ligand, the observed rate constants are composite terms since the two solvent ligands are in non-equivalent sites, and initial ligand loss from both sites occurs. N.m.r. experiments reveal that this loss proceeds at similar rates for each site.

The quadridentate ligand *N,N*-bis(2-aminoethyl)-1,2-ethanediamine (tren) is of interest since it can co-ordinate about an octahedral ion in only one way.[1] Consequently, a stereochemical rigidity is introduced in the reactions of complexes of this ligand, which is absent, for example, in bis(1,2-ethanediamine) complexes where hydrolysis reactions may be accompanied by geometrical rearrangement.[2] The ligand geometry (I) requires the two remaining sites to be non-equivalent, since one is *trans* to a tertiary nitrogen (L_t) and the other *trans* to a primary nitrogen (L_p).

Acid-hydrolysis studies of tren complexes of bis(halogeno)-cobalt(III) reported previously have identified the two sites as unique.[3-9] Results have been interpreted, further, in terms of steric strain arising from the geometry of the tren ligand.[1] At least in the solid state there is some evidence for steric strain in octahedral cobalt(III)[10,11] and nickel(II) complexes,[12] since the unidentate ligand adjacent to the tertiary nitrogen is bent away from the ideal situation. Since all previous studies have dealt with ionic leaving groups, it was of interest to synthesize and examine the behaviour of complexes with neutral leaving groups, where considerations related to electrostriction differences between the precursor and transition state are markedly diminished compared with ionic leaving groups. This study reports syntheses of (tren)cobalt(III) complexes with neutral leaving groups, and an initial examination of their hydrolysis behaviour. The syntheses reported are greatly facilitated by proceeding through the bis(trifluoromethanesulphonato) precursor complex.



(I)

Experimental

Syntheses.—[Co(tren)Cl_2]Cl·HCl·H_2O. The precursor complex was prepared essentially as previously described,[11] except that it was isolated as the hydrochloride monohydrate (Found: C, 19.5; H, 5.2; Cl, 38.6; N, 15.1. Calc. for $C_6H_{21}Cl_4CoN_4O$: C, 19.7; H, 5.8; Cl, 38.7; N, 15.3%).

[Co(tren)$(OSO_2CF_3)_2$][CF_3SO_3]. To distilled anhydrous CF_3SO_3H (25 cm^3) was added in portions [Co(tren)Cl_2]Cl·HCl·H_2O (5.0 g). [**CAUTION:** CF_3SO_3H is a strong protic acid. HCl is released on addition. A fume hood should be employed.] A nitrogen bubbler was connected to the reaction flask, which was lowered into an oil-bath and heated at 100 °C for 3 h with gentle bubbling of nitrogen. The flask was removed from the oil-bath and allowed to cool to room temperature with the nitrogen still passing through the solution. The gas flow was disconnected, and the product precipitated by slow addition to diethyl ether (200 cm^3). [**CAUTION:** Exothermic process. The initial addition must be performed slowly, preferably dropwise, with vigorous stirring.] The product was collected on a fine-porosity sintered-glass funnel, initially under gravity, and once a bed of precipitate had formed under suction. The purple powder was washed well with diethyl ether (3 × 50 cm^3), and dried in a vacuum desiccator over P_4O_{10}. It must be stored protected from moisture, but is otherwise stable (yield 8.9 g, 100%) (Found: C, 16.8; H, 2.8; N, 8.5. Calc. for $C_9H_{18}CoF_9N_4O_9S_3$: C, 16.5; H, 2.8; N, 8.6%). Electronic spectrum in CF_3SO_3H: 371 (93) and 516 nm (ε 122 dm^3 mol^{-1} cm^{-1}).

[Co(tren){$OS(CH_3)_2$}$_2$][CF_3SO_3]$_3$. To dry dimethyl sulphoxide (10 cm^3) was added [Co(tren)$(OSO_2CF_3)_2$][CF_3SO_3] (4.0 g), and the mixture was heated on a steam-bath for 10 min. After cooling to room temperature, the solution was transferred to a larger flask with ethanol (20 cm^3). Slow addition of diethyl ether (200 cm^3) to the rapidly stirring solution effected the precipitation of a purple powder. This was collected, resuspended in cold ethanol (25 cm^3), and ether (200 cm^3) slowly added. The product was filtered off, washed with ether (2 × 50 cm^3), and dried (yield 4.4 g, 90%) (Found: C, 19.2; H, 4.0; F, 21.1; N, 6.9; S, 19.5. Calc. for $C_{10}H_{30}CoF_9N_4O_{11}S_5$: C, 19.3, H, 3.75; F, 20.7; N, 6.95; S, 19.8%).

[Co(tren){$OS(CH_3)_2$}$_2$][ClO_4]$_3$. The crude $CF_3SO_3^-$ salt was prepared as above from 5 g of [Co(tren)$(OSO_2CF_3)_2$][CF_3SO_3] in dimethyl sulphoxide (20 cm^3). This was dissolved in water (25 cm^3) and $NaClO_4$ (10 g in 10 cm^3) was added. Purple needles appeared on standing and these were collected, washed with ethanol (2 × 20 cm^3), ether (2 × 20

cm^3), and dried (yield 3.75 g, 75%) (Found: C, 18.4; H, 5.0; Cl, 15.8; N, 8.4; S, 10.3. Calc. for $C_{10}H_{30}Cl_3CoN_4O_{14}S_2$: C, 18.2; H, 4.6; Cl, 16.1; N, 8.5; S, 9.7%). Electronic spectrum in aqueous 0.1 mol dm^{-3} $HClO_4$–0.9 mol dm^{-3} $NaClO_4$: 371 (112) and 520 nm (ε 154 dm^3 mol^{-1} cm^{-1}).

$[Co(tren)\{OP(OCH_3)_3\}_2][CF_3SO_3]_3$. To dry trimethyl phosphate (10 cm^3) was added $[Co(tren)(OSO_2CF_3)_2][CF_3SO_3]$ (2.0 g), and the mixture was heated on a steam-bath for 10 min. The blue-purple solution was cooled to room temperature and washed into a large flask with ethanol (20 cm^3). Slow addition of diethyl ether (200 cm^3) to the stirring solution precipitated a purple powder. The powder was collected, stirred in ethanol (50 cm^3), and reprecipitated with ether (200 cm^3). The product was filtered off, washed with ether (2 × 20 cm^3), and dried (yield 2.0 g, 70%) (Found: C, 19.6; H, 4.4; N, 5.9; P, 6.7; S, 10.1. Calc. for $C_{15}H_{36}CoF_9N_4O_{17}P_2S_3$: C, 19.3; H, 3.9; N, 6.0; P, 6.65; S, 10.3%). Electronic spectrum in aqueous 0.1 mol dm^{-3} CF_3SO_3H–0.9 mol dm^{-3} $NaOSO_2CF_3$: 372 (87) and 520 nm (ε 128 dm^3 mol^{-1} cm^{-1}).

$[Co(tren)(NCCH_3)_2][CF_3SO_3]_3$. The product was prepared by reaction of $[Co(tren)(OSO_2CF_3)_2][CF_3SO_3]$ (2.0 g) with dry acetonitrile (10 cm^3) exactly as described above for the trimethyl phosphate analogue, and was isolated as bright yellow microcrystals (yield 2.1 g, 90%) (Found: C, 21.0; H, 3.8; F, 23.0; N, 11.6; S, 13.3. Calc. for $C_{13}H_{24}CoF_9N_6O_9S_3$: C, 21.25; H, 3.3; F, 23.3; N, 11.45; S, 13.1%). It may be recrystallized further, if required, by dissolution in a minimum volume of hot ethanol containing some $NaOSO_2CF_3$, followed by slow addition of diethyl ether to the cooling solution in portions over several hours. Electronic spectrum in aqueous 0.1 mol dm^{-3} $HClO_4$–0.9 mol dm^{-3} $NaClO_4$: 341 (113) and 462 (ε 145 dm^3 mol^{-1} cm^{-1}).

$[Co(tren)\{HCON(CH_3)_2\}_2][CF_3SO_3]_3$. The complex was prepared by reaction of $[Co(tren)(OSO_2CF_3)_2][CF_3SO_3]$ (2.0 g) with dry dimethylformamide (10 cm^3) on a steam-bath for 10 min. After cooling to room temperature, the red solution was added to 500 cm^3 of rapidly stirring diethyl ether. The resultant oil was separated by decantation of the supernatant, and was mixed by stirring with ethanol (50 cm^3) to yield a carmine powder in suspension. After stirring for 20 min, ether (50 cm^3) was added to complete precipitation. The product was collected after a further 10 min, washed with ether (2 × 20 cm^3), and dried (yield 2.1 g, 90%) (Found: C, 22.5; H, 3.9; F, 21.0; N, 10.4; S, 12.4. Calc. for $C_{15}H_{32}CoF_9N_6O_{11}S_3$: C, 22.55; H, 4.05; F, 21.4; N, 10.5; S, 12.05%). If required, the product may be recrystallized as described for the acetonitrile analogue. Electronic spectrum in aqueous 0.1 mol dm^{-3} $HClO_4$–0.9 mol dm^{-3} $NaClO_4$: 361 (117) and 512 nm (ε 212 dm^3 mol^{-1} cm^{-1}).

Spectroscopic and Kinetic Methods.—Electronic spectra were recorded using Hewlett-Packard 8450A or Hitachi 220A spectrophotometers. Nuclear magnetic resonance spectra were recorded using a JEOL FNM FX200 spectrometer, in D_2O or $DClO_4$; shifts are with respect to sodium 3-trimethylsilylpropionate as internal reference, which occurs at −0.02 p.p.m. *versus* $SiMe_4$. Infrared spectra were recorded for KBr discs using a Pye Unicam SP-3 300 spectrometer. Microanalyses were performed by the Australian National University Microanalytical Service.

Acid-aquation reactions were followed by spectrophotometry in thermostatted (±0.1 °C) cell holders using 0.1 mol dm^{-3} HX–0.9 mol dm^{-3} NaX (X = ClO_4^- or $CF_3SO_3^-$) aqueous solutions. Samples of the complex were dissolved directly in pre-equilibrated solutions in the spectrophotometer cell, and reactions were monitored continuously to about four half-lives (*ca.* 95% completion of reaction) of the second reaction, with the final absorbance routinely recorded a day later (>98% completion of reaction). Plots of ln $(A_t - A_\infty)$ *versus* time are non-linear due to the two consecutive reactions, and separation into two components to yield two sequential rate constants was performed by conventional graphical[13] or computational methods where the fit by two exponentials was determined by an iterative program.[14]

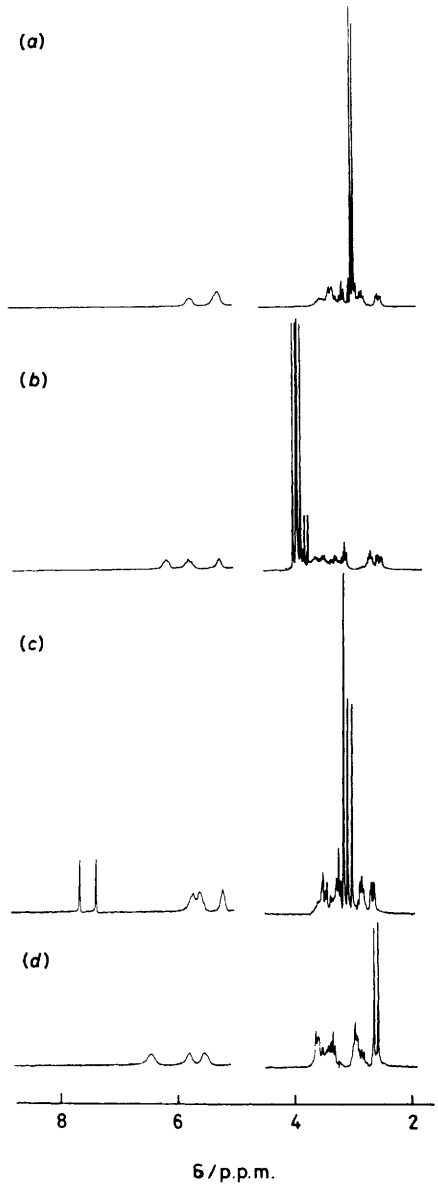


Figure 1. 200-MHz Proton n.m.r. spectra of $[Co(tren)L_2]^{3+}$ compounds in D_2O. L = dimethyl sulphoxide (*a*), trimethyl phosphate (the small doublet to the right of the major part of doublets is due to free trimethyl phosphate, since some hydrolysis occurs on the time-scale of the experiment) (*b*), dimethylformamide (*c*), and acetonitrile (*d*)

Results

Applications of recently established methods for synthesis of (trifluoromethanesulphonato-*O*)cobalt(III) complexes[15,16] in this case allowed the facile synthesis of $[Co(tren)(OSO_2CF_3)_2][CF_3SO_3]$ in essentially quantitative yield. The purple product is required to co-ordinate the two $^-OSO_2CF_3$ ligands in *cis* dispositions, which is the preferred arrangement since *cis*-$[Co(en)_2(OSO_2CF_3)_2]^+$ (en = 1,2-ethanediamine) is the only product of reaction of either *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ with

CF_3SO_3H at or above room temperature.[15] The substitution lability of co-ordinated $^-OSO_2CF_3$ on cobalt(III) established previously is also apparent in this complex. Aquation in 0.1 mol dm^{-3} $HClO_4$–0.9 mol dm^{-3} $NaClO_4$ is rapid. Only a single exponential was observed in this case, with $k_{obs.}$ (25 °C) 1.55×10^{-2} s^{-1}. This compares with $k_{obs.}$ 2.7×10^{-2} s^{-1} for $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ and consecutive rate constants for *cis*-$[Co(en)_2(OSO_2CF_3)_2]^+$ of 2.2×10^{-2} and 8.6×10^{-3} s^{-1}.[15] The observation of a single exponential for the tren complex may be interpreted in terms of a very rapid loss of the first $^-OSO_2CF_3$, which is therefore not measured, or alternatively in terms of a ratio $k_1:k_2$ of 2:1, when a single exponential would apply.[17] It is notable that $k_1:k_2$ for the $(en)_2$ analogue approaches 2:1,[15] so the latter may apply. If this is so, then it implies no special lability for tren compared to 2en or $5NH_3$. The variation of the rate of aquation of the tren complex with temperature (15, 5.0×10^{-3}; 20, 9.15×10^{-3}; 30 °C, 2.67×10^{-2} s^{-1}) yields activation parameters of $\Delta H^{\ddagger}$ 78.2 ± 1.3 kJ mol^{-1} and $\Delta S^{\ddagger}$ −16 ± 4 J K^{-1} mol^{-1}. The sole product of acid aquation of $[Co(tren)(OSO_2CF_3)_2][CF_3SO_3]$ is the $[Co(tren)(OH_2)_2]^{3+}$ complex, the electronic spectrum of which in aqueous 0.1 mol dm^{-3} CF_3SO_3H–0.9 mol dm^{-3} $NaOSO_2CF_3$ has maxima at 359 (77) and 502 nm (ε 101 dm^3 mol^{-1} cm^{-1}).

Table 1. Consecutive rate constants for acid hydrolysis of $[Co(tren)L_2]^{n+}$ complexes at 50 °C*

L	k_1/s^{-1}	k_2/s^{-1}	k_1/k_2
$OS(CH_3)_2$	1.3×10^{-3}	2.6×10^{-4}	5.0
$HCON(CH_3)_2$	2.1×10^{-4}	3.8×10^{-5}	5.5
$OP(OCH_3)_3$	1.05×10^{-2}	1.85×10^{-3}	5.8
$NCCH_3$	3.5×10^{-5}	3.4×10^{-6}	10.2
Cl^-	3.2×10^{-2}	6.8×10^{-5}	470
Br^-	2.5×10^{-1}	9.4×10^{-5}	2 660

* Neutral ligands: I = 1.0 mol dm^{-3}, H^+ = 0.1 mol dm^{-3}; standard error ≤ 5% (this work). Anionic ligands: rates extrapolated from data in refs. 4 and 5; we determined an aquation rate constant for $[Co(tren)Cl_2]^+$ in acid which was identical with the literature value at 25 °C.

The lability of the co-ordinated $^-OSO_2CF_3$ anions permits facile substitution by co-ordinating solvents such as water, dimethyl sulphoxide, dimethylformamide, trimethyl phosphate, and acetonitrile. Infrared spectroscopy of recrystallized samples clearly established the presence of these solvents as ligands, which is also established from microanalyses and proton n.m.r. spectroscopy. Further, the low-energy absorption maximum of the dimethyl sulphoxide (520 nm), dimethylformamide (512 nm), trimethyl phosphate (520 nm), and acetonitrile (462 nm) complexes differs from that for the aqua-complex (502 nm), and is consistent with O-bonding for all but the acetonitrile ligand, which must be N-bonded.

The non-equivalence of the two unidentate ligands is clearly established by proton n.m.r. spectra (Figure 1). Separate but equal peaks or groups of peaks occur for the two ligands. For the dimethyl sulphoxide complex, two sharp methyl singlets occur at 2.95 and 3.00 p.p.m. for the non-equivalent dimethyl sulphoxide ligands. With acetonitrile, two sharp methyl singlets occur at 2.62 and 2.69 p.p.m. The non-equivalent methyl doublets for the trimethyl phosphate complex occur at 3.91 and 3.99 p.p.m., with a coupling constant of 11 Hz in each case. The dimethylformamide complex is best characterized by the non-equivalent aldehyde-proton signals at 7.40 and 7.69 p.p.m. For this compound, the *N*-methyl groups are non-equivalent on any one ligand, so a doublet is observed; overall, a pattern of two overlapping doublets with a coincidence of chemical shifts at low field occurs, and the $\Delta[\delta(Me_A) - \delta(Me_B)]$ is different for the two sites. From structure (I), it was expected that the NH_2 group *trans* to L_p would be unique, so a 1:2 ratio of amine-proton chemical shifts would be seen. This is the case only for the dimethyl sulphoxide complex (Figure 1); other complexes show three amine-proton signals, and even for the dimethyl sulphoxide complex there is asymmetry in the major amine-proton signal. The separation of the signal for the two primary amines *trans* to each other is probably related to non-equivalence of the protons on each amine leading to two NH_a and two NH_b protons. This is not unreasonable in view of the unique nature of the L_p and L_t sites, and the presumed specific hydrogen-bonding interactions with the adjacent amine protons.

Acid hydrolysis (0.1 mol dm^{-3} H^+, I = 1.0 mol dm^{-3}) of all

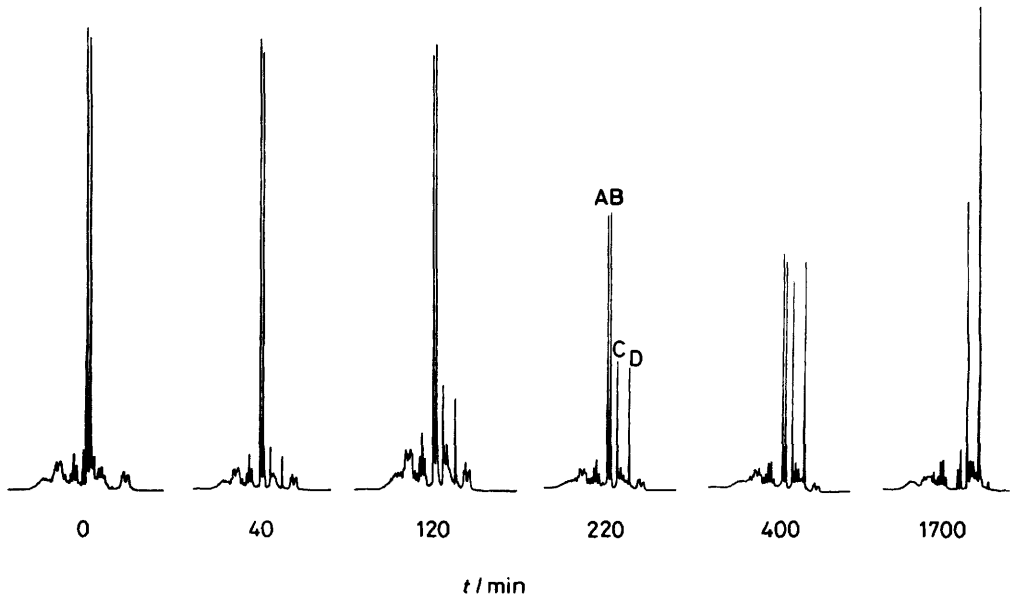


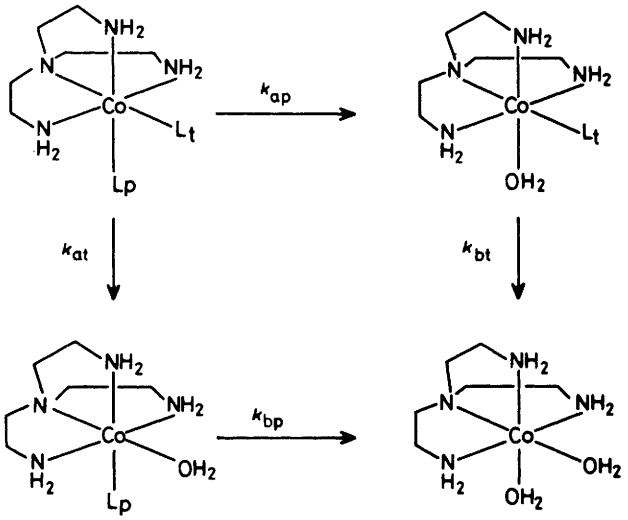
Figure 2. 200-MHz Proton n.m.r. spectrum of $[Co(tren)\{OS(CH_3)_2\}_2]^{3+}$ recorded at time intervals mainly during the initial part of the reaction. The two initial non-equivalent co-ordinated dimethyl sulphoxide signals (A, B), the signal of the intermediate (C), and that of free dimethyl sulphoxide (D) are identified on one of the spectra, all recorded in 0.1 mol dm^{-3} $DClO_4$ at 25 °C

four bis(solvent) tren complexes proceeds with two consecutive steps discernible. Rate constants for the processes are collected in Table 1, and compared with data for dihalogeno-analogues therein. For the bis(solvent) tren compounds the ratio $k_1:k_2$ is small at 50 °C, being 5.8 for trimethyl phosphate, 5.0 for dimethyl sulphoxide, 5.5 for dimethylformamide, and 10.2:1 for acetonitrile. In each case the only product of the acid hydrolysis is the $[Co(tren)(OH_2)_2]^{3+}$ ion, from spectroscopic comparison with an authentic sample.

As elaborated in the Discussion section, the unique nature of the L_p and L_t sites requires the observed rate constants to be composite terms, since both L_p and L_t can leave in the initial step, presumably at different rates. The different behaviour for L_p and L_t has not been addressed previously in a quantitative sense. In an attempt to obtain some information on the relative labilities of the L_p and L_t sites for initial hydrolysis, we have followed the hydrolysis reaction of the bis(dimethyl sulphoxide) complex in 0.1 mol dm^{-3} $DClO_4$ by n.m.r. spectroscopy (Figure 2); for this complex, the results indicate that loss of ligand from the L_p and L_t sites occurs at comparable rates. The decay of the two dimethyl sulphoxide signals (A and B, Figure 2) over the early part of the reaction occurs at almost equal rates. A single intermediate peak (C) is observed, while free dimethyl sulphoxide (D) is also observed. The absence of coincidences for the intermediate with precursor signals is clear from the final (1 700 min) spectrum shown in Figure 2, where almost all of the precursor complex has been consumed, and only two signals due to the intermediate and free dimethyl sulphoxide are observed. An identical experiment with the bis(dimethylformamide) complex yielded a comparable result, although in the aldehydic proton region two intermediates were clearly detected; in addition to the initial signals at 7.40 and 7.69 p.p.m., two new signals grew in at 7.55 and 7.61 p.p.m., in addition to the signal from free dimethylformamide at 7.91 p.p.m. The initial rates of loss from each site differ by a factor of no more than two. For the acetonitrile case, loss from each site proceeds at comparable rates; the initial signals at 2.62 and 2.69 p.p.m. are replaced by new signals of almost equal intensity at 2.64 and 2.70 p.p.m. and a free acetonitrile signal at 2.03 p.p.m. Therefore for all three cases, initial loss of L_p and L_t occurs at essentially the same rate.

Discussion

The existence of two unique sites for the unidentate ligands, L_p and L_t in (I) requires stepwise loss of these ligands to follow alternate paths (Scheme). Under these circumstances, the observed rate constants k_1 and k_2 are composite terms, with $k_1 = k_{ap} + k_{at}$ and $k_2 = k_{bp} + k_{bt}$. Previous work with the chloroaqua-complex has shown that this aquation proceeds with two different reaction rates,[6] ascribed to the presence of two isomers with the Cl^- *cis* to the tertiary nitrogen or *trans* to the tertiary nitrogen. Since this intermediate was prepared from the dichloro-complex, some loss of the first Cl^- from both L_p and L_t sites is implied, although no definitive experiments on the isomeric purity of the first hydrolysis have appeared.



Scheme.

Loss of one halide from $[Co(tren)X_2]^+$ is appreciably faster than the analogous reaction of $[Co(en)_2X_2]^+$.[4,5,18,19] This behaviour was ascribed to the particular geometry of the tren complexes. An early crystal structure determination of Ni(tren)-$(SCN)_2$ found that the metal–ligand bond *trans* to the tertiary nitrogen of the tren ligand is shorter than the metal–ligand *cis* bond,[12] suggesting that the latter position is sterically crowded. More recently, however, strain-energy calculations for isomers of $[Co(tren)(NH_3)Cl]^{2+}$ have been published, and there is little difference, though *trans*-Cl is slightly more strained.[20] Hydrolysis rate constants for the two isomers in acidic media are very similar,[21] consistent with this analysis. Nevertheless, in all crystal structures determined there is some deviation from the ideal with the unidentate ligand *cis* to the tertiary nitrogen bent away.[10–12]

The apparently special nature of the site *cis* to tertiary N seen in the solid state has been extrapolated to interpret the solution kinetics. Acid hydrolysis of $[Co(tren)BrCl]^+$ where both possible isomers exist is asserted to occur with loss of the ligand (Cl^- or Br^-) *cis* to the tertiary N in the first step.[8] There is certainly a marked increase in the rate of the first process compared with both the first step for aquation of the bis(1,2-ethanediamine) analogue, and with the second step for the tren complexes. At 25 °C, k_1(tren):k_1(2en) for the initial hydrolysis is 12 for X = Cl^- and 25:1 for X = Br^-. The ratio for the second stage falls to *ca.* 1.5:1 with X = Cl^-, and has been ascribed to less strain in the intermediate tren complex.[8] In these assessments, essentially exclusive release initially at the *cis*-tertiary N site is implied, though not proven. For comparison, it is notable that steric acceleration in simple pentachlorocobalt(III) complexes has been reported, with $k[Co(NH_2CH_3)_5Cl^{2+}]:k[Co(NH_3)_5Cl^{2+}]$ of 20 and $k[Co(NH_2CH_2CH_3)_5Cl^{2+}]:k[Co(NH_3)_5Cl^{2+}]$ of 95:1.[22] Ascribing a rate-constant ratio as low as 12:1 for $[Co(tren)Cl_2]^+$ to a specific effect is not particularly compelling, since the small energy differences involved may well be brought about by other minor factors such as specific solvation differences.

At least for the $[Co(tren)L_2]^{3+}$ complexes, loss of the neutral ligand L from the L_p and L_t sites is competitive, and the n.m.r. experiments show that both leave at nearly the same rates in the initial step. Therefore no special lability can be ascribed to the L_p compared with the L_t site in that situation. This is borne out by comparison of the data in Table 2, where the rate ratio for loss of neutral ligand from $[Co(NH_3)_5L]^{3+}$ [23] *versus* $[Co(tren)L_2]^{3+}$ is less than 10:1 in all cases. This ratio is statistically reduced further, given that two leaving sites are available initially in the tren compared with the penta-amine case. The results for charged leaving groups differ substantially (Table 2), except for $CF_3SO_3^-$, and in that case the observed single exponential may imply a very rapid first step which is not observed, although this cannot be substantiated.

Loss of the second neutral ligand is not much slower than the first process (Table 1). This is reasonable, since apart from minor ligand-field and solvation differences, no special differences are inferred for $[Co(tren)L_2]^{3+}$ over $[Co(tren)(OH_2)L]^{3+}$. The variation with charged leaving groups (Cl^-, Br^-) is markedly different,[1] however (Table 1). This may imply some special steric effect with charged ligands in the first step. However, this is improbable, since the molar volume of $Cl(aq)^-$,

Table 2. Comparative aquation rate constants (25 °C) for $[Co(tren)L_2]^{n+}$ and $[Co(NH_3)_5L]^{n+}$ cations

L	k_1(tren)/s^{-1}	k_1(5NH$_3$)/s^{-1}	k_1 ratio	Ref.
$OP(OCH_3)_3$	4.3×10^{-4}	2.5×10^{-4}	1.7.	*a*, 23
$OS(CH_3)_2$	7.4×10^{-5}	1.8×10^{-5}	4.1	*a*, 23
$HCON(CH_3)_2$	1.5×10^{-5}	1.6×10^{-6}	9.4	*a*, 23
$NCCH_3$	7.2×10^{-7}	$\leqslant 2 \times 10^{-8}$ [b]	*ca.* 35	*a*
$^-OSO_2CF_3$	1.55×10^{-2}	2.7×10^{-2}	0.6	*a*, 15
Cl^-	3.2×10^{-2}	1.7×10^{-6}	18 800	4, 25
Br^-	2.5×10^{-1}	6.3×10^{-6}	39 700	5, 25

[a] This work. [b] A value of $k_1(5NH_3)$ of 4.3×10^{-7} s^{-1} has been reported,[23] but this differs substantially from our own estimate at 25 °C.

for example, is actually less than those of the neutral ligands employed in this study.[24] Rather, the difference may be related to departure of an ionic leaving group. Both the charge on the complex and the electrostriction of the cation change with the departure of ionic leaving groups, and the solvent rearrangements concomitant with these processes may dominate the kinetic behaviour. Loss of Cl^- from *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ is very much slower than from any *cis*-$[Co(en)_2(X)Cl]^+$ where Cl^- leaves first, and no special steric effects can be invoked in these cases.[25] The same behaviour is seen for *cis*-$[Co(trien)(NH_3)Cl]^{2+}$ *versus* *cis*-$[Co(trien)Cl_2]^+$ (trien = triethylenetetramine).[25] The general observation that $k \gg k'$ for Cl^- loss in $[Co(N_4)(X)Cl]^+$ *versus* $[Co(N_4)(L)Cl]^{2+}$ (N_4 represents N_4-donor ligand) is certainly maintained for $[Co(tren)Cl_2]^+$ *versus* $[Co(tren)(OH_2)Cl]^{2+}$, and need not be considered remarkable. It is notable for the $[Co(tren)L_2]^{3+}$ system that when L = dimethyl sulphoxide n.m.r. spectroscopy reveals a single signal for the intermediate rather than two separate signals. Given the small separation of the signals for the precursor, this may simply imply that the signals for the two isomers are coincident; the absence of coincidences with L = acetonitrile and L = dimethylformamide supports this interpretation. Of course, given the tendency for tren to participate in five-co-ordinate trigonal-bipyramidal geometries, it is conceivable that a common trigonal-bipyramidal transition state exists for loss of either L_p or L_t. This could generate a common geometry in an intermediate, although any compelling reasons for entry of a water molecule at a specific site in the transition state, required for formation of only one isomer as intermediate, are not immediately obvious.

It is notable from the data in Table 2 that for the neutral O-bound ligands the k(tren):k(5NH$_3$) ratio gets progressively smaller as the rate increases, *i.e.* the better the leaving group the smaller is the ratio. For this albeit limited data set there is a linear relationship between log k(tren) and log k(5NH$_3$); data for acetonitrile also fit the line moderately well, although the rate of acid hydrolysis of (acetonitrile)penta-amminecobalt(III) is apparently not well determined at 25 °C. The implication of this observation is that a uniform dissociative mechanism applies for both complexes with the various leaving groups. Differences in the rate constants for the tren or penta-ammine complex with any one ligand then relate to the amount of bond stretching necessary to generate the transition state in each case. Presumably, as the lability of the ligand increases, the differences in the amount of extension necessary to attain the transition state with the two non-leaving-group sets diminishes, and this is seen as a diminution in the rate constant ratio, although effects specific for each complex, such as solvation differences, will not produce an exact relationship. The behaviour with anionic leaving groups is not clear due to significant charge and electrostriction changes in those cases, although data for $CF_3SO_3^-$ appear to fit the relationship discussed above.

The advantage of employing a multidentate ligand which imparts a fixed geometry in the precursor, intermediates, and products is obvious, since it removes the necessity to consider geometric isomerization and to separate product isomers. Carrying the system further and employing neutral rather than ionic leaving groups imparts a further simplification, since it limits electrostrictive changes during reaction, and may provide the further bonus of allowing the process to be followed by proton n.m.r. techniques. The results reported above represent the first study where loss of a range of neutral ligands from stereochemically rigid cobalt(III) complexes has been pursued. We are currently extending our study of this system to include a detailed analysis of the rate–pH profile, since the first step is base dependent and the second apparently acid dependent, and intend to make like studies with other stereochemically rigid complexes.

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Received 30*th November* 1984; *Paper* 4/2039