

Copper(II), iron(III) and cobalt(III) complexes of the pendent-arm cyclam derivative 6,6,13-trimethyl-13-amino-1,4,8,11-tetraazacyclotetradecane

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Abstract The interaction of Cu(II), Fe(III) and Co(III) with 6,6,13-trimethyl-13-amino-1,4,8,11-tetraazacyclotetradecane (L^3) incorporating a pendent amine group has led to isolation of the new octahedral complexes $[Cu(HL^3)(ClO_4)_2]Cl \cdot H_2O$ (**1**), $[Fe(L^3)Cl](S_2O_6) \cdot H_2O$ (**2**), $[Co(L^3)Cl](ClO_4)_{1.5}Cl_{0.5} \cdot 0.25H_2O$ (**3**), $[Co(HL^3)Cl_2](ClO_4)_2 \cdot H_2O$ (**4**) and $[Co(L^3)Cl]_2(S_2O_4)(ClO_4)_2$ (**5**). In (**1**) the copper ion occupies the macrocyclic cavity of protonated ($-NH_3^+$) L^3 which is present in its *trans*-III configuration; weakly bound ClO_4^- ligands occupy the axial positions. The X-ray structure of (**2**) showed that Fe(III) occupies the N_4 -macrocyclic cavity of L^3 in a *trans*-III configuration, with the pendent amine group binding in an axial position. The remaining axial position is occupied by a Cl^- ligand. Chromatography of the product obtained from the reaction

of $Na_3[Co(CO_3)_3]$ with L^3 yielded three fractions. Fraction 1 yielded crystals (**3**) composed of three crystallographically independent species incorporating cations of type $[Co(L^3)Cl]^{2+}$ with very similar structures; in each case the macrocyclic ring nitrogens of L^3 are bound to the Co(III) in an asymmetric *cis*-fashion. Fraction 2 yielded the *trans*-III octahedral cationic complex (**4**) incorporating L^3 in its protonated form. The Co(III) complex (**5**) from fraction 3 shows a different coordination arrangement to the products from fractions 1 or 2. The macrocyclic ring coordinates in its *trans*-III form, but the axial sites in this case are occupied by the pendent- NH_2 group and a Cl^- ligand.

Keywords Copper(II) · Iron(III) · Cobalt(III) · Cyclam · Macrocycle · X-ray

Authors dedicate this manuscript to Prof. Jack Harrowfield and Dr. Jacques Vicens in celebration of their 65th birthdays.

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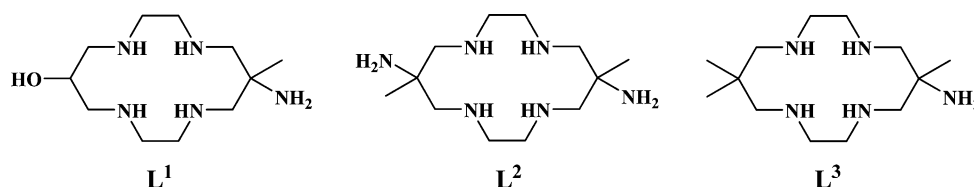
Introduction

Substituted derivatives of tetraazamacrocycles, such as the 14-membered ring cyclam (1,4,8,11-tetraazacyclotetradecane), incorporating different functional groups appended to the macrocyclic framework [1–9] exhibit a number of features which make them attractive as potential ligands for the development of imaging agents, therapeutic radiopharmaceuticals, sensing devices and heterogeneous catalysts [10–16]. Such features include the presence of a pendent functional group, the ability to form both kinetically and thermodynamically stable complexes (the macrocyclic effect) and easy synthesis from readily available starting materials. While substitution at the nitrogen donor sites often results in the lowering of the stability of the resulting metal complexes due to steric interferences [17, 18], the influence on complex stability is usually less when the substitution is present on the carbon backbone

somewhat remote from the donor nitrogens. Nevertheless such substitution may still have a marked effect on metal coordination, and, for example, its presence may promote or restrict particular ligand conformations or configurations and hence affect any stereo-isomerism that the complex may have a propensity to adopt [19, 20]. It has been shown previously that the hydroxyl-functionalized macrocycle **L**¹ exists predominantly as its *trans* (anti-) isomer, although the *cis* form does also occur; different coordination modes of **L**¹ to Co(III) have been observed, with both axial and equatorial orientations of the hydroxyl substituents being documented [21]. Similarly the '*trans*-diammac' ligand **L**² also forms Co(III) complexes in which it is quadridentate, quinquedentate and sexidentate [22–26]. We now report the synthesis of the related amino-substituted derivative **L**³ together with an investigation of its complexes with Cu(II), Fe(III) and Co(III). Emphasis in this study has been given to a comparative X-ray structural study of the stereochemistries adopted by this ligand across all three metal complex types.

by dropwise addition of 2 M HCl (100 mL). The purplish pink solution turned colorless after ~2 h, stirring was continued for a further 3 h, and unreacted Zn powder was removed by filtration. The filtrate was diluted to 1 L with water and adsorbed onto a column of Dowex 50 W × 2 (H⁺ form) resin. This was washed with water (500 mL) and the Zn(II) present was eluted off with 0.5 M HCl (1 L) before the protonated free ligand was eluted with 4 M HCl. The eluate was evaporated to dryness under reduced pressure to give a white powder of the hydrochloride salt (**L**³·5HCl). Yield, 9.8 g. IR spectrum (KBr disc, selected peaks) 3420 (OH), 3250(sh) (NH), 2960 (CH), 2363 (RNH₃⁺) cm⁻¹.

Free **L**³ was obtained from the above hydrochloride salt by neutralizing a suspension of the latter in methanol with sodium hydroxide in methanol and taking the resulting solution to dryness on a rotary evaporator. The residue was then treated with hot acetonitrile, filtered to remove sodium chloride, and the solution again taken to dryness on a rotary evaporator. The yellow oily **L**³ that remained was dried under vacuum. ¹H NMR (CD₃OD): δ = 0.96 (s, 3H, CH₃),



Experimental

Materials and instrumentation

[CuLCl]PF₆ (**L** = 6,6,13-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradecane) was available from an earlier study [27]. Cation-exchange chromatography employed analytical grade 200–400 mesh Dowex 50 W × 2 or SP Sephadex C-25 ion exchange resins, initially present as the H⁺ and Na⁺ forms, respectively. Reagents were purchased from Aldrich and used as received. Electronic absorption spectra were measured with a SCINCO S-2100 diode array spectrophotometer, IR spectra on a JASCO 715 spectrometer, elemental analyses on a Chemtronics TEA-3000 analyser and ¹H NMR spectra on a Varian 300NB spectrometer operating at 300 MHz.

6,6,13-Trimethyl-13-amino-1,4,8,11-tetraazacyclotetradecane (**L**³)

Zn powder (5.0 g) was added to a stirred solution of [CuLCl]PF₆ (**L** = 6,6,13-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradecane) (10.0 g) in water (200 mL) followed

0.97 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.2–2.7 (m, overlapping CH₂ and/or NH signals).



CuCl₂·2H₂O (0.75 g) in 10 mL methanol was added to **L**³ (1.1 g) in methanol (20 mL) and the solution was stirred for 2 h. The solution was evaporated to dryness under reduced pressure and the residue then redissolved in water (100 mL) and adsorbed onto Dowex 50 W × 2 (H⁺-form) in a column. The column was washed with water (500 mL) then with HCl (0.5 M, 500 mL) before eluting with HCl (3 M). The eluate was evaporated to dryness under reduced pressure to yield a reddish purple powder which was dried under vacuum. Yield, 1.7 g. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution of this product containing excess LiClO₄; the crystals were dried in air. Calc. for C₁₃H₃₄Cl₃CuN₅O₉: C, 27.19; H, 5.97; N, 12.19. Found: C, 26.7; H, 5.74; N, 11.8%. Visible spectrum in water λ_{max} (nm) (log ε_{max} (M⁻¹ cm⁻¹)) 510 (1.87), 601 (sh, 1.44). IR spectrum (KBr disc, selected peaks) 3393 (OH), 3247, 3230 (sh) (NH), 2961 (CH), 2566, 2477 (RNH₃⁺), 1106 br (ClO₄⁻) cm⁻¹.

$[\text{Fe}(\text{L}^3)\text{Cl}]\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$

L^3 (1.2 g) in methanol (20 mL) was mixed with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.3 g) in methanol (10 mL) and the solution was stirred for 2 h. The brown precipitate that formed was removed by filtration, washed with cold methanol, and dried under vacuum. Yield, 1.2 g. Addition of $\text{Li}_2\text{S}_2\text{O}_6$ to a solution of this chloride complex in methanol resulted in brown crystals of the mixed $\text{Cl}^-/\text{S}_2\text{O}_6^{2-}$ salt that proved suitable for X-ray diffraction. The crystals were dried in air. Calc. for $[\text{Fe}(\text{L}^3)\text{Cl}]\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O} = \text{C}_{13}\text{H}_{33}\text{ClFeN}_5\text{O}_7\text{S}_2$: C, 29.64; H, 6.31; N, 13.29. Found: C, 29.4; H, 6.2; N, 13.3%. Visible spectrum in water, λ_{max} (nm) ($\log \epsilon_{\text{max}}$ ($\text{M}^{-1} \text{cm}^{-1}$)) 339 (3.13), 495 (2.21). IR spectrum (KBr disc, selected peaks) 3437 s(br) (OH), 3209 (s), 3143 (sh) (NH, NH_2), 2965 (CH), 1230s, 978 (SO) cm^{-1} .

Co(III) complexes of 6,13,13-trimethyl-1,4,8,11-tetraazacyclotetradecane-6-amine: $[\text{Co}(\text{L}^3)\text{Cl}](\text{ClO}_4)_{1.5}\text{Cl}_{0.5} \cdot 0.25\text{H}_2\text{O}$ (fraction 1), $[\text{Co}(\text{HL}^3)\text{Cl}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (fraction 2) and $[\text{Co}(\text{L}^3)\text{Cl}]_2(\text{S}_2\text{O}_6)(\text{ClO}_4)_2$ (fraction 3)

$\text{L}^3 \cdot n\text{HCl}$ (2.5 g) was suspended in methanol (50 mL) and the solution partially neutralized with NaOH (0.68 g in 50 mL methanol). The NaCl that formed was filtered off and $\text{Na}_3[\text{Co}(\text{CO})_3]_3$ (1.8 g) was added to the filtrate. The solution was stirred for 24 h then HCl (2 M, 10 mL) was added to the reddish brown solution and stirring was continued for 1 h before evaporation of the solution to dryness under reduced pressure. The residue was dissolved in water (200 mL) and adsorbed onto Dowex 50 W \times 2 in its H^+ -form. The column was washed with water (500 mL) before elution with 3 M HCl to give three bands, fraction 1 (red), fraction 2 (green) and fraction 3 (red). The eluate corresponding to each band was taken to dryness under reduced pressure, and the respective residues recrystallized from the minimum volume of water after addition of a precipitating anion(s) as its lithium salt (LiClO_4 for fraction 1 and fraction 2, LiClO_4 and $\text{Li}_2\text{S}_2\text{O}_6$ for fraction 3). Yields: fraction 1, 1.0 g; fraction 2, 0.42 g; fraction 3, 0.70 g. In the case of the fraction 1, a crystal from the initial few crystals that formed in the recrystallization solution was used for the X-ray structure determination; the filtrate was then allowed to concentrate through evaporation in air over one week and the bulk product obtained in this manner was used for the microanalysis. (Fraction 1) Calc. for $\text{C}_{13}\text{H}_{31.5}\text{Cl}_3\text{CoN}_5\text{O}_{6.25}$: C, 29.84; H, 6.07; N, 13.39. Found C, 30.1; H, 6.19; N, 13.0%. $^1\text{H NMR}$ (0.05 M DCl): $\delta = 0.77$ (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.9–3.6 (several complex multiplets due to overlapping CH_2 and/or NH signals). UV–Vis spectrum in water, λ_{max} (nm) ($\log \epsilon_{\text{max}}$ ($\text{M}^{-1} \text{cm}^{-1}$)) 363 (2.10), 475 (1.97), 528 (1.98). IR spectrum (KBr disc, selected peaks) 3435s (OH), 3240, (NH), 2969 (CH) 1097s

(ClO_4^-) cm^{-1} . (Fraction 2) Calc. for $\text{C}_{13}\text{H}_{34}\text{Cl}_4\text{CoN}_5\text{O}_9$: C, 25.80; H, 5.66; N, 11.57. Found C, 26.6; H, 5.70; N, 11.8%. $^1\text{H NMR}$ (0.05 M DCl): $\delta = 1.01$ (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.1–3.2 (overlapping CH_2 and/or NH signals). UV–Vis spectrum in methanol, λ_{max} (nm) ($\log \epsilon_{\text{max}}$ ($\text{M}^{-1} \text{cm}^{-1}$)) 382 (1.78), 433 (1.55), 620 (1.59). IR spectrum (KBr disc, selected peaks) 3356s (OH), 3207, 3142(NH), 2957, 2901 (CH), 2557 (br), (RNH_3^+), 1100s br (ClO_4^-) cm^{-1} . (Fraction 3) Calc. for $\text{C}_{13}\text{H}_{31}\text{Cl}_2\text{CoN}_5\text{O}_7\text{S}$: C, 29.39; H, 5.88; N, 13.18. Found C, 29.3; H, 5.85; N, 12.9%. $^1\text{H NMR}$ (0.05 M DCl): $\delta = 0.83$ (s, 6H, CH_3), 1.10 (s, 3H, CH_3), 2.1–3.3 (several complex multiplets due to overlapping CH_2 and/or NH signals). UV–Vis spectrum in water, λ_{max} (nm) ($\log \epsilon_{\text{max}}$ ($\text{M}^{-1} \text{cm}^{-1}$)) 359 (1.99), 454 (sh, 1.65), 533 (1.85). IR spectrum (KBr disc, selected peaks) 3436 br (OH), 3248, 3206s (NH), 2966, 2397 (CH) 1097s (ClO_4^-) cm^{-1} .

X-ray structure determinations

Data for $[\text{Fe}(\text{L}^3)\text{Cl}](\text{S}_2\text{O}_6) \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{L}^3)\text{Cl}](\text{ClO}_4)_{1.5}\text{Cl}_{0.5} \cdot 0.25\text{H}_2\text{O}$ and $[\text{Co}(\text{L}^3)\text{Cl}]_2(\text{S}_2\text{O}_6)(\text{ClO}_4)_2$ were collected with ω scans to approximately $56^\circ 2\theta$ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å) at 150(2) K. Data integration and reduction were undertaken with SAINT and XPREP [28]. Data for $[\text{Cu}(\text{HL}^3)(\text{ClO}_4)_2]\text{Cl} \cdot \text{H}_2\text{O}$ were collected on a Nonius Kappa-CCD diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans to approximately $51^\circ 2\theta$ at 100(2) K. Data for $[\text{CoHL}^3\text{Cl}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ were collected using graphite monochromated synchrotron radiation (0.76999 Å) and an ADSC Quantum210 detector with ω and ψ scans at 100(2) K. Data integration and reduction for these two structures were undertaken with COLLECT [29] and HKL2000 [30]. Subsequent computations were carried out using the WinGX-32 graphical user interface.¹ Structures were solved by direct methods using SIR97 [32] or SHELXS-97 [33]. Multi-scan empirical absorption corrections were applied to each of the data sets except $[\text{CoHL}^3\text{Cl}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ using the programs SADABS [34] or SCALEPACK [30]. Data were refined and extended with SHELXL-97 [35]. All non-hydrogen atoms with occupancy greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Oxygen- and nitrogen-bound hydrogen atoms were first located in the difference Fourier map before refinement. Disorder, where present, was modeled with standard crystallographic

¹ WinGX-32: System of programs for solving, refining and analysing single crystal X-ray diffraction data for small molecules, see [31].

Table 1 Crystal data and structure refinement details

Compound	[FeL ³ Cl](S ₂ O ₆)·H ₂ O	[CuHL ³ (ClO ₄) ₂ Cl]·H ₂ O	[CoL ³ Cl](ClO ₄) _{1.5} Cl _{0.5} ·0.25H ₂ O	[CoHL ³ Cl ₂](ClO ₄) ₂ ·H ₂ O	[CoL ³ Cl] ₂ (S ₂ O ₆)(ClO ₄) ₂
Formula of refinement model	C ₂₆ H ₆₆ Cl ₂ Fe ₂ N ₁₀ O ₁₄ S ₄	C ₁₃ H ₃₄ Cl ₃ CuN ₅ O ₉	C ₇₈ H ₁₉₄ Cl ₁₈ Co ₆ N ₃₀ O _{37.63}	C ₁₃ H ₃₄ Cl ₄ CoN ₅ O ₉	C ₁₃ H ₃₁ Cl ₂ CoN ₅ O _{7.5}
<i>M</i> (g mol ⁻¹)	1053.73	574.34	3146.31	605.18	531.32
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> bam	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> (Å)	9.9126(13)	8.0450(6)	21.3217(19)	12.139(2)	25.363(2)
<i>b</i> (Å)	14.608(2)	36.984(2)	50.853(5)	13.936(3)	13.3841(12)
<i>c</i> (Å)	15.658(2)	8.1409(10)	26.167(2)	14.272(3)	15.7798(14)
α (°)	95.241(2)	90.00	90.00	90.00	90.00
β (°)	105.115(2)	110.033(5)	90.00	97.50(3)	125.9350(10)
γ (°)	97.640(2)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	2150.5(5)	2275.7(4)	28372(4)	2393.7(8)	4337.1(7)
<i>D</i> _c (g cm ⁻³)	1.627	1.676	1.473	1.679	1.627
<i>Z</i>	2	4	8	4	8
Crystal size (mm)	0.45 × 0.35 × 0.25	0.2 × 0.07 × 0.05	0.50 × 0.40 × 0.30	0.5 × 0.15 × 0.1	0.47 × 0.32 × 0.28
<i>T</i> (K)	150(2)	100(2)	150(2)	100(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.065	1.367	1.102	1.217	1.179
<i>T</i> _{min,max}	0.663, 0.766	0.721, 0.934	0.585, 0.718	N/A	0.584, 0.719
2 θ _{max} (°)	28.33	25.67	25.00	30.41	28.38
<i>hkl</i> range	-13 ≤ <i>h</i> ≤ 13, -19 ≤ <i>k</i> ≤ 18, -20 ≤ <i>l</i> ≤ 20	-9 ≤ <i>h</i> ≤ 9, -45 ≤ <i>k</i> ≤ 42, -9 ≤ <i>l</i> ≤ 9	-59 ≤ <i>h</i> ≤ 60, 25 ≤ <i>k</i> ≤ 25, -31 ≤ <i>l</i> ≤ 31	-15 ≤ <i>h</i> ≤ 0, -17 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 18	-20 ≤ <i>h</i> ≤ 20, 17 ≤ <i>k</i> ≤ 17, -27 ≤ <i>l</i> ≤ 27
<i>N</i>	21637	30622	114009	10114	21591
<i>N</i> _{ind} (<i>R</i> _{merge})	10047 (0.0350)	4262 (0.0590)	12793 (0.0477)	5578 (0.1648)	5424 (0.0238)
<i>N</i> _{obs} (<i>I</i> > 2σ(<i>I</i>))	7548	2901	8567	4624	4738
<i>N</i> _{var}	569	283	881	294	308
<i>R</i> 1(<i>F</i>)	0.0419	0.0493	0.0854	0.1080	0.0294
<i>wR</i> 2(<i>F</i> ²)	0.1096	0.1229	0.2669	0.3278	0.0775
GoF(all)	1.024	1.029	1.077	1.336	1.030
$\Delta\rho$ _{min} (eÅ ⁻³)	-0.489	-0.843	-1.560	-0.023	-0.382
$\Delta\rho$ _{max} (eÅ ⁻³)	1.299	1.330	1.313	0.004	0.509

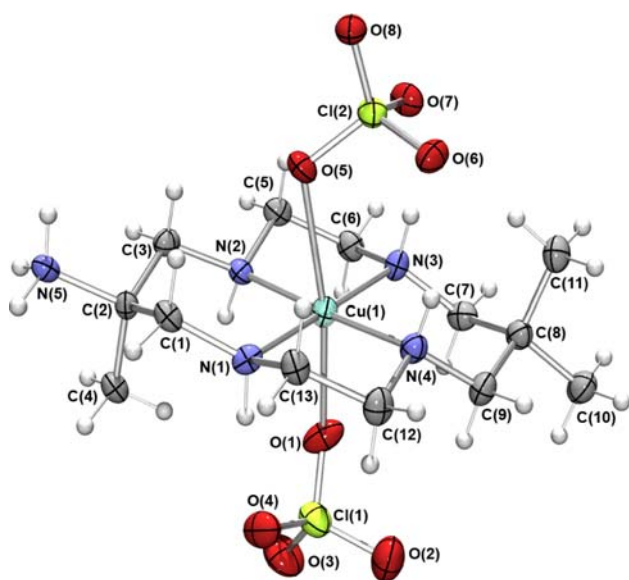


Fig. 1 ORTEP representation of $[\text{Cu}(\text{HL}^3)(\text{ClO}_4)_2]\text{Cl}\cdot\text{H}_2\text{O}$ shown with 50% probability ellipsoids. The non-coordinated anion and water of solvation have been omitted for clarity

Fig. 2 ORTEP representations of the two chemically identical but crystallographically independent cations in $[\text{Fe}(\text{L}^3)\text{Cl}](\text{S}_2\text{O}_6)\cdot\text{H}_2\text{O}$ shown with 50% probability ellipsoids. Anions and water molecules have been omitted for clarity

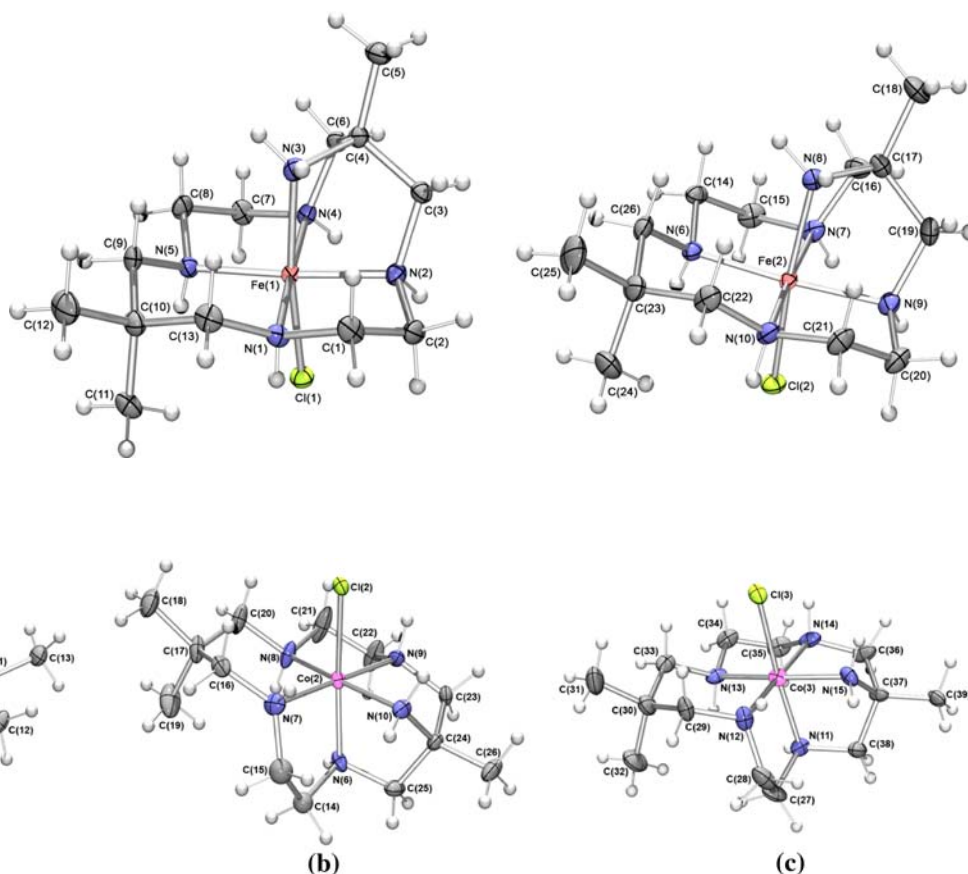


Fig. 3 ORTEP representations of the three crystallographically independent $[\text{CoL}^3\text{Cl}]^{2+}$ cations in the crystals derived from fraction 1 shown with 50% probability ellipsoids; regions of disorder, anions

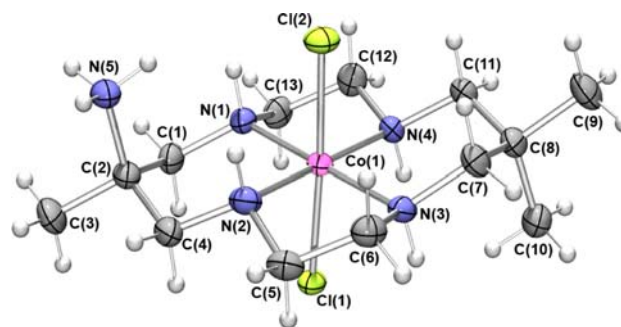


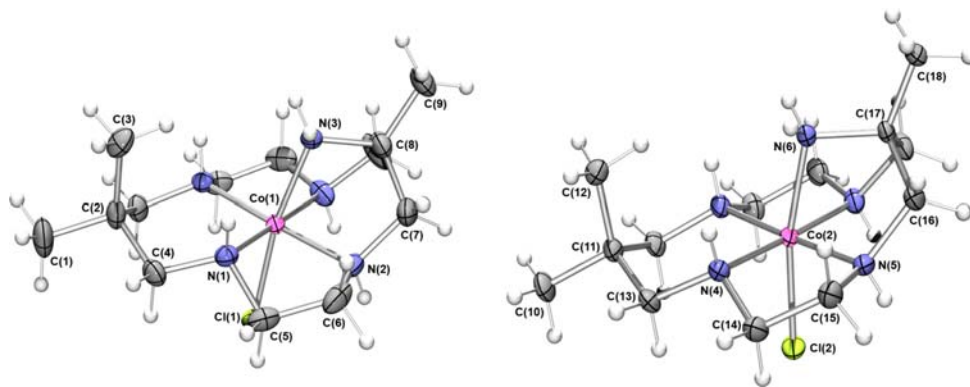
Fig. 4 ORTEP representation of the cation in $[\text{CoHL}^3\text{Cl}_2](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ obtained from fraction 2; shown with 50% probability ellipsoids; anions and solvent water molecules omitted for clarity

techniques including bond length and angle restraints where appropriate.

Crystal and structure refinement data are summarized in Table 1 and ORTEP [36] depictions of the structures are provided in Figs. 1, 2, 3, 4 and 5. Tables of selected bond lengths, angles and hydrogen bonding geometry are given in the electronic supplementary material.

and waters of crystallisation are omitted for clarity; **a** is a non-superimposable mirror image of **(b)** and **(c)**

Fig. 5 ORTEP representations of the two chemically identical but crystallographically distinct $[\text{CoL}^3\text{Cl}]^{2+}$ cations in $[\text{CoL}^3\text{Cl}]_2(\text{S}_2\text{O}_6)(\text{ClO}_4)_2$ shown with 50% probability ellipsoids; anions have been removed for clarity; symmetry code used for generating equivalent atoms: $x, 2 - y, z$



Results and discussion

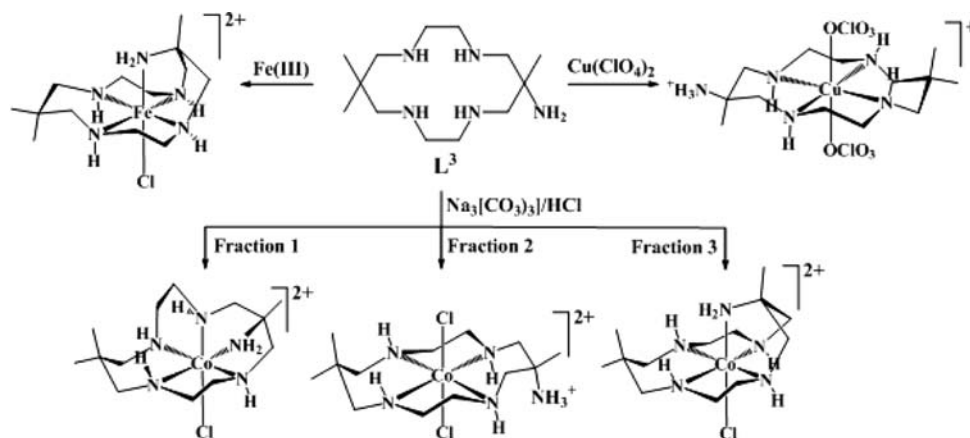
The pendent amine ligand L^3 was obtained directly from the previously reported [27] Cu(II) complex of the corresponding pendent nitro ligand L by simultaneous Zn/HCl reduction and demetallation as shown in Scheme 1; L^3 was isolated as its hydrochloride salt.

Reaction of Cu(II) chloride with L^3 in methanol followed by ion exchange chromatography (elution with dilute aqueous HCl) yielded a reddish purple complex which was recrystallized from water in the presence of excess perchlorate. The infrared spectrum of this complex confirmed the presence of perchlorate (strong perchlorate stretch centered at 1106 cm^{-1}) [37] and also contained absorptions in the $2750\text{--}2475\text{ cm}^{-1}$ region characteristic of a primary ammonium group [38]; its microanalysis was in accord with the stoichiometry $\text{Cu}(\text{HL}^3)\text{Cl}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$. With respect to this, it is noted that the protonation of the pendent amine group attached to the cyclam framework of several other related metal-bound tetraaza-macrocyclic ligands (including coordinated *trans*-diammac, L^2) has been well documented previously [9, 19, 20, 39–41].

The X-ray structure (Fig. 1) of the above complex showed that the Cu(II) occupies the central cavity of the protonated form of L^3 which adopts the most common

'*trans* III' configuration [42]. The in-plane Cu–N bonds fall in the range $2.004(3)\text{--}2.035(3)\text{ \AA}$ and are hence unremarkable. Weakly bound monodentate perchlorato ligands occupy each of the axial positions giving rise to extended (Jahn-Teller) distorted bonds, with the central copper achieving elongated tetragonal coordination. The perchlorate ligands are not equivalent with the Cu–O bond lengths being $2.457(3)\text{ \AA}$ (Cu–O1), and $2.634(3)\text{ \AA}$ (Cu–O5), respectively. One of the non-coordinated perchlorate oxygens is hydrogen bonded to a secondary amine of the substituted cyclam ring (N1–O4, 3.03 \AA) while the other perchlorato group has two of its oxygens hydrogen bonded to two further (adjacent) secondary amines (N3–O7, 3.08 \AA ; N4–O6, 3.15 \AA) of the cyclam ring backbone. The structure confirms the presence of a pendent ammonium group which is hydrogen bonded to a lattice water molecule (N5–O9w, 2.79 \AA). This, in turn, is hydrogen bonded (twice) to the non-coordinated chloride counterion (O9w–Cl3, 3.19 and O9w–Cl3', 3.16 \AA)—the latter being required to maintain neutrality. Overall, these hydrogen bonds form a two-dimensional sheet-like arrangement extending parallel to the crystallographic *ac*-plane. The ammonium group adopts an equatorial position with respect to the corresponding 6-membered chelate ring of the macrocyclic complex.

Scheme 1 Synthesis of the respective Cu(II), Fe(III) and Co(III) complexes of L^3



Reaction of Fe(III) chloride with L^3 in methanol yielded a brown complex which crystallized on addition of excess $S_2O_6^{2-}$. The infrared spectrum showed no peaks in the primary ammonium region but contained the expected peaks for the presence of amine ($3209, 3170 \text{ cm}^{-1}$) and the $S_2O_6^{2-}$ dianion ($1227, 984 \text{ cm}^{-1}$) [43]. An X-ray structure (Fig. 2) showed the complex to be of type $[Fe(L^3)Cl](S_2O_6) \cdot H_2O$; there are two independent complex molecules in the asymmetric unit. The four secondary amine donors of the macrocyclic ring coordinate in an equatorial manner to the central Fe(III) with the cyclam backbone once again approximating a *trans*-III configuration. However, in this case the pendent primary amine group coordinates to the metal centre in one of the axial positions, with the remaining axial position occupied by a chloro ligand to yield a slightly distorted octahedral coordination geometry. The Fe–N_{axial} distance, at $1.999(2) \text{ \AA}$, is only marginally longer than the in-plane Fe–N bond lengths which fall in the range $1.977(2)–1.984(2) \text{ \AA}$.

Adjacent complexes are linked by a hydrogen bonding network involving primary and secondary amine protons on the macrocyclic rings, the $S_2O_6^{2-}$ anion, and the lattice water molecules: (O13w–N8, 3.04; O13w–O5, 2.82; O13w–O7, 2.84; O1–N8, 3.03; O7–N3, 2.89; O10–N5, 2.99 \AA). The majority of the published X-ray reports [44] of complex structures incorporating $S_2O_6^{2-}$ show that this anion readily acts as a ‘network builder’ by acting as a bridging hydrogen bond acceptor for adjacent –NH or –OH donors, in a similar manner to that in the present structure; in many of these published structures hydrogen bonding solvent molecules are also incorporated in the resulting three-dimensional network.

Reaction of $Na_3[Co(CO)_3]_3$ with L^3 in acidified methanol followed by chromatography of the product in water on Dowex 50 W \times 2 (H^+ form) using dilute aqueous HCl as eluent resulted in three bands which were separated and the respective fractions collected. Each fraction was taken to dryness on a rotary evaporator and the product recrystallised from water after addition of ClO_4^- (fractions 1 and 2) or $S_2O_6^{2-}$ (fraction 3).

The infrared spectrum of the red–violet complex obtained from fraction 1 confirmed the presence of perchlorate anion (strong broad absorption at 1097 cm^{-1}) and the 1H NMR spectrum of this product in D_2O gave three methyl peaks of equal intensity in accordance with the presence of different environments for the three methyl groups of the bound macrocycle.

The X-ray structure (Fig. 3) determination using crystals obtained from fraction 1 showed the presence of three independent complex molecules (Fig. 3a–c) in the unit cell with the Co(III) centre in each complex exhibiting its normal octahedral coordination. While all three cationic species have the same stoichiometry of $[Co(L^3)Cl]^{2+}$ and are

essentially identical structurally, two enantiomeric forms are present (two molecules have the same hand and one has an opposite hand). In contrast to the Cu(II) and Fe(III) complexes just discussed L^3 is coordinated in an ‘unsymmetrical’ *cis*-octahedral fashion in these complexes, with the equatorial plane being occupied by three nitrogens from the macrocyclic ring and one from the pendent amine group. Axial positions are filled by the remaining ring nitrogen and a chloro ligand. As the complexes crystallize in the orthorhombic space group *Ibam*, which has inversion and mirror symmetry, overall there are equal numbers of the two hands present in the lattice and hence single crystals correspond to a racemic mixture. Hydrogen bonding interactions are present in the lattice between the amine hydrogens, anions and water solvate molecules, resulting in the formation of infinite one-dimensional chains throughout the lattice.

The infrared spectrum of the green complex derived from fraction 2 confirmed the presence of perchlorate and also contained bands in the region corresponding to the presence of an ammonium group. The 1H NMR showed three methyl singlets of equal intensity indicating different environments for these groups. An X-ray structure determination (Fig. 4) confirmed that the complex is of type $[CoHL^3Cl_2](ClO_4)_2 \cdot H_2O$ in which the macrocycle is coordinated, as before, in its planar ‘*trans*-III’ configuration with the axial sites occupied by chloro ligands; all metal to donor bond distances are unremarkable. The protonated primary amine is orientated axially with respect to the attached six-membered chelate ring. This latter amine group is involved in a network of hydrogen bonds linking lattice water molecules, perchlorate anions, chloro groups on adjacent complexes and secondary amine groups on the same complex. The structure of the present complex cation is similar to that of the copper complex of L^3 discussed earlier, except that chloro groups replace the axial perchlorate groups and the ammonium group is orientated equatorially in the latter.

The purple complex isolated from fraction 3 was confirmed by its infrared spectrum to contain an $S_2O_6^{2-}$ anion and not to incorporate an ammonium group. The 1H NMR showed the presence of two methyl singlets of intensity 1:2 indicating equivalent environments for two of the three methyl groups in the coordinated macrocycle. The X-ray structure (Fig. 5) of the solid showed that the complex has an overall composition of $[CoL^3Cl]_2(S_2O_6)(ClO_4)_2$. While it has a similar stoichiometry to the complex cations isolated from fraction 1, it contains a different macrocycle coordination mode to either of these. This product has its four secondary macrocyclic ring nitrogens occupying the equatorial coordination plane (*trans*-III configuration), with the pendent primary amine group bound in an axial position. The remaining (*trans*) axial position is occupied by a chloro ligand to complete the overall octahedral geometry. The arrangement is similar to that in $[Fe(L^3)Cl](S_2O_6) \cdot H_2O$,

with amine nitrogen atoms hydrogen bonded to both the $\text{S}_2\text{O}_6^{2-}$ and ClO_4^- anions to form an intricate three-dimensional network.

Conclusion

The aim of the present study was to undertake an initial investigation of the coordination chemistry of the new cyclam derivative **L**³, bearing a pendent primary amine group, towards Cu(II), Fe(III) and Co(III). It has been demonstrated that this ligand readily gives rise to five new complexes with these ions that show a range of coordination and lattice structures involving in individual complexes both coordination and non-coordination/protonation of the pendent amine group.

Supplementary material

Crystallographic data for compounds **1–5** have been deposited with CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and are identified by deposition numbers of CCDC 735298–735302. Copies of this information can be obtained free of charge on request by e-mail at deposit@ccdc.cam.ac.uk or at <http://www.ccdc.cam.ac.uk>.

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