

A tetrapodal pentaamine for stabilizing square pyramidal co-ordination modules: synthesis, structure and reactivity of cobalt(III) complexes of 2,2'-dimethyl-2,2'-iminodimethylenebis(1,3-propanediamine)

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A facile synthesis of the tetrapodal pentaamine ligand 2,2'-dimethyl-2,2'-iminodimethylenebis(1,3-propanediamine), ditame, has been achieved and some unusual effects of its topology and preference for square pyramidal co-ordination in cobalt(III) complexes explored. Potential influences of the ditame structure on substitution chemistry in $[\text{Co}(\text{ditame})\text{X}]^{n+}$ systems are defined by crystal structure analyses for $[\text{Co}(\text{ditame})\text{Cl}][\text{ZnCl}_4]$ and $[\text{Co}(\text{ditame})(\text{NH}_3)]\text{Cl}[\text{ZnCl}_4]$. Proton exchange, nitrogen inversion and chloride anation reactivity, and substitution stereochemistry studies have been carried out on the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and $[\text{Co}(\text{ditame})(\text{OD}_2)]^{3+}$ complexes by using ^{13}C NMR spectroscopy. The base hydrolysis rate constant for $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ($68 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , I 1.0 mol dm^{-3}) is 250 fold greater than that for the analogous $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion. This difference is attributed to an enhanced *trans* influence and a bond-coupled co-operative mechanism that facilitate the Cl^- dissociation in the conjugate base of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$. The bond-coupled mechanism also aids dissociative processes for the relatively fast aquation and anation chemistry of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and $[\text{Co}(\text{ditame})(\text{OH}_2)]^{3+}$. Two results for the reactivity of the $[\text{Co}(\text{ditame})\text{X}]^{n+}$ ($\text{X} = \text{Cl}^-$ or H_2O) ions are attributed to restricted rearrangement of the square pyramidal $\text{Co}(\text{ditame})$ fragment in the course of X^{n-3} substitutions. One is the very small amount of $[\text{Co}(\text{ditame})(\text{N}_3)]^{2+}$ ($1.1 \pm 0.3\%$) formed in competition with $[\text{Co}(\text{ditame})(\text{OH})]^{2+}$ during base hydrolysis in aqueous $1 \text{ mol dm}^{-3} \text{ NaN}_3$, which indicates an unusually short lifetime for the proposed intermediate. Also, there were no species detected that arise from partial dissociation of the amine, neither in the base hydrolysis nor in the aquation and anation experiments, even at temperatures $>50^\circ\text{C}$ and in the presence of strong acids. There are important consequences for substitution chemistry in other $[\text{M}(\text{pentaamine})\text{X}]^{n+}$ systems where rearrangement of the $\text{MN}_5(\text{amine})$ fragment is restricted. The quantitatively simple substitution processes also make these reagents valuable as protective groups in synthetic applications such as peptide cleavage and synthesis.

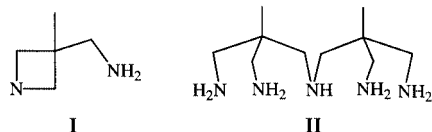
Pentadentate ligands which co-ordinate to five of the six apical sites in an octahedral metal complex essentially impose a donor atom subfield with square pyramidal (*SP*) geometry.¹ Rare examples in this class have the potential to enforce *SP* configurations for intermediates in dissociative substitutions at the sixth octahedral site,^{1,2} or to form stable *SP* complexes³ with metal ions that are typically five- or six-co-ordinate, when aided by derivatives that block the sixth site.^{2,3} Several intrinsic structural features are needed by the ligand to achieve these results. In order preferentially to stabilize square pyramidal transients in substitution reactions the pentadentate bite angles should be resistant to expansion so that rearrangement to a trigonal bipyramidal (*TBPY*) form³ is sterically restricted. At the same time, any potential metal–ligand π -bonding interactions² should be restricted in the rearranged configuration. To stabilize five-co-ordinate *SP* complexes when octahedral co-ordination is electronically preferred the ligand should be able to accommodate the introduction of suitable steric blocking

groups, ideally by a template procedure. It is also crucial that the five-co-ordinate intermediates or complexes are inert to reaction pathways involving partial dissociation of the pentadentate ligand.

In the course of probing the synthesis of ethylidynetris(methanamine) (tame) by ammonolysis^{4–6} of (ethylidynetrimethyl)tris(benzenesulfonate) under forcing conditions, several unusual polyamine chelates have been formed and isolated in moderate quantities.⁴ One of these was the bidentate (aminomethyl)azetidide **I** which forms novel bis- and tris-(ligand) complexes with cobalt(III) and nickel(II) ions, and some unusual properties of these complexes were investigated in a previous publication.⁶ Another important polyamine product is the tetrapodal pentaamine 2,2'-dimethyl-2,2'-iminodimethylenebis(1,3-propanediamine) or ditame **II**. Qualitatively this ligand seems likely to promote *SP* co-ordination geometry for metal ions that usually form five- and six-co-ordinate complexes, at least for those metals which favour metal–nitrogen σ binding.

The current study involves the synthesis, structure and substitution reactivity of cobalt(III) complexes of ditame, and includes a simple efficient two-step isolation of the pentaden-

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tate chelate, which advances further studies of its complex formation and reactivity with other metal ions.⁷ Crystal structural analyses have defined the ligand and the cobalt(III) complexes, and also carry implications for the reactivity of the molecules.

Experimental

Materials, instrumentation and general procedures

Analytical grade commercially available reagents were used except for CoCl_2 (anhydrous) from Alfa Products, Danvers, Massachusetts. Bio-Rad analytical grade Dowex 50W-X2 (200–400 mesh, H^+ form) and Pharmacia SP-Sephadex C-25 (Na^+ form) cation-exchange resins were used for column chromatography.

The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were recorded with a Varian XL-300 or Varian Gemini 300 spectrometer and a broad band (5 mm) probe at 20 °C. Chemical shifts (δ positive downfield) are reported in ppm relative to external SiMe_4 with 1,4-dioxane as internal standard in D_2O at δ 3.70 (^1H) and 67.4 (^{13}C). A Hewlett-Packard 8450A UV/VIS or a Cary 210 spectrophotometer thermostatted at 25.0 ± 0.1 °C was used to measure electronic absorption spectra. Measurements of pH were carried out using a Metrohm 654 pH meter and a Ross combination electrode with 1.0 mol dm^{-3} NaCl as the internal electrolyte. The slope (mV/pH) was determined using standard (NBS) phthalate and phosphate buffers, and mV readings (± 0.1) were converted into pH using $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ HCl ($I = 1.0 \text{ mol dm}^{-3}$, NaClO_4 , pH 3.00) as the standard. The pH of ethanolamine and diethanolamine buffers for kinetics (0.2 mol dm^{-3} in total base) was adjusted by partial neutralization with standardized HClO_4 and the ionic strength was adjusted to 1.0 mol dm^{-3} with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

Büchi rotary evaporators were used to perform evaporations at ≤ 20 Torr pressure with bath temperatures of normally ≤ 50 °C. A 6 l Teflon sealed stainless steel autoclave fitted with an internal pressure probe, a pressure release valve, and independent thermocouple probes for temperature control and monitoring was employed for the syntheses involving liquid ammonia. The autoclave was suitable for reaction temperatures and pressures up to 250 °C and 350 atm. A moulded Teflon liner (5 mm, vol *ca.* 4.5 l) fitted with a removable Teflon cap contained the reaction mixtures. Reaction temperature (± 2 °C) was regulated from a remote site using a Eurotherm 902P microprocessor control unit incorporated in the heating circuit and connected with the thermocouple control probe. The unit had an automatic self-tuning facility which determined ideal critically damped parameter values for optimum approach to and maintenance of the selected reaction temperature. Outputs from both the control and monitor probes were recorded using digital displays as well as a 2-pen recorder.

Synthesis

2,2'-Dimethyl-2,2'-iminodimethylenebis(1,3-propanediamine) pentahydrochloride, ditame·5HCl. (Ethyldynetrimethyl)tris(benzenesulfonate) was synthesized using reported procedures⁸ although vacuum drying proved to be unnecessary. The triester (500 g, 0.925 mol) and liquid NH_3 (3.5 l) were loaded into the Teflon liner, which was inserted in the high pressure autoclave before finally securing the Teflon-sealed cap and connecting the temperature probes. The vessel was then heated to an equilibrium internal reaction temperature of 126 °C and pressure of *ca.* 100 atm using the remote control unit. These temperature

and pressure conditions were maintained for 15 h before shut-down and cooling to *ca.* 20 °C. The NH_3 was then removed through the release valve connected to an efficient water aspirator, and water (2 l) was reintroduced through the valve to dissolve the reaction residues. The pale yellow solution was diluted with water (to *ca.* 4 l) and HCl (*ca.* 250 ml, 36%) slowly added until the pH was about 2. This solution was then sorbed onto Dowex 50W-X2 resin (12 × 35 cm column, H^+ form) and the column washed with water (5 l) and 1 mol dm^{-3} HCl (5 l) to remove the excess of ammonium ion and some minor reaction products. The main light coloured polyamine band (F_1) was then eluted with 2 mol dm^{-3} HCl (12 l from band front). A second distinct light band (F_2) was subsequently eluted with 6 mol dm^{-3} HCl (2.5 l from band front), and a third fraction finally removed with more 6 mol dm^{-3} HCl (5 l).

Band F_1 was reduced in volume to *ca.* 300 ml using a Büchi Rotavapor R-151 fitted with 10 l evaporating and receiving flasks and connected to a Büchi B-160 Vacobox operating at 40–45 mbar pressure. White crystals of the hydrochloride salt formed as the concentrations of F_1 and HCl increased, and crystallization from the 300 ml mixture was completed by addition of methanol (1.5 l). The solid was isolated by filtration, washed with methanol and diethyl ether and air dried (98 g). It was identified by ^1H , ^{13}C NMR spectra and analytical methods⁸ as ethyldynetris(methanamine)trihydrochloride (tame·3HCl) (yield 47%).

Band F_2 was evaporated to *ca.* 200 ml in volume whereupon white crystals of the hydrochloride salt began to form. Crystallization was completed by slow addition of methanol while cooling and scratching. The solid was filtered off, stirred and washed with ethanol and then diethyl ether and air dried. It was identified as ditame·5HCl by NMR spectra and analytical procedures and confirmed by the X-ray analyses reported herein (yield 55 g, 30%) (Found: C, 30.1; H, 7.8; N, 17.3. $\text{C}_{10}\text{H}_{32}\text{Cl}_5\text{N}_5$ requires C, 30.1; H, 8.1; N, 17.5%). ^1H NMR (D_2O): δ 1.26 (s, 6 H, CH_3), 3.10, 3.16, 3.21, 3.25 and 3.33 (s plus AB q, 12 H, CH_2). ^{13}C NMR (D_2O): δ 18.5 (CH_3), 36.7 (C_{quat}), 44.1 (CH_2NH_2) and 54.4 (CH_2NH).

The isolation and characterization of species in the third main fraction, which was shown by ^1H , ^{13}C NMR and analytical work⁴ to contain mainly trimeric molecules (yield *ca.* 5%), will be addressed in a future publication along with that of other unusual minor polyamine products.

Chloro[2,2'-dimethyl-2,2'-iminodimethylenebis(1,3-propanediamine)]cobalt(III) dichloride hydrate (1/2.5), [Co(ditame)Cl] \cdot Cl $_2$ ·2.5H $_2$ O. The compound ditame·5HCl (840.5 g crude, <2.1 mol) was stirred with $\text{LiOH} \cdot \text{H}_2\text{O}$ (352.8 g, 8.4 mol) in methanol (5.0 l) until all had dissolved. A solution of CoCl_2 (273 g, 2.1 mol) in methanol (2.5 l) was then slowly added while stirring vigorously in air, and the mixture stirred for five days at 25 °C. The lilac precipitate was collected by filtration, washed with cold ethanol and diethyl ether and air dried (crude yield 548 g, >60%). Samples of the crude chloride salt were recrystallized as fibrous pinkish lilac needles from HCl (*ca.* 2 mol dm^{-3}) in water by addition of HCl (36%) and methanol or ethanol–diethyl-ether. The crystals were collected, washed with 2-butanol or ice cold ethanol and air dried (Found: C, 28.2; H, 7.2; Cl, 24.7; Co, 12.9; N, 16.1. $\text{C}_{10}\text{H}_{32}\text{Cl}_3\text{CoN}_5\text{O}_{2.5}$ requires C, 28.1; H, 7.5; Cl, 24.9; Co, 13.8; N, 16.4%). ^1H NMR (0.1 mol dm^{-3} $\text{DCl-D}_2\text{O}$): δ 0.89 (s, 6 H, CH_3), 1.9–2.9 (complex multiplets, 12 H, CH_2), 4.7–5.9 (complex multiplets, NH and NH_2 , overlap with HOD). ^{13}C NMR (D_2O , pD *ca.* 5): δ 21.3 (CH_3), 40.4 (C_{quat}), 45.5, 46.4 (CH_2NH_2) and 56.2 (CH_2NH). Visible absorption spectrum in water λ_{max} (ϵ) 517 (82.1) and 360 nm ($78.3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

The sparingly soluble diperchlorate salt was obtained from an aqueous solution of the chloride by addition of HClO_4 (70%). It proved to be the monohydrate $[\text{Co}(\text{ditame})\text{Cl}][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ which was analysed by using ^1H NMR in $(\text{CD}_3)_2\text{SO}$. The tetrachlorozincate salt (anhydrous) was crystallized by slow

addition of aqueous $\text{ZnCl}_2\text{-HCl}$ (pH *ca.* 2) to a solution of the chloride salt in HCl -water (1 mol dm^{-3}) (Found: C, 23.0; H, 4.9; Cl, 33.9; Co, 10.2; N, 13.3. $\text{C}_{10}\text{H}_{27}\text{Cl}_5\text{CoN}_5\text{Zn}$ requires C, 23.1; H, 5.2; Cl, 34.2; Co, 11.4; N, 13.5%). Crimson crystals of the $[\text{ZnCl}_4]^{2-}$ compound suitable for X-ray crystallographic analysis were acquired by slow diffusion of ethanol into a solution of the chloride salt in 2 mol dm^{-3} HCl containing an excess of ZnCl_2 , accompanied by slow evaporation of the mixed solvent.

[Co(ditame)(N₃)]ClO₄·2.5H₂O. The complex $[\text{Co}(\text{ditame})\text{Cl}]\text{Cl}_2\cdot 2.5\text{H}_2\text{O}$ (1.0 g) was dissolved in water (25 ml) containing NaN_3 (0.5 g) and warmed at 60 °C for 30 min. Addition of NaClO_4 (5 ml of 10 mol dm^{-3}) to the resulting deep violet solution effected the deposition of $[\text{Co}(\text{ditame})(\text{N}_3)]\text{ClO}_4\cdot 2.5\text{H}_2\text{O}$ crystals, which were collected after 2 h at 0 °C, washed with ethanol and diethyl ether and air dried. This material was recrystallized from water- NaClO_4 (Found: C, 23.2; H, 5.6; Cl, 13.8; N, 21.4. $\text{C}_{10}\text{H}_{27}\text{Cl}_2\text{CoN}_8\text{O}_8$ requires C, 23.2; H, 5.3; Cl, 13.7; N, 21.7%). ¹³C NMR (D_2O): δ 21.3 (CH_3), 40.1 (C_{quat}), 45.6, 46.7 (CH_2NH_2) and 56.4 (CH_2NH). Visible absorption spectrum in water: λ_{max} (ϵ) 503 nm (369 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

[Co(ditame)(OH₂)]NO₃·3H₂O. A suspension of $[\text{Co}(\text{ditame})\text{Cl}]\text{Cl}_2\cdot 2.5\text{H}_2\text{O}$ (0.5 g) in water (5 ml) was treated with NaOH (5 mol dm^{-3}) until it just dissolved to yield $[\text{Co}(\text{ditame})(\text{OH})]^{2+}$, several extra drops being added to bring the final pH to greater than 10. The pink solution was cooled on ice and treated with cold HNO_3 (4 ml, 16 mol dm^{-3}) to give an orange solution. Orange crystals quickly deposited on standing and were recrystallized from cold water- HNO_3 (Found: C, 25.3; H, 6.1; N, 23.5. $\text{C}_{10}\text{H}_{29}\text{CoN}_8\text{O}_{10}$ requires C, 25.0; H, 6.1; N, 23.3%). ¹³C NMR (D_2O): δ 21.2 (CH_3), 41.1 (C_{quat}), 45.3, 46.6 (CH_2NH_2) and 55.7 (CH_2NH). Visible absorption spectrum: in 0.1 mol dm^{-3} HClO_4 , λ_{max} (ϵ) 484 (73.5) and 346 nm (84.6 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$); in 0.01 mol dm^{-3} OH^- , 489 (86.5) and 355 nm (80.4 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

[Co(ditame)(NH₃)]Cl₃·3H₂O. The complex $[\text{Co}(\text{ditame})\text{Cl}]\text{Cl}_2\cdot 2.5\text{H}_2\text{O}$ (517 g of crude chloride salt) was dissolved in liquid NH_3 (2.5 l) in the 4.5 l Teflon vessel described earlier. This was heated to an equilibrium internal reaction temperature of 125 °C (pressure *ca.* 100 atm) for 24 h using the high pressure autoclave and remote control unit in accord with aforesaid procedures. After allowing the autoclave to cool to ambient temperature the NH_3 was removed through the release valve by an efficient water aspirator. The yellow-orange residues were dissolved in water (2 l) and sorbed onto a column of Dowex 50W-X2 resin (12 × 72 cm, H^+ form). The column was washed with water (10 l) and 1 mol dm^{-3} HCl (10 l) to remove ammonium and other minor low charge impurities, and then some other minor products (mainly chloro- and aqua-pentaamine species) were eluted with 2 mol dm^{-3} HCl . A final large orange band was eluted with 4 mol dm^{-3} HCl and the eluent evaporated to *ca.* 1 l at a bath temperature of 60 to 65 °C. This solution was cooled on an ice-bath, while an ethanol-diethyl ether solution was slowly added with scratching until no further precipitation occurred. The yellow-orange powder was collected by filtration, washed with ethanol-diethyl ether solution and diethyl ether and air dried (yield 339 g, *ca.* 70%) (Found: C, 26.2; H, 8.3; Cl, 24.8; Co, 12.6; N, 17.9. $\text{C}_{10}\text{H}_{36}\text{Cl}_3\text{CoN}_6\text{O}_3$ requires C, 26.5; H, 8.0; Cl, 23.4, Co, 13.0; N, 18.5%). ¹H NMR (D_2O): δ 0.89 (s, 6 H, CH_3), 2.2–2.9 (complex multiplets, 12 H, CH_2). ¹³C NMR (D_2O): δ 21.4 (CH_3), 39.7 (C_{quat}), 45.2, 46.2 (CH_2NH_2) and 55.5 (CH_2NH). Electronic absorption spectrum in water: λ_{max} (ϵ) 466 (89), 337 (101) and 225 nm (20700 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

Orange, needle like crystals of the $\text{Cl}[\text{ZnCl}_4]$ hydrate suitable for X-ray studies were obtained by adding an excess of $\text{ZnCl}_2\text{-HCl}$ solution (aqueous, *ca.* 0.8 mol dm^{-3} ZnCl_2) to a solution

of the trichloride in the minimum volume of water, and slow evaporation in air (Found: C, 22.2; H, 6.0; Cl, 32.0; N, 15.6. $\text{C}_{10}\text{H}_{31}\text{Cl}_5\text{CoN}_6\text{O}_{0.5}\text{Zn}$ requires C, 22.0; H, 5.7; Cl, 32.5; N, 15.4%).

Kinetics

Repetitive spectral scanning of reacting $[\text{Co}(\text{ditame})\text{Cl}]\text{Cl}_2$ solutions in ethanolamine buffer (pH 9.90, $I = 1.0\text{ mol dm}^{-3}$) in the 660–350 nm range revealed sharp isosbestic points at 510 and *ca.* 360 nm, as expected for the simple reaction: $[\text{Co}(\text{ditame})\text{Cl}]^{2+} + \text{OH}^- \longrightarrow [\text{Co}(\text{ditame})(\text{OH})]^{2+} + \text{Cl}^-$. With the spectrophotometer in the A, t trace mode, the kinetics was followed by utilizing the large proportional absorbance change at 530 nm. Runs were performed in triplicate for each of the ethanolamine and diethanolamine buffers. Pseudo first order kinetics was observed at each pH over the range 9–11. The specific base hydrolysis rate constant k_{OH} ($68 \pm 5\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ at 25 °C, $I = 1.0\text{ mol dm}^{-3}$) was determined from $k(\text{obs.})/[\text{OH}^-]$ where $[\text{OH}^-]$ was obtained from pH using $\text{p}K_w = 13.77$ at 25 °C. Background aquation was negligible at the pH values employed.

Azide ion competition

Samples of $[\text{Co}(\text{ditame})\text{Cl}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (*ca.* 200 mg) were dissolved in 1.00 mol dm^{-3} $\text{NaN}_3\text{-}0.1\text{ mol dm}^{-3}$ NaOH (25 ml, 25 °C) and allowed to react for 2 min before quenching with NH_4ClO_4 (1 g). The product mixtures were diluted with water (to 500 ml), sorbed onto SP-Sephadex C-25 cation exchange resin (Na^+ form) and eluted with 0.5 mol dm^{-3} NaClO_4 (pH 3, HClO_4), to separate two bands. The first was $[\text{Co}(\text{ditame})(\text{N}_3)]^{2+}$, determined spectrophotometrically using ϵ 369 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ at λ_{max} 503 nm, and the second band $[\text{Co}(\text{ditame})(\text{OH}_2)]^{3+}$ was removed from the column with 1.0 mol dm^{-3} NaClO_4 (pH 3) and determined using ϵ 73.5 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ at λ_{max} 484 nm. Light was excluded in all these experiments because of the photosensitivity of the azido species. Total cobalt recovery from the column exceeded 98%. A control experiment (N_3^- excluded) demonstrated the absence of any other 2+ ion which may have been in the starting material as a trace impurity. The amount of azido complex found in duplicate experiments and normalized to 100% recovery was $1.1 \pm 0.3\%$. This is the lowest N_3^- ion *versus* H_2O competition so far reported for a chloro amine cobalt(III) complex in a base hydrolysis reaction. Control experiments indicated that the azido complex was recovered unchanged from 0.1 mol dm^{-3} NaOH solutions after a 2 min reaction period.

X-Ray crystallography

The structures of $[\text{Co}(\text{ditame})\text{Cl}][\text{ZnCl}_4]$ and $[\text{Co}(\text{ditame})(\text{NH}_3)]\text{Cl}[\text{ZnCl}_4]$ have been determined. A summary of crystal data, data collection and refinement is given in Table 1. Data were collected on a HUBER four-circle diffractometer. For $[\text{Co}(\text{ditame})\text{Cl}][\text{ZnCl}_4]$ refinement of the structure using isotropic thermal parameters converged at an unusually high value of the discrepancy factor ($R(F)$ 0.175), although subsequent anisotropic refinement of the non-hydrogen atoms converged with more acceptable values. Hydrogen atoms were included at their calculated positions and not explicitly refined in the least-squares procedure. For the $[\text{Co}(\text{ditame})(\text{NH}_3)]\text{Cl}[\text{ZnCl}_4]$ compound the structure was solved by direct methods.⁹ The hydrogen atoms were included at calculated positions and refined.

CCDC reference number 186/1651.

Results and discussion

Synthesis and structure

The pentaamine chelate 2,2'-dimethyl-2,2'-iminodimethylene-

Table 1 Summary of crystallographic data

	[Co(ditame)Cl][ZnCl ₄]	[Co(ditame)(NH ₃)Cl][ZnCl ₄]
Empirical formula	C ₁₀ H ₂₇ Cl ₅ CoN ₅ Zn	C ₁₀ H ₃₀ Cl ₅ CoN ₆ Zn
<i>M</i>	518.94	535.97
<i>T</i> /K	294	294
Crystallographic system	Orthorhombic	Monoclinic
Space group	<i>Pnma</i> or <i>Pn2₁a</i>	<i>P2₁/c</i>
<i>a</i> /Å	16.175(5)	9.870(1)
<i>b</i> /Å	7.771(3)	25.131(4)
<i>c</i> /Å	15.772(4)	9.054(1)
β /°		67.41(1)
<i>U</i> /Å ³	1982	2073.6
<i>Z</i>	4	4
μ (Mo-K α)/cm ⁻¹	27.59	26.62
No. reflections collected	7929	7010
No. reflections independent	3626	4140
<i>R</i> _{int}	0.028	
<i>R</i> (<i>F</i>)	0.064	0.036
<i>R</i> _w (<i>F</i>)	0.071	0.045

bis(1,3-propanediamine) (ditame, **II**) was synthesized by a relatively straightforward two-step procedure in which two molecules of (ethyldiynetrimeethyl)tris(benzenesulfonate) were co-condensed with ammonia in liquid ammonia at 125 °C and *ca.* 100 atm. An established cation-exchange chromatographic technique,⁸ followed by crystallization as the pentahydrochloride salt, enabled the ditame ligand to be isolated cleanly in moderate yield (30%) despite the large amount of tame co-product (45–50%) and several other minor products present in the reaction mixture. The ¹³C NMR spectrum revealed four signals in D₂O, consistent with an average C_{2v} symmetry for the solution structure of ditame under these conditions. The ¹H NMR spectrum confirmed this assertion and all individual assignments were based on reported chemical shift data for analogous carbon and proton chromophores.

Conventional methods for complex formation and substitution chemistry were used to obtain the [Co(ditame)Cl]²⁺, [Co(ditame)(N₃)]²⁺ and [Co(ditame)(OH₂)]³⁺ species, whereas the [Co(ditame)(NH₃)]³⁺ complex was synthesized in good yield by a dissociative conjugate base solvolysis in liquid ammonia at 125 °C. Five resonances were observed in the ¹³C NMR spectrum of each ion, and this result shows that on the ¹³C NMR timescale a mirror plane relates the two cap fragments of the complex molecules in aqueous solution. Accordingly, the ¹H NMR spectra of the [Co(ditame)Cl]²⁺ and [Co(ditame)(NH₃)]³⁺ ions showed a singlet resonance for the methyl protons of the ditame ligand.

The structures of [Co(ditame)Cl]²⁺ and [Co(ditame)(NH₃)]³⁺ were established by single crystal X-ray analyses of their [ZnCl₄] and Cl[ZnCl₄] salts respectively, and ORTEP¹⁰ views of the cations are shown in Figs. 1 and 2. They clearly illustrate the dimeric nature of the pentaamine ligand with two tame residues fused at the secondary nitrogen atom, which gives rise to the trivial name "ditame". The bond length and angle data for the structures are given in Tables 2 and 3. Although the anisotropic refinement of the [Co(ditame)Cl][ZnCl₄] structure in the centrosymmetric space group *Pnma* converged with an acceptable *R* value of 0.064, a closer analysis showed that the structure must be disordered in this space group. For this reason some of the data presented in Table 2 are not expected accurately to reflect the intramolecular geometry. In order to identify the problem, formulate a solution and also to offer a clear realistic description of the chelated ligand configuration, the two crystal structures are briefly discussed in separate sections.

Structure of [Co(ditame)Cl][ZnCl₄]. Several results from the structure solution and refinement collectively imply that this structure is statistically disordered in space group *Pnma*. First the complex cation (Fig. 1(a)) lies on a mirror plane containing the C(51)H₃C(41)C(31)H₂N(3)HC(32)H₂C(42)C(52)H₃ fragment as well as the cobalt and chlorine atoms. This is incompat-

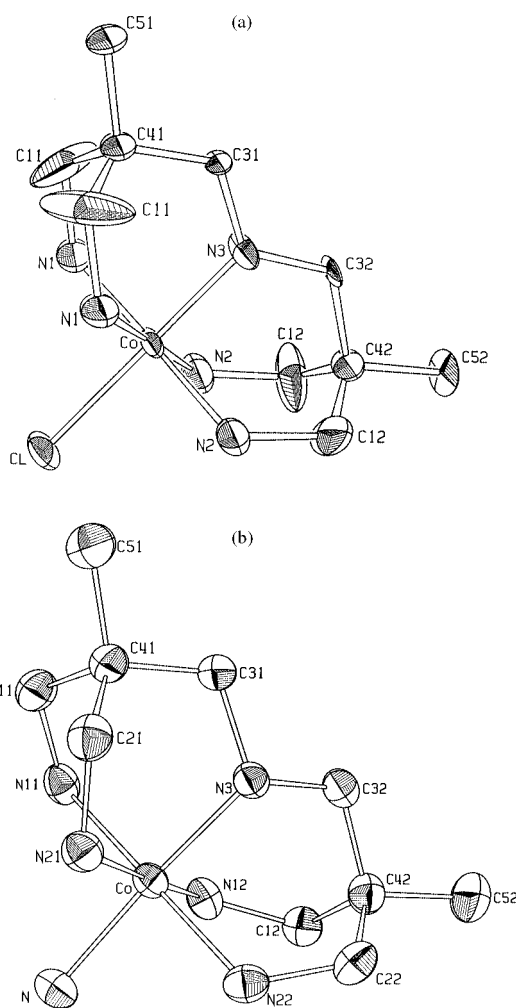


Fig. 1 (a) View of the [Co(ditame)Cl]²⁺ cation in the [Co(ditame)Cl][ZnCl₄] structure (H atoms omitted). (b) View of the [Co(ditame)(NH₃)]³⁺ cation in the [Co(ditame)(NH₃)Cl][ZnCl₄] structure (H atoms omitted). Atomic displacement ellipsoids enclose 50% probability.

ible with spectroscopic and microanalytical data which show that the secondary nitrogen atom N(3) is protonated and has essentially sp³ hybrid valence orbitals, thereby enforcing a puckered conformation for the CCH₂NHCH₂C moiety. The exceptionally short N(3)–C(31) and N(3)–C(32) distances are consistent with the projection of a puckered chain onto the mirror plane. Also, the sizes and shapes of several anisotropic displacement ellipsoids (Fig. 1(a)) appear to be unrealistic for thermal motion. Another result supporting the disordered *Pnma* model arises from a refinement of the structure in the

Table 2 Bond lengths (Å) and angles (°) for [Co(ditame)Cl][ZnCl₄]^a

Co–N(1)	1.956(10)	C(41)–C(31)	1.488(16)
Co–N(2)	1.968(10)	C(41)–C(51)	1.522(17)
Co–N(3)	1.936(11)	C(32)–C(42)	1.512(16)
Co–Cl	2.305(4)	C(42)–C(12)	1.512(17)
N(1)–C(11)	1.457(13)	C(42)–C(52)	1.514(17)
N(2)–C(12)	1.475(12)	Zn–Cl(1)	2.267(3)
N(3)–C(31)	1.396(14)	Zn–Cl(2)	2.372(4)
N(3)–C(32)	1.395(15)	Zn–Cl(3)	2.209(4)
C(41)–C(11)	1.481(17)		
N(1)–Co–N(3)	89.8(3)	Co–N(3)–C(31)	117.1(8)
N(2)–Co–N(3)	90.4(3)	Co–N(3)–C(32)	119.0(7)
Cl–Co–N(3)	179.7(6)	C(32)–N(3)–C(31)	123.9(10)
N(1)–Co–N(1')	88.2(6)	N(3)–C(31)–C(41)	119.9(10)
N(2)–Co–N(1)	179.8(3)	N(3)–C(32)–C(42)	118.4(10)
N(2)–Co–N(1')	92.0(4)	N(1)–C(11)–C(41)	114.5(11)
Cl–Co–N(1)	90.0(2)	N(2)–C(12)–C(42)	114.5(12)
N(2)–Co–N(2')	87.9(6)	C(11)–C(41)–C(11')	109.7(19)
Cl–Co–N(2)	89.8(2)	C(31)–C(41)–C(11)	109.9(9)
Cl(1)–Zn–Cl(1')	106.6(2)	C(51)–C(41)–C(11)	109.3(7)
Cl(1)–Zn–Cl(2)	107.6(1)	C(51)–C(41)–C(31)	108.7(10)
Cl(1)–Zn–Cl(3)	114.0(1)	C(32)–C(42)–C(12)	108.8(8)
Cl(2)–Zn–Cl(3)	106.6(2)	C(32)–C(42)–C(52)	110.5(10)
Co–N(2)–C(12)	118.9(9)	C(12)–C(42)–C(12')	111.6(15)
Co–N(1)–C(11)	119.3(10)	C(52)–C(42)–C(12)	108.6(7)

^a Primes indicate atoms generated by the symmetry operation ($x, 0.5 - y, z$).

Table 3 Bond lengths (Å) and angles (°) for [Co(ditame)(NH₃)Cl][ZnCl₄]

Co–N(3)	1.945(3)	C(11)–C(41)	1.528(4)
Co–N(12)	1.964(3)	C(12)–C(42)	1.528(4)
Co–N(21)	1.972(3)	C(21)–C(41)	1.527(4)
Co–N(22)	1.980(3)	C(22)–C(42)	1.532(4)
Co–N(11)	1.981(3)	C(31)–C(41)	1.536(4)
Co–N	1.982(3)	C(32)–C(42)	1.539(4)
N(3)–C(31)	1.488(4)	C(41)–C(51)	1.539(5)
N(3)–C(32)	1.495(4)	C(42)–C(52)	1.536(4)
N(11)–C(11)	1.486(4)	Zn–Cl(3)	2.240(1)
N(12)–C(12)	1.484(4)	Zn–Cl(2)	2.250(1)
N(21)–C(21)	1.498(4)	Zn–Cl(4)	2.274(1)
N(22)–C(22)	1.493(4)	Zn–Cl(1)	2.284(1)
N(12)–Co–N(3)	91.3(1)	N(12)–C(12)–C(42)	111.3(3)
N(21)–Co–N(3)	88.4(1)	N(21)–C(21)–C(41)	112.5(3)
N(22)–Co–N(3)	86.9(1)	C(11)–C(41)–C(21)	110.1(3)
N(11)–Co–N(3)	93.0(1)	C(11)–C(41)–C(31)	109.3(3)
N–Co–N(3)	174.4(1)	C(11)–C(41)–C(51)	109.7(3)
N(12)–Co–N(21)	175.9(1)	C(21)–C(41)–C(31)	111.8(2)
N(12)–Co–N(22)	89.0(1)	C(21)–C(41)–C(51)	107.9(3)
N(11)–Co–N(12)	89.6(1)	C(31)–C(41)–C(51)	108.0(3)
N–Co–N(12)	91.2(1)	N(22)–C(22)–C(42)	112.1(2)
N(21)–Co–N(22)	95.1(1)	C(12)–C(42)–C(22)	110.0(3)
N(11)–Co–N(21)	86.4(1)	C(12)–C(42)–C(52)	109.2(3)
N–Co–N(21)	89.4(1)	C(12)–C(42)–C(32)	109.5(3)
N(11)–Co–N(22)	178.6(2)	C(22)–C(42)–C(52)	109.1(3)
N–Co–N(22)	88.1(1)	C(22)–C(42)–C(32)	110.0(3)
N–Co–N(11)	92.0(1)	C(32)–C(42)–C(52)	108.9(3)
C(31)–N(3)–C(32)	110.9(2)	N(3)–C(31)–C(41)	110.9(2)
Co–N(11)–C(11)	118.9(2)	N(3)–C(32)–C(42)	111.7(2)
Co–N(12)–C(12)	118.5(2)	Cl(2)–Zn–Cl(3)	111.35(4)
Co–N(21)–C(21)	116.9(2)	Cl(3)–Zn–Cl(4)	108.33(4)
Co–N(22)–C(22)	117.5(2)	Cl(1)–Zn–Cl(3)	111.25(4)
Co–N(3)–C(31)	117.1(2)	Cl(2)–Zn–Cl(4)	114.12(4)
Co–N(3)–C(32)	115.9(2)	Cl(1)–Zn–Cl(2)	108.84(4)
N(11)–C(11)–C(41)	112.3(2)	Cl(1)–Zn–Cl(4)	102.67(4)

alternative non-centrosymmetric space group $Pn2_1a$. The best fit puckered chain model converged with $R = 0.166$ for an isotropic atom refinement, but attempts to advance the process in this space group using anisotropic thermal parameters always resulted in the atoms close to the mirror plane sites of $Pnma$ moving toward those positions.

A double atom model was used to represent the disorder in

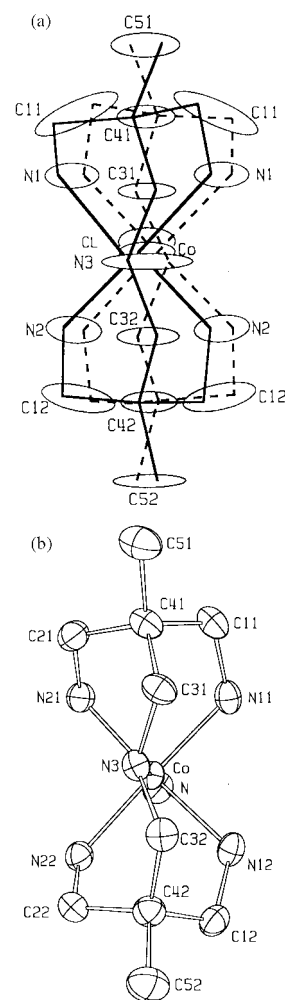


Fig. 2 (a) The [Co(ditame)Cl]²⁺ cation viewed along the N(3)–Co direction for the [Co(ditame)Cl][ZnCl₄] structure refined in space group $Pnma$. (b) Similar view of [Co(ditame)(NH₃)]³⁺ in the [Co(ditame)(NH₃)Cl][ZnCl₄] structure.

the space group $Pnma$ and the idea is illustrated in Fig. 2(a), which portrays a view of the [Co(ditame)Cl]²⁺ cation along the N(3)–Co direction. Each atom, described in the figure by its refined anisotropic displacement ellipsoid, was replaced by two half-weight isotropic atoms which were separated with a distance calculated according to Kartha and Ahmed.¹¹ The full line and broken line representations in Fig. 2(a) depict two puckered configurations obtained by linking atoms in the double atom model. The conformations are stereochemically reasonable according to Dreiding models of the complex cation and are in fact mirror images related by the mirror planes of $Pnma$. Refinement of the double isotropic atom model converged with $R = 0.12$, a considerable improvement over any previous isotropic refinement in $Pnma$.

Structure of [Co(ditame)(NH₃)Cl][ZnCl₄]. This well determined structure (R 0.036, R_w 0.045) is pictured in Figs. 1(b) and 2(b), and establishes the NMR spectra–structure relationship for the cobalt(III) complex ion in solution that was discussed earlier. A virtual mirror plane relates the two cap conformations in the cation and the structure should average rigorous mirror symmetry in solution, consistent with the NMR data. The cobalt to nitrogen distances (Table 3) are close to typical for Co^{III}–N bonds, with the average Co–N(H₂) distance being 1.974 (range ± 0.010) Å. The Co–N(H) bond length of 1.945(3) Å is somewhat shorter than normal, whereas Co–N(H₃) (1.982(3) Å) is slightly longer than the Co–N bonds in [Co(NH₃)₆]³⁺ (1.965(1) Å).¹² Bond angles for the structure are given in Table 3 and have rather characteristic values for this

kind of cobalt(III) polyamine complex. The N–Co–N angles are close to the corresponding octahedral values whereas Co–N–C angles are 7–9° larger than the tetrahedral ones. One interesting aspect is the rigorous planarity of the chromophoric fragment Co, N(11), N(12), N(21), N(22), which forms the base of an essentially square pyramidal donor atom subfield imposed by the tetrapodal ditame ligand. The maximum deviation from the least-squares plane defined by these atoms is only $\pm 0.003(3)$ Å, and it seems likely that the bonding topology of the ligand buffers the steric interaction between the cap moieties to constrain the planar arrangement. A similar small deviation of $\pm 0.002(10)$ Å occurs in the $[\text{Co}(\text{ditame})\text{Cl}][\text{ZnCl}_4]$ structure despite the different ligand substituents. Although this result is less convincing because of the structure disorder and lower precision, it qualitatively supports the argument for an enforced square pyramidal donor atom configuration in co-ordinated ditame, and implies that this geometry is resistant to quite substantial changes in the nature of the substituent at the sixth site.

Topological implications. The potential influence of the structure and configuration of the co-ordinated pentaamine on the reactivity of its associated five- and six-co-ordinate metal complexes bears some discussion.

Dissociative substitution reactions at the sixth site in pseudo-octahedral species containing the ditame ligand are not expected to involve rearrangement to trigonal bipyramidal intermediates. The preferred geometry of the co-ordinated ligand framework should strongly resist the large expansion in two bite angles required for such a transformation. Also, subsequent addition of nucleophiles to the pseudo square pyramidal intermediates is expected to be extremely rapid, and probably faster than ion atmosphere equilibration rates, and this should influence the nucleophile competition experiments.^{13,14}

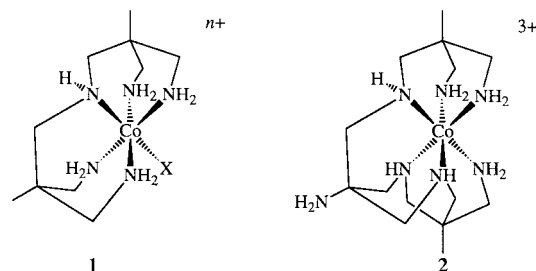
Both the structures of $[\text{Co}(\text{ditame})\text{Cl}][\text{ZnCl}_4]$ and $[\text{Co}(\text{ditame})(\text{NH}_3)\text{Cl}][\text{ZnCl}_4]$, as well as Dreiding stereomodels of the complex cations, indicate that contraction of any of the ditame bite angles would lead to large increases in angular strain energy and interatomic steric repulsion energy. This could hamper spontaneous substitution reactions in any six-co-ordinate metal complexes of ditame where the rate determining process might be associative,¹⁵ such as $[\text{M}^{\text{III}}(\text{ditame})\text{L}]^{3+}$ ($\text{M} = \text{Cr}$ or Ru , $\text{L} =$ neutral ligand) complexes, and may even promote dissociative chemistry in such cases.

The nature of the cobalt(III)–ditame configuration also has implications for the stability of the metal–ditame moiety in other more labile five- and six-co-ordinate metal complexes. It is expected that dissociation of any one of the primary nitrogen atoms would move the methyl group towards an axial position in the remaining chelate ring of the partly dissociated cap. The increase in steric energy should resist this dissociation and promote a rapid re-coordination of the unbound amine group. Sequential dissociation of the ditame ligand is therefore likely to be slow, and the metal–ditame fragment itself should be relatively stable in complexes with the more labile metal ions.⁷

NMR studies

Proton exchange. ¹³C NMR spectroscopy was used to monitor amine proton exchange reactions for the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion **1** ($\text{X} = \text{Cl}^-$) in D_2O (pD 5) at 20 °C. Multiple peaks and upfield chemical shifts were observed for the carbon atoms bound to primary and secondary amine groups, as deuteration proceeded at the amine centres. The assignments for the methyl and quaternary carbon atom signals were therefore readily confirmed by their shift invariance to N-deuteration. Signals for the individual isotopomers CNH_2 , CNHD and CND_2 were clearly resolved in the 75 MHz ¹³C NMR spectra, each D sub-

stitution resulting in an upfield shift of about 0.1 ppm. Accordingly, after *ca.* 24 h the resonances for the two non-equivalent CNH_2 carbon atoms first appeared as doublets followed by triplets, corresponding to exchange of the first and then the second protons at comparable rates. Ultimately, each carbon atom bound to a fully deuterated primary amine gave rise to a singlet *ca.* 0.2 ppm upfield from the corresponding signal for the undeuterated species. Some aquation accompanied the proton exchange in the parent chloro complex but the two processes are independent.



More significantly, the assignment of the signal associated with the carbon atoms bound to the secondary amine group was confirmed by the appearance of just one upfield (0.1 ppm) signal even up to complete N-deuteration. This was observed in <1 min at pD 5, 20 °C and the exchange process was complete in <1 h ($k_{\text{ex}} 7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Clearly H^+ exchange at this site, *trans* to co-ordinated Cl^- , is faster (estimated as *ca.* 10^3 fold) than that at any of the primary amine sites. Also the base-catalysed exchange at the secondary amine site is much faster than base hydrolysis. Indeed, at higher pH where background aquation became relatively insignificant, all the amine sites were deuterated before appreciable base hydrolysis occurred.

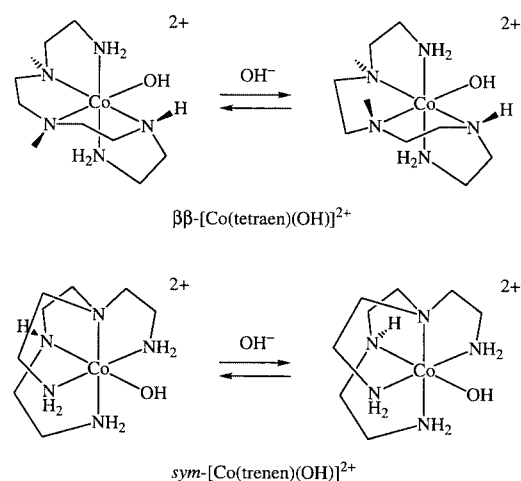
Base hydrolysis stereochemistry and chloride anation. A solution of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ **1** ($\text{X} = \text{Cl}^-$) in 0.1 mol dm^{-3} NaOD (D_2O) rapidly yielded the $[\text{Co}(\text{ditame})(\text{OD})]^{2+}$ **1** ($\text{X} = \text{OD}^-$) species which showed ¹³C NMR singlet signals at δ 56.3 ($\text{CH}_2\text{-N}_{\text{sec}}$), 40.0 (C_{quat}) and 21.4 (CH_3), and indicated that a single product was formed. The ¹³C signals for the two non-equivalent carbon atoms bound to the primary amine groups appeared as a broad unresolved doublet in the range δ 45.7 to 46.7, but on reacidification (DCl , 2 mol dm^{-3} in D^+) the resulting $[\text{Co}(\text{ditame})(\text{OD})]^{3+}$ **1** ($\text{X} = \text{D}_2\text{O}$) ion gave rise to a clean five-signal ¹³C NMR spectrum. It also became apparent that more than 80% of the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ reactant was regenerated after standing overnight at *ca.* 20 °C, at which point the anation was completed by warming the sample. These results confirm that each $[\text{Co}(\text{ditame})\text{X}]^{n+}$ species has the same pentadentate structure on the 75 MHz ¹³C NMR timescale, and that no observable dissociation of any of the N atoms occurs during the substitution reactions.

The formation of *ca.* 80% $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ over *ca.* 12 h from $[\text{Co}(\text{ditame})(\text{OD})]^{3+}$ in *ca.* 2 mol dm^{-3} Cl^- indicates that Cl^- anation for the $[\text{Co}(\text{ditame})(\text{OH})]^{3+}$ species is more than 10^2 fold faster than that for the pentaammine complex $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{3+}$ under comparable conditions. The reverse reaction, namely aquation of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ($k_{\text{aq}} 7.2 \times 10^{-5} \text{ s}^{-1}$),¹⁶ is also faster (400 fold) than that of its $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ analogue ($k_{\text{aq}} 1.8 \times 10^{-7} \text{ s}^{-1}$).¹⁶

Nitrogen inversion. The broad, almost coalesced signals observed for the two non-equivalent CND_2 carbon atoms of $[\text{Co}(\text{ditame})(\text{OD})]^{2+}$ are attributed to a fluxional interconversion process. Each CND_2 carbon atom undergoes a configurational exchange between the same pair of non-equivalent sites as inversion at the secondary amine nitrogen proceeds. Since a deprotonation must precede the inversion in this case, it follows

that the exchange broadening should not be observed when proton or deuterium exchange at the secondary amine centre is relatively slow on the ^{13}C NMR time frame. These conditions apparently prevail at $\text{pD} < 7$ in D_2O at 25°C for the $[\text{Co}(\text{ditame})\text{X}]^{n+}$ **1** complexes studied here, as the CNH_2 carbon atom signals all appeared as well resolved sharp doublets. For example, the observed half-life for the sec-NH proton exchange in $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ at $\text{pD} 5$ (D_2O , 20°C) is $>10^3$ s, which is much too long to cause line broadening of CNH_2 carbon signals by inversion at the secondary nitrogen atom. In 0.1 mol dm^{-3} NaOD (D_2O , 20°C) however, $t_{1/2}$ for the analogous deuterium exchange in $[\text{Co}(\text{ditame})(\text{OD})]^{2+}$ is expected to be of the order of 10^{-5} to 10^{-6} s, which would be short on the ^{13}C time-scale. The presence of a very broad band for the CND_2 carbon atoms and its persistence over a range of $[\text{OD}^-]$ (0.1 – 1.0 mol dm^{-3}) imply that under these conditions the inversion and attendant conformational change limit the exchange rate between the non-equivalent sites, rather than the sec-ND deuterium exchange. Increasing the temperature of the $[\text{Co}(\text{ditame})(\text{OD})]^{2+}$ **1** ($\text{X} = \text{OD}^-$) solution in 1.0 mol dm^{-3} NaOD by 35°C served to collapse the broad band CND_2 carbon resonance to a sharp singlet, and a quantitative temperature dependent NMR study of the inversion and conformational dynamics may be feasible in this region. A closely analogous fluxional phenomenon has been observed in a ^{13}C NMR study⁵ of the tricapped complex $[\text{Co}(\text{NH}_2\text{tritame})]^{3+}$ **2** ($\text{NH}_2\text{tritame} = 3\text{-amino-7-aminomethyl-3-(4,4-bis(aminomethyl)-2-azapentyl)-7-methyl-1,5-diazacyclooctane}$) in which the hexadentate ligand $\text{NH}_2\text{tritame}$ has essentially three tame fragments fused together as shown. Although this ligand was synthesized by unrelated template methods,^{5,17} the cobalt(III) complex **2** contains a ditame fragment which is analogous to that of the $[\text{Co}(\text{ditame})\text{X}]^{n+}$ species **1**. The two non-equivalent carbon atoms bound to the primary amine groups in the upper cap displayed ^{13}C NMR properties which were virtually identical to those observed for $[\text{Co}(\text{ditame})(\text{OD})]^{2+}$ in D_2O . At 25°C however, the exchange broadening was observed at a lower $[\text{OD}^-]$ ($\text{pD} 6$) for the $[\text{Co}(\text{NH}_2\text{tritame})]^{3+}$ complex because of faster proton exchange at the analogous secondary nitrogen atom. Under these conditions the broad coalesced signal for the two CND_2 carbon atoms finally collapsed to a sharp singlet when the temperature was raised by *ca.* 20°C .⁵ The Arrhenius activation energies for the secondary amine inversion and associated configurational changes involved in these fluxional processes are likely to be 60 – 70 kJ mol^{-1} , by comparison with values obtained from temperature dependent NMR studies of other stereochemical interconversions occurring at similar rates.

Previous studies have reported two other hydroxopentaamine cobalt(III) complexes in which sec-NH proton exchange and nitrogen inversion formally cause pairs of carbon atoms to exchange between two non-equivalent sites. These are the $\beta\beta$ - $[\text{Co}(\text{tetraen})(\text{OH})]^{2+}$ (tetraen = 3,6,9-triazaundecane-1,11-diamine)¹⁸ and *sym*- $[\text{Co}(\text{trenen})(\text{OH})]^{2+}$ (trenen = 3-(2-aminoethyl)-3,6-diazaoctane-1,8-diamine)^{18,19} ions depicted in Scheme 1. The $\beta\beta$ - $[\text{Co}(\text{tetraen})(\text{OH})]^{2+}$ isomer shows an eight line ^{13}C NMR spectrum in D_2O at 20°C , which collapses to four lines in high $[\text{OD}^-]$ ($>0.1 \text{ mol dm}^{-3}$). This indicates that nitrogen inversion is fast on the ^{13}C NMR timescale at 20°C when the central sec-NH proton exchange rate is sufficiently fast. It follows that the activation energy for the inversion and conformational change is somewhat lower than that for the $[\text{Co}(\text{ditame})(\text{OH})]^{2+}$ ion if chemical shift differences are ignored. The fluxional interconversion phenomenon also serves uniquely to identify the topology of the $\beta\beta$ diastereoisomer of $[\text{Co}(\text{tetraen})(\text{OH})]^{2+}$ which has eight possible diastereoisomeric forms. In contrast, the *sym*- $[\text{Co}(\text{trenen})(\text{OH})]^{2+}$ species does not exhibit rapid inversion on the ^{13}C NMR timescale in strong base at 20°C and shows eight distinct carbon resonances under these conditions, even though the secondary N-H proton undergoes rapid exchange.¹⁹ However, in this case inversion at



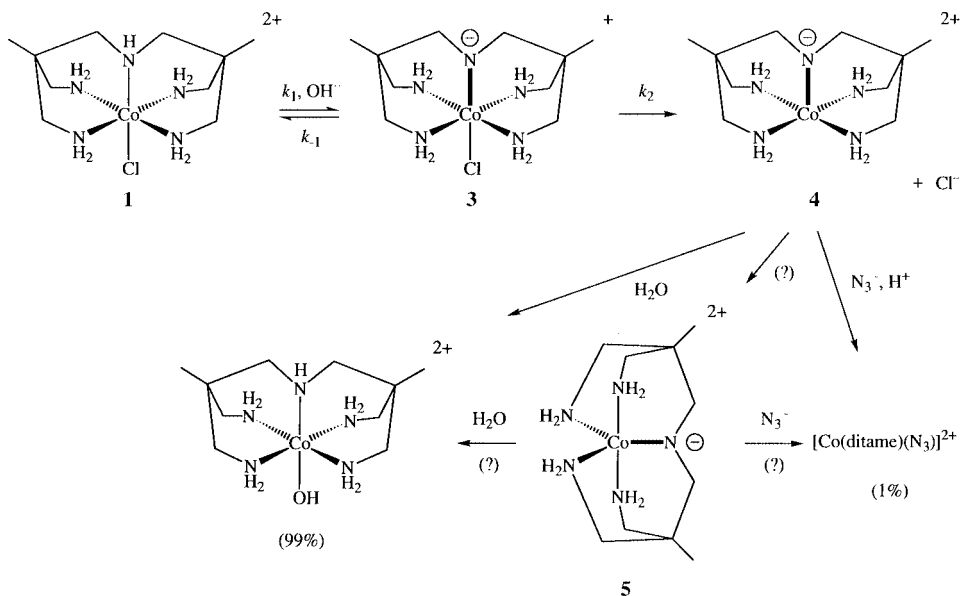
Scheme 1

the secondary nitrogen atom leads to racemization of an enantiomer of the resolved complex, and the inversion kinetics for $[\text{Co}(\text{trenen})\text{X}]^{n+}$ ($\text{X} = \text{N}_3^-, \text{Cl}^-, \text{H}_2\text{O}$ or OH^-) complexes were determined by using a spectropolarimeter to follow the racemization.¹⁹ These results imply that the activation energy of the NH inversion and conformational change for $[\text{Co}(\text{trenen})(\text{OH})]^{2+}$ is considerably higher than that for $[\text{Co}(\text{ditame})(\text{OH})]^{2+}$ and probably well over 100 kJ mol^{-1} .

Reactivity

One result from the base hydrolysis study of the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion is exceptional for acidopentaamine cobalt(III) complex systems. This is the limited extent of N_3^- competition, shown by the very small amount of $[\text{Co}(\text{ditame})(\text{N}_3)]^{2+}$ ion formed (*ca.* 1%) during base hydrolysis in aqueous 1 mol dm^{-3} NaN_3 . Another significant point is that only one pentadentate configuration is feasible and that was observed rigorously. Also, there was no dissociation of an arm of the ditame ligand. However, this is characteristic of much of cobalt(III) amine chemistry under these conditions, and is therefore not so surprising.

The amine proton exchange rates ($k_{\text{ex}} 7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for NH , $<10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for NH_2 at 20°C) and the base hydrolysis rate ($k_{\text{OH}} 68 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $I = 1.0 \text{ mol dm}^{-3}$) of complex **1** ($\text{X} = \text{Cl}^-$) are relatively standard for chloropentaamine cobalt(III) type complexes, with values for k_{ex} being near the lower end and that for k_{OH} near the middle of the observed ranges at $I \text{ ca. } 1 \text{ mol dm}^{-3}$, 25°C . For example, the related NH_3 protons *trans* and *cis* to the chloro substituent in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ exchange at similar rates ($k_{\text{trans}} 3 \times 10^6$, $k_{\text{cis}} 5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $I = 0.1$),²⁰ whereas the NH group *trans* to Cl^- in the *sym*- $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$ ion¹⁹ has $k_{\text{ex}} 5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 34°C , $I = 1.2 \text{ mol dm}^{-3}$, more than 10^4 fold faster than that for deuteration at any of the *cis* primary amine sites. Closer comparisons between the proton exchange rate constants require statistical corrections but these would not alter the qualitative discussion here. Base hydrolysis rates for cobalt(III) chloropentaamines at 25°C , $I \text{ ca. } 1.0 \text{ mol dm}^{-3}$ range from $k_{\text{OH}} 2.1 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for *t*- $[\text{Co}(\text{tren})(\text{NH}_3)_5\text{Cl}]^{2+}$ (tren = 2,2',2''-nitrilotris(ethan-1-amine))²¹ to 2.2×10^5 – $2.3 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for β_2 - (RR,SS) - $[\text{Co}(\text{trien})(\text{glyOEt})\text{Cl}]^{2+}$ (trien = 3,6-diazaoctane-1,8-diamine, glyOEt = ethyl glycinate)^{22a} and β_2 - (RS,SR) - $[\text{Co}(\text{trien})(\text{NH}_3)_5\text{Cl}]^{2+}$ (β_2 is a diastereoisomeric form of the unsymmetrically co-ordinated trien complexes in which Cl^- is located *trans* to the NH_2 group).^{22b} The value of k_{OH} (*ca.* $2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $I = 1.0 \text{ mol dm}^{-3}$) found for one isomer of $[\text{Co}(\text{dien})(\text{tn})\text{Cl}]^{2+}$ (dien = 2,2'-iminobis(ethan-1-amine) tn = 1,3-propanediamine) also lies at the upper end of the range.²³



Scheme 2

Base hydrolysis. Mechanism and rate law. The nature and reactivity of key intermediates in the base hydrolysis of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ are intimately tied to the configurational retention and low competition values for N_3^- . There are implications for this system and others in which square pyramidal donor atom configurations are enforced by the ligand steric requirements. There is therefore a need to rationalize the rate data using the commonly accepted $\text{S}_{\text{N}}1\text{CB}$ or D_{CB} mechanism^{24–26} and incorporating relevant structural features of the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ complex. The leading steps in the proposed mechanism for the base hydrolysis reaction are depicted in Scheme 2. A pre-equilibrium is rapidly established between the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion **1** ($\text{X} = \text{Cl}^-$) and its conjugate base **3**, followed by the dissociation of Cl^- and a fast product forming step in which nucleophiles are scavenged by the five-co-ordinate intermediate **4** (or **5**) from its solution atmosphere.

A substantial body of evidence supporting the integral components of the D_{CB} mechanism has been accumulated from base hydrolysis studies on a broad spectrum of cobalt(III) pentaamine complexes, especially for $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ (X^{n-3} varies widely with $n = 0$ to 3) systems.^{14,24–28} Overall, the data are well accommodated by the D_{CB} mechanism, even when the deprotonation is rate determining.²⁹ In particular, cogent evidence for the dissociation of the leaving group and the existence of a short-lived five-co-ordinate intermediate has consistently arisen from studies of nucleophilic competition for the intermediate^{14,27,28,30–32} and stereochemical studies^{32,33} of base hydrolysis and competition products. Large rate enhancements caused by a systematic increase in steric energy relative to that of a $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ parent complex also imply a dissociative mechanism.³⁴ For $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ ions of the same charge the competition ratios ($[\text{Co}(\text{NH}_3)_5\text{Y}^{m+}]/[\text{Co}(\text{NH}_3)_5(\text{OH})^{2+}][\text{Y}^{m-3}]$) and product stereochemistries for a given nucleophile Y^{m-3} ($m = 0$ to 3) were found to be virtually invariant to the leaving group X^{n-3} , and this was also the case for $[\text{Co}(\text{en})_2(\text{NH}_3)\text{X}]^{2+}$ complexes³² ($\text{en} = 1,2$ -ethanediamine). The dependence of competition ratios on the formal ionic charge of the reactants^{13,14,28} and the correlation of the ratios with the degree of hydration for different nucleophiles²⁸ (rather than ion association effects and nucleophilic capacity) have also been convincingly demonstrated. At least for the relatively uncongested $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ ions, these results implied that the lifetime of the apparent five-co-ordinate species was similar to the relaxation time of its precursor's solution atmosphere, whose com-

position is influenced by the overall complex charge. In more sterically crowded systems such as $[\text{Co}(\text{en})_2(\text{NH}_3)\text{X}]^{2+}$ and $[\text{Co}(\text{CH}_3\text{NH}_2)_5\text{Cl}]^{2+}$, competition ratios were enhanced for selected competitors,^{32,34} (e.g. N_3^-) indicating greater stabilization and substantially longer lifetimes for the five-ordinate intermediates. Some insight into the structure of the intermediates was obtained by analysis of the product stereochemistries,^{21–23,32,33} and donor atom rearrangement was normally observed in rigorous studies of this kind. Partial or complete rearrangement to trigonal bipyramidal five-co-ordinate forms²⁴ was used to rationalize these observations, although other intermediate structures have been considered.^{32,33} With the aforementioned evidence in mind, it is possible to rationalize the rate data and the unusually low N_3^- competition ratio for the base hydrolysis of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$.

The proposed D_{CB} mechanism in Scheme 2 leads to the familiar²⁴ rate law $-\text{d}[\text{Co}(\text{ditame})\text{Cl}]^{2+}/\text{d}t = k_2k_1/k_{-1}[\text{Co}(\text{ditame})\text{Cl}]^{2+}[\text{OH}^-]$, provided the first step is a pre-equilibrium and k_2 is rate determining, which is commonly the case. These conditions require proton exchange to be much faster than base hydrolysis as $k_{\text{OH}} = k_2k_1/k_{-1} \ll k_1$. For the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion both the secondary amine (*trans* to Cl^-) and the primary amine (*cis* to Cl^-) groups exchange protons much faster than Cl^- is lost, being *ca.* 10^5 fold and 10^2 fold greater than k_{OH} respectively. Also, the base hydrolysis rate data followed a rate law of the form $-\text{d}[\text{Co}(\text{ditame})\text{Cl}]^{2+}/\text{d}t = k_{\text{OH}}[\text{Co}(\text{ditame})\text{Cl}]^{2+}[\text{OH}^-]$ over the pH range 9 to 11. Factors influencing the observed k_{OH} value may then be inferred, from the derived rate constant k_2k_1/k_{-1} , to be largely those which affect the deprotonation equilibrium ($k_1/k_{-1} = K_a/K_w$) or the rate constant (k_2) for the dissociative step leading to the square pyramidal intermediate **4**. The following comparison of rate data and certain structural features of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ with data for the simpler pentaamine complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ helps to identify possible reasons for the difference in their base hydrolysis rate constants (k_{OH} 68 vs. 0.25³⁵ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 25 °C, $I = 1.0 \text{ mol dm}^{-3}$).

Factors affecting k_1/k_{-1} . Since the $\text{p}K_a$ values for the amine sites in $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ are >15 , reprotonation is close to diffusion controlled and the differences in proton exchange rates therefore reflect the differences in acidity of the sites. It follows that for these two complexes the amine sites *trans* to Cl^- have roughly the same acidity, and that is also the case for the *cis* amine sites. Recently, a chloro complex containing a pentadentate ligand similar to ditame has

been examined for its base hydrolysis reactivity.³⁶ In this instance a pyridine residue substitutes for the CH₂NHCH₂ fragment linking the same moieties, and the base hydrolysis rate constant under similar conditions to those used here is 0.057 dm³ mol⁻¹ s⁻¹ at 25 °C. This is 10³ fold slower than that for [Co(ditame)Cl]²⁺ and indicates to a degree that deprotonation *trans* to bound Cl⁻ gives the effective intermediate for the latter molecule. If the effective conjugate base in the base hydrolysis of [Co(NH₃)₅Cl]²⁺ is also *trans* deprotonated as implied by some previous results,^{21,32,33} then k_1/k_{-1} should be similar for both the [Co(ditame)Cl]²⁺ and [Co(NH₃)₅Cl]²⁺ systems.

Factors affecting k_2 . For reasons discussed previously,³⁴ reactivity differences arising from alkyl substituent inductive effects and ground to transition state activity coefficient ratios in the conjugate base complexes **3** and *trans*-[Co(NH₃)₄(NH₂)Cl]⁺ are not likely to account for a 10²–10³ fold difference in base hydrolysis rates.

X-Ray crystallographic studies on the [Co(ditame)Cl]²⁺ and [Co(NH₃)₅Cl]²⁺ ions³⁷ show no marked differences in co-ordination geometry between their CoN₅Cl chromophores, and at first sight imply similar and relatively marginal steric influences on the chromophore structures. It might then be expected that as the Co–Cl bond stretches the bulk of any decrease in steric repulsion energy would be similar for the two 2+ cations in the absence of CoN₅ rearrangement. Also, in the discussion of the [Co(ditame)Cl]²⁺ and [Co(ditame)(NH₃)₃]³⁺ structures, it was argued that the square pyramidal CoN₅ geometry in the cobalt–ditame moiety is stabilized by means of a counterbalance between the intraligand steric repulsion forces and the preferred bond length and angle restoring forces. This would largely eliminate decreases in steric energy within the bound ditame ligand as Cl⁻ is released, and would restrict progression of the CoN₅ fragment towards a trigonal bipyramid. Similar arguments apply to the dissociation of Cl⁻ from the [Co(ditame – H)Cl]⁺ conjugate base complex **3**.

An important factor affecting k_2 is the fine structure of the CoN₅Cl chromophore within the conjugate base **3** or the *trans*-[Co(NH₃)₄(NH₂)Cl]⁺ ion, and in particular the labilizing effect of the amido group on the Co–Cl bond. Owing to the high p*K*_a values (usually >15) of chloropentamine cobalt(III) complexes, and their reactivity, structures have not yet been obtained for the deprotonated species and no detailed structural information is therefore available. Ultimately, such data should reveal one of the more substantial contributions to the enhanced rates for base hydrolysis compared with those for spontaneous aquation reactions of these complexes. In the meantime, however, indirect information provides some insight into the nature of the conjugate bases, and how this might explain the difference in base hydrolysis rates for the [Co(ditame)Cl]²⁺ and [Co(NH₃)₅Cl]²⁺ ions.

It is well known, both experimentally and theoretically, that relatively strong σ bonding ligand donors have a high *trans* influence in octahedral and square planar complexes.³⁸ This affects the observable ground state electronic properties and reactivity of the more weakly σ bonded *trans*-located ligand donors, and is often clearly revealed by X-ray, infrared and NMR techniques and by the lability of the *trans* donor groups. Although the electronic origin of the *trans* influence is well founded (from molecular orbital calculations) on electron exchange interactions between metal and donor atoms, steric effects are invariably present and may contribute significantly. It has also been shown that very effective σ donors weaken *cis* M–L bonds but to a much smaller degree,³⁸ and the effect may not be obvious from ground state data such as metal–ligand bond distances. These phenomena can be expected to contribute to the reactivity of the conjugate base **3** compared with [Co(NH₃)₄(NH₂)Cl]⁺, because the amido group should be a strong σ donor for cobalt(III) whereas Cl⁻ is relatively weak. The crystal structure of the deprotonated hexaminecobalt(III)

complex [Co((NO₂)₂-sar – H)]²⁺ (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane; 1,8 substituted) provides compelling evidence for the high σ donor strength of the nearly tetrahedral NR₂⁻ group as well as its high *trans* and low *cis* influences on NHR₂ σ donors.³⁹ The *trans*-Co–NHR₂ distance of 2.016(7) Å and the Co–NR₂⁻ distance of 1.946(7) Å are significantly longer and shorter than the *cis*-Co–NHR₂ bond lengths which vary from 1.967(7) to 1.980(7) Å, none being significantly different from the mean of 1.974 Å. Moreover, the *cis*-Co–NHR₂ values are the same as the Co–N distances found in structures of [Co((NO₂)₂-sar)]³⁺ and several functionalized analogues,⁴⁰ and the *cis* influence of σ -bonded NR₂⁻ is not apparent from the observed X-ray data. Since the p*K*_a for a metal bound NHR₂ group in cobalt(III) chloropentamines is usually more than 5 units greater than that of 9.9 found for [Co((NO₂)₂-sar)]³⁺ at *I* = 1.0 mol dm⁻³,²⁹ the NR₂⁻ and NH₂⁻ groups in the conjugate bases **3** and *trans*-[Co(NH₃)₄(NH₂)Cl]⁺ should be even better σ donors and the *trans* influences magnified. Also, Cl⁻ is a weaker σ ligand for Co^{III} than NHR₂. A large increase in the Co–Cl bond distance of the conjugate base would reduce the dissociative activation energy (δr 0.2 Å equates to *ca.* 20 kJ mol⁻¹)[‡] and lead to a substantial labilizing effect on the Co–Cl bond.

There is some experimental evidence for the relative importance of the *trans*- and *cis*-Co–Cl labilizing effects by NHR⁻ and NH₂⁻ groups in cobalt(III) chloropentamines. An appropriate example is the 2 × 10⁴ fold increase in base hydrolysis rate on going from the **t** to the **p** isomer of [Co(tren)(NH₃)Cl]²⁺ (**t** and **p** define Cl⁻ as *trans* to the tertiary or a primary N atom of the tren ligand).²¹ From the preceding rationale and the observed proton exchange rates,²¹ it is expected that the active conjugate base for the **p** isomer has a NHR⁻ group *trans* to Cl⁻, whereas for the **t** form it *must* be *cis* to Cl⁻. Based on the proton exchange rates the presumed *trans*-NH₂R group of **p** is *ca.* 100 fold more acidic than the *cis* related groups of **t**. This leaves a factor of 10²–10³ favouring the reactivity of the *trans* conjugate base complex over that of the *cis* species. A comparative analysis of minimized potential energy terms for the **p** and **t** structures²¹ failed to reveal any obvious reactivity differences for the conjugate bases that could be attributed to steric effects. Accepting this, it is proposed that the increased dissociation rate largely arises from the higher *trans* NHR⁻ Co–Cl labilizing effect in the deprotonated **p** complex. The *interesting* result is that the π bonding interaction between the *cis*-NH₂⁻ group and the cobalt *p* orbital in the Co–Cl direction of the **t** species does not appear to activate the dissociation nearly as much as the *trans*-NHR⁻ group of the deprotonated **p** species acting through the σ bond system. The data then imply that the factor favouring the *trans*-NHR⁻ activation of Co–Cl over that of *cis*-NH₂⁻ could be between 10² and 10³. Since the *cis*-NH₃ and -NH₂R protons of the **t** isomer exchange at similar rates and the *cis*-NHR⁻ groups are not well oriented for π bonding with the relevant *p* orbital, it is likely that the *cis*-NH₂⁻ form is the reactive deprotonated intermediate, although the conclusions would be much the same if a *cis*-NHR⁻ analogue dominated the reactivity.

Structural influences of ditame on k_2 . Two implicit features of the conjugate base (**3**) structure emerge from the [Co(ditame)-X]ⁿ⁺ (X = Cl or NH₃) structural results, that have the potential to increase the electron exchange stabilization of the Co–NR₂⁻ σ bond, and thus to enhance the *trans* labilizing effect on the Co–Cl bond and the reactivity of **3** compared with that of [Co(NH₃)₄(NH₂)Cl]⁺. One involves the strongly coupled nature of the bound ditame ligand configuration, with its square pyramidal co-ordination geometry and stereospecifically oriented NH₂ groups. The other arises from the short Co–NHR₂ bond

‡ Estimate, based on an observed diagonal-valence force constant for the Co–Cl stretch in cobalt(III) chloropentamines.

lengths observed in the $[\text{Co}(\text{ditame})\text{X}]^{n+}$ ($\text{X} = \text{Cl}$ or NH_3) structures and the longer than usual *trans* Co–Cl and Co–NH₃ distances, and is largely attributed to the steric demands of the ligand in its stabilized *SP* configuration. It is likely that these steric forces would motivate a shortening of the Co–NR₂[–] bond in **3** relative to Co–NH₂[–] in $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$, thereby promoting the Co–NR₂[–] σ bond electron exchange interaction, the *trans* influence and the Co–Cl bond lability. Also, the strong, relatively rigid coupling between the nitrogen donor atoms that is imposed by the co-ordinated ditame ligand can co-operate with the *trans* influence of the Co–NR₂[–] bond to aid chloride ion dissociation from **3**. Thus any movement of the NH₂ groups along the Co→Cl vector must shorten the Co–NR₂[–] bond, and the converse is also true. It follows that in the course of a vibrational period the rigid coupling would cause synchronous increases in the *trans* influence and in the steric impact of the NH₂ groups on the chloride atom. Both of these factors would assist the chloride ion dissociation. This mechanism is not possible in *trans*-deprotonated $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ as there is no rigid coupling between the four in-plane NH₃ groups and NH₂[–]. Although a modest sterically motivated rearrangement in the CoN₅ fragment of $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ may contribute in that case, it is thought at present that the stronger Co–NR₂[–] σ electron exchange and the co-operative mechanism in **3** would be more effective, and could well account for the *ca.* 3×10^2 fold increase in the base hydrolysis rate of the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion over that of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.

Stereochemistry and azide ion competition. Studies on the stereochemistry of base hydrolysis and competition products for cobalt(III) acidopentaamine complexes have often shown some degree of donor atom configurational change,^{24–26} even for systems such as $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ in which the five-co-ordinate intermediates have relatively short lifetimes.^{14,28,33} As noted earlier, rearrangement of the intermediate to a pseudo trigonal bipyramid was argued to account for the product stereochemistries. The retention of CoN₅ configuration in the base hydrolysis and azide ion competition products of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ **1** ($\text{X} = \text{Cl}$) was established by the chromatographic and NMR studies, which revealed just the two product species $[\text{Co}(\text{ditame})(\text{OH})]^{2+}$ and $[\text{Co}(\text{ditame})(\text{N}_3)]^{2+}$, each bearing the fully co-ordinated ditame ligand. This result is certainly consistent with the formation of a square pyramidal five-co-ordinate intermediate (**4**), which rapidly adds nucleophiles exclusively at the vacated chloride ion site *trans* to the secondary nitrogen atom. Since it is not possible to co-ordinate the sec-N atom *trans* to any one of the primary amines, the only feasible rearrangement of donor atoms would require the dissociation of an amine group on nucleophilic addition. This is clearly inconsistent with the results, and it must be concluded that little or no rearrangement of the CoN₅ configuration occurs in the process of forming the base hydrolysis products **1** ($\text{X} = \text{OH}$ or N_3). Although exclusive nucleophilic attack *trans* to the NR₂[–] group of an intermediate like **5** may give the same results, it is felt that the excessive angular strain energy introduced into the ditame framework, an unfavourable σ ligand field stabilization for low spin Co^{III}, and limited prospects for π stabilization all would oppose a configurational change from **4** toward **5**. The $[\text{Rh}^{\text{III}}(\text{pentaamine})\text{X}]^{n+}$ systems have similar characteristics due to the inherently stronger ligand field stabilization energy and weaker steric factors arising from longer Rh–N bonds (see ref. 24, pp. 273, 274). Generally it should be more difficult to rearrange the Rh^{III}N₅ moiety than Co^{III}N₅, and five-co-ordinate intermediates would in any event be relatively less favourable for Rh^{III} and shorter lived.

The poor competition by N₃[–] ion for the square pyramidal intermediate **4** (*ca.* 1% captured in 1 mol dm^{–3} NaN₃) indicates that it is exceptionally short-lived, even compared with $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)]^{2+}$ in the base hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$,

where 8.5% of the intermediate was captured by N₃[–] in 1 mol dm^{–3} NaN₃.³¹ In the $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co}(\text{CH}_3\text{NH}_2)_5\text{Cl}]^{2+}$ complexes, where steric factors help to stabilize and increase the lifetimes of *TBPY* (or rearranged) intermediates during base hydrolysis, the amounts captured by N₃[–] under similar conditions were 25%³² and 53%³⁴ respectively. The implication here is that M(pentaamine)Xⁿ⁺ systems containing ligands which restrict rearrangement of the MN₅ fragment in dissociative substitution reactions should show characteristics that are similar to those of the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ ion: the lifetimes for the M(pentaamine)^{m+} intermediates should be very short and product distributions should favour the nearest nucleophile adjacent to the basal plane. The analogous tetrapodal ligand complex referred to earlier³⁶ may well follow this pattern when the competition experiments are carried out. Also, pentadentate complexes with similar stereochemistry to that of the $[\text{Co}(\text{ditame})\text{X}]^{2+}$ ions should be stable to dissociation of the amine in the course of a substitution reaction, as the forces that oppose rearrangement of the MN₅ fragment will usually help to maintain its stability to dissociation. The lack of observed partially dissociated species have certainly demonstrated this stability in the base hydrolysis reactivity of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$, and in the spontaneous aquation and Cl[–] anation experiments discussed below.

Aquation and anation. Although there is a need to acquire rate and competition data for the spontaneous aquation of sufficiently labile $[\text{Co}(\text{ditame})\text{X}]^{n+}$ complexes (*e.g.* $\text{X} = \text{CF}_3\text{SO}_3^-$ or ClO_4^-), some important inferences already follow from the limited results of this study. The ¹³C NMR studies on the aquation of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and the chloride anation of $[\text{Co}(\text{ditame})(\text{OD}_2)]^{3+}$ clearly attest to the stability of the cobalt–ditame module in the course of $[\text{Co}(\text{ditame})\text{X}]^{n+}$ substitutions. No dissociation of the amine was detected in the aquation and anation experiments under elevated temperature conditions (>50 °C) nor in the presence of strong acid (up to 6 mol dm^{–3} in HCl or CF₃SO₃H).

The NMR experiments on aquation and chloride anation also showed that these processes for the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and $[\text{Co}(\text{ditame})(\text{OH}_2)]^{3+}$ complexes were more than 10² fold faster than those for the simpler $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ analogues, when measured under comparable conditions. These rate increases are consistent with an essentially dissociative mechanism in which an enhanced Co–NR₂H σ bonding interaction, indicated by the $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ and $[\text{Co}(\text{ditame})(\text{NH}_3)]^{3+}$ structural data, would act in conjunction with the strongly coupled ditame co-operative mechanism to facilitate the dissociation. The essential rationale is discussed in some detail in the base hydrolysis section. Also, the rate increases are inconsistent with covalent bond formation by the entering nucleophile prior to loss of the leaving group, because of the strong resistance to contraction of the co-ordinated ditame bite angles.

Implications for substitution and template chemistry. It remains to be seen if the correlations, linking configurational constraints on the MN₅ module with the properties of M(pentaamine)^{m+} intermediates, hold in a pervasive way for dissociative substitutions with other metal ions and ligands. However, the high stability of the cobalt–ditame fragment in $[\text{Co}(\text{ditame})\text{X}]^{n+}$ complexes, complemented by the relatively fast anation and aquation kinetics of the aqua and chloro derivatives, has led to some interesting synthetic applications⁴¹ along with stability and reactivity studies in other metal–ditame systems.⁷ One recent example exploits the virtually quantitative anation chemistry of $[\text{Co}(\text{ditame})(\text{OH}_2)]^{3+}$ under moderate reaction conditions, and employs the $[\text{Co}(\text{ditame})]^{3+}$ moiety as a carboxylate protecting group in chemical and enzyme-catalysed peptide synthesis.⁴² In this context, it should also be possible quantitatively to recover the protecting group. There is

also an implication that intermediates in other $[M(\text{ditame})X]^{n+}$ substitution reactions might be resistant to ditame dissociation. Therefore there are good prospects for relatively simple substitution and synthetic chemistry that involves more labile metal ions and photoactive MN_5X centres.

Other prospects follow from the use of the $[\text{Co}(\text{ditame})X]^{n+}$ ion (where X is a replaceable non-reactive substituent) as a template for molecular assembly. A sizeable diversity of new structural units and derivatives are accessible *via* efficient condensations of the Co^{III} bound NH_2 groups with formaldehyde to form methylideneimine reagents,⁴³ and with mixed aldehydes^{43,44} or formaldehyde-alkyl aryl ketone mixtures⁴⁵ to give two substituted imino (or saturated) tricarbon straps linking pairs of NH_2 groups. Such intermediates could then be used, for example, to introduce groups which would block co-ordination at the sixth site, or to form stable five-co-ordinate square pyramidal cage systems with a variety of functional group attachments, including photoactive centres. These advances should lead to new redox chemistry and photochemistry for a number of metal ions, and further developments in the chromophore electron chemistry of five-co-ordinate metal complexes. The many ways of attaching various functional groups to these types of amine and imine cage molecules⁴³⁻⁴⁷ also enhance the possibilities for using stable MN_5 chromophores with unusual properties in biological and photobiological applications, some of which have been alluded to in previous reports.^{43,45-47}

Generally, these studies of the template reactivity of $[\text{Co}(\text{ditame})X]^{n+}$ and others based on the $[\text{Co}(\text{ditame})(\text{NH}_3)]^{3+}$ complex aim to promote fundamental transformations in the properties of MN_5 and MN_6 chromophores.⁴¹ Several striking effects have been achieved for MN_6 species using other strategies,^{5,17,44,48} where profound changes were observed for chromophore electron phenomena such as electron transfer rates, redox potentials and electronic absorption and emission spectroscopies. At the same time, a high intrinsic stability is a common feature of the molecules displaying these new properties. This largely results from the three-dimensional encapsulating nature of the ligands, complemented by other important steric factors. It is expected that the templates described here will enhance and diversify these efforts as well as give rise to new stable MN_5 and MN_6 chromophores.

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