

## N-Methylation of macrocyclic hexaaminocobalt(III) complexes

Paul V. Bernhardt\*† and Lathe A. Jones

Department of Chemistry, University of Queensland, Brisbane 4072, Australia

Reaction between formaldehyde and the pendant arm macrocyclic complex (*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)cobalt(III)  $[\text{CoL}^1]^{3+}$  yielded the diimine derivative *trans*-6,13-dimethyl-6,13-bis(methyleneamino)-1,4,8,11-tetraazacyclotetradecane ( $\text{L}^3$ ) as its cobalt(III) complex. Reduction of the imines has been achieved with  $\text{NaBH}_4$  and the *meso* and *rac* cobalt(III) complexes of *trans*-6,13-dimethyl-6,13-bis(methylamino)-1,4,8,11-tetraazacyclotetradecane ( $\text{L}^5$ ) have been prepared. Crystal structures of the macrocyclic complexes  $[\text{CoL}^1][\text{ClO}_4]_3$ ,  $[\text{CoL}^3][\text{ClO}_4]_3$  and *meso*- $[\text{CoL}^5][\text{ClO}_4]_3 \cdot 2\text{H}_2\text{O}$  were determined and some unusual structural, spectroscopic and electrochemical variations observed going from the parent hexaamine  $[\text{CoL}^1]^{3+}$  to  $[\text{CoL}^3]^{3+}$  (diimine) and ultimately to  $[\text{CoL}^5]^{3+}$  (bis-N-methylated hexaamine).

The elaboration of macrocyclic ligands by the attachment of so-called pendant arms provides an added dimension to their co-ordination chemistry.<sup>1</sup> For example, the hexaamine *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine  $\text{L}^1$ , a substituted cyclam, may co-ordinate in a hexadentate manner<sup>2</sup> whereas the unsubstituted parent can only bind in a tetradentate mode.<sup>3</sup> The pendant primary amines may also be used as links to other metal centres or active functional groups *via* conventional organic synthetic routes. However, the basicity, and hence, nucleophilicity, of the pendant amines is lowered<sup>4</sup> relative to simple primary amines when a four-co-ordinate metal ion enters the macrocyclic ring, *i.e.* when the primary amines do not directly participate in binding.

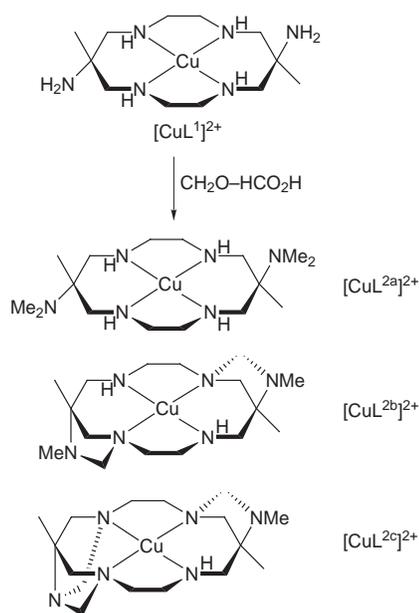
Macrocyclic aliphatic and aromatic (Schiff-base) imines and their complexes have been known for some time.<sup>5</sup> By contrast, terminal aliphatic imines are much more reactive and relatively few examples of this type of ligand are known.<sup>6,7</sup> Non-chelated co-ordinated imines are highly electrophilic, and typically unstable with respect to hydrolysis under basic conditions. Previously,<sup>8,9</sup> we found that reaction of the non-co-ordinated pendant primary amines of  $[\text{CuL}^1]^{2+}$  with formaldehyde and formic acid leads to the bis(dimethylamino)-substituted macrocycle  $[\text{CuL}^{2a}]^{2+}$  in addition to some tri- and tetra-cyclic condensation products (Scheme 1). The intermediate methyleneimines formed through condensation between formaldehyde and the pendant primary amines of  $\text{L}^1$  were not isolated.

In this work we investigate the reaction of  $[\text{CoL}^1]^{3+}$  with formaldehyde where both pendant amines are bound to the metal ion (Scheme 2). We shall show that this reaction leads to some rather different chemistry compared with that seen previously for the copper(II) system. In particular, we have isolated and characterised the highly reactive diimine  $[\text{CoL}^3]^{3+}$ , and its potential use as a precursor to functionalised macrocycles will be demonstrated.

## Experimental

### Syntheses

*trans*-(6,13-Dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)cobalt(III) perchlorate,  $[\text{CoL}^1][\text{ClO}_4]_3$ , was prepared as previously described.<sup>2</sup> X-Ray-quality crystals were obtained by slow evaporation of an aqueous solution of the complex in the presence of an excess of  $\text{NaClO}_4$ . For all new complexes, satisfactory analyses (C, H and N) were obtained.



Scheme 1

### Anion exchange

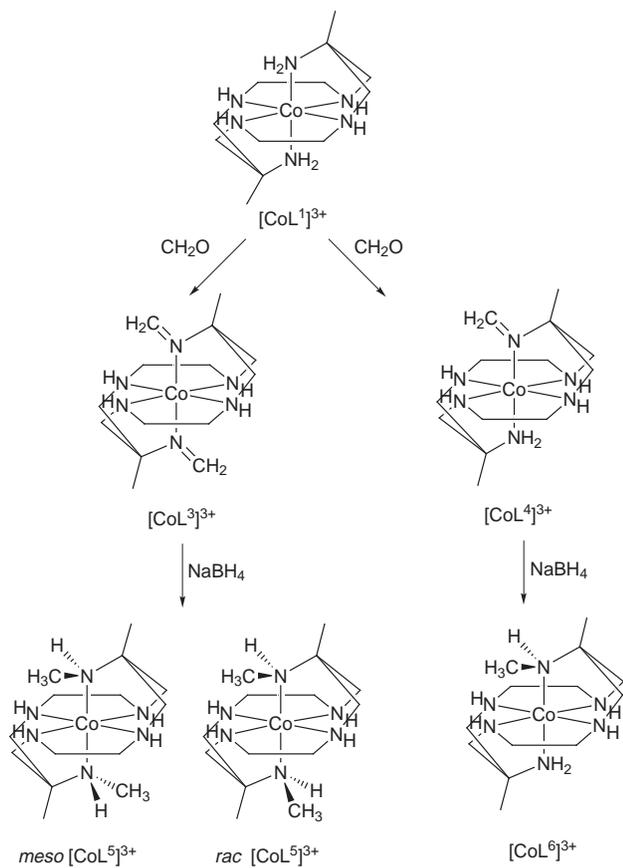
$[\text{CoL}^1]\text{Cl}_3$ . A solution of  $[\text{CoL}^1][\text{ClO}_4]_3$  (7.0 g in 100  $\text{cm}^3$  water) was sorbed onto a Dowex 50W  $\times 2$  cation-exchange column (15  $\times$  4 cm,  $\text{H}^+$  form) and eluted with 3 mol  $\text{dm}^{-3}$  HCl solution. The eluate was taken to dryness on a rotary evaporator to afford  $[\text{CoL}^1]\text{Cl}_3$  as a yellow powder (4.83 g).

$[\text{CoL}^1][\text{O}_2\text{CMe}]_3$ . A solution of  $[\text{CoL}^1]\text{Cl}_3$  (4.83 g) was sorbed on a Dowex 1-X8 anion-exchange column (15  $\times$  4 cm,  $^-\text{O}_2\text{CMe}$  form). The complex now in its acetate form was collected as it passed through the column, which was washed with water until the eluate became colourless. The eluate was evaporated to a syrup, redissolved in EtOH and evaporated to dryness. Finally, the solid was suspended in benzene and once again evaporated to dryness to leave a yellow powder that was dried in a vacuum desiccator. A stock solution (0.057 mol  $\text{dm}^{-3}$ ) was prepared by dissolving the solid in dry MeOH (200  $\text{cm}^3$ ).

### Condensation reaction

*trans*-(6,13-Dimethyl-6,13-dimethyleneamino-1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate,  $[\text{CoL}^3][\text{ClO}_4]_3$ . To the above methanolic solution of  $[\text{CoL}^1][\text{O}_2\text{CMe}]_3$  (100  $\text{cm}^3$ ,

† E-Mail: bernhardt@chemistry.uq.edu.au



Scheme 2

0.057 mol dm<sup>-3</sup>) was added paraformaldehyde (9.0 g), triethylamine (1.6 cm<sup>3</sup>) and triethyl orthoformate (5 cm<sup>3</sup>). The mixture was refluxed for 4 h, cooled to room temperature and acidified with dilute HCl (200 cm<sup>3</sup>, 0.5 mol dm<sup>-3</sup>). The solution was charged onto a Dowex 50W × 2 column (80 × 2 cm, H<sup>+</sup> form) and the eluent was 2 mol dm<sup>-3</sup> HCl. Visual separation of the reaction products was not apparent, so the yellow eluate was collected in fifteen 50 cm<sup>3</sup> fractions. Each fraction was evaporated to dryness and <sup>1</sup>H NMR spectroscopy was used to identify the composition of each fraction. Fractions 1–4 contained pure diimine [CoL<sup>3</sup>]Cl<sub>3</sub>. <sup>1</sup>H NMR (D<sub>2</sub>O, pD 5): δ 1.52 (s, 6 H), 2.67 and 3.54 (AB q, <sup>3</sup>J = 12.9, 8 H), 2.58 and 3.15 (AA'BB' m, 8 H), 7.95 and 8.50 (d, of d., <sup>3</sup>J = 6.3 Hz, 4 H). This spectrum was run approximately 30 min after dissolution when deuterium exchange of the amine protons was complete. In acidified D<sub>2</sub>O the NH resonances were observed at δ 7.46 as a broad singlet, in addition to coupling with the methylene protons. Recrystallisation of this compound from dilute HClO<sub>4</sub> solution afforded crystals of the triperchlorate salt that were suitable for X-ray work.

Later fractions comprised mixtures of the monoimine [CoL<sup>4</sup>]³⁺, the diimine [CoL<sup>3</sup>]³⁺ and some starting material [CoL<sup>1</sup>]³⁺. Overall the ratio of these species was approximately 4 ([CoL<sup>4</sup>]³⁺):1 ([CoL<sup>3</sup>]³⁺):1 ([CoL<sup>1</sup>]³⁺).

#### Imine reduction

In a separate experiment the 4 ([CoL<sup>4</sup>]³⁺):1 ([CoL<sup>3</sup>]³⁺):1 ([CoL<sup>1</sup>]³⁺) mixture of complexes was collected as a single band from the chromatography column (Dowex 50W × 2, 15 × 4 cm, 2 mol dm<sup>-3</sup> HCl eluent) and evaporated to dryness. This solid was taken up in water (100 cm<sup>3</sup>), and a solution of pH 1.5 resulted from residual HCl in the solid. To this solution was added NaBH<sub>4</sub> (1 g) in several portions to avoid excessive frothing and the mixture was stirred at room temperature for 16 h. The solution was diluted to 1 dm<sup>3</sup> (pH had risen to 9) and charged onto a Sephadex C-25 cation-exchange column (80 × 2

cm, Na<sup>+</sup> form). Two diffuse, close running bands were observed using 0.1 mol dm<sup>-3</sup> trisodium citrate as the eluent. Both bands were, separately, charged onto a small Dowex 50W × 2 column (10 × 3 cm, H<sup>+</sup> form) and eluted with 3 mol dm<sup>-3</sup> HCl solution. Proton and <sup>13</sup>C NMR spectroscopy revealed band 1 to be a 1:2 mixture of [CoL<sup>1</sup>]Cl<sub>3</sub> and [CoL<sup>6</sup>]Cl<sub>3</sub> respectively, whereas band 2 was a 3:2 mixture of *meso*- and *rac*-[CoL<sup>5</sup>]Cl<sub>3</sub>. Final purification of these mixtures is described below.

***trans*-(6,13-Dimethyl-13-methylamino-1,4,8,11-tetraazacyclo-tetradecan-6-amine)cobalt(III) chloride, [CoL<sup>6</sup>]Cl<sub>3</sub>.** The mixture of [CoL<sup>1</sup>]Cl<sub>3</sub> and [CoL<sup>6</sup>]Cl<sub>3</sub> from band 1 was dissolved in water (500 cm<sup>3</sup>) and charged on a Sephadex C-25 cation-exchange column (80 × 2 cm, Na<sup>+</sup> form). Elution with Na<sub>2</sub>HPO<sub>4</sub> (0.1 mol dm<sup>-3</sup>) gave two well separated bands, the first being [CoL<sup>1</sup>]³⁺ followed by the major band [CoL<sup>6</sup>]³⁺. The latter band was charged on a small Dowex 50W × 2 column and eluted with 3 mol dm<sup>-3</sup> HCl. The eluate was evaporated to dryness to afford the desired product as its trichloride salt. <sup>1</sup>H NMR (D<sub>2</sub>O, pD 7): δ 1.24 (s, 3 H), 1.36 (s, 3 H), 2.47 (s, 3 H) and 2.6–3.8 (m, 16 H, CH<sub>2</sub>). In acidified D<sub>2</sub>O, the resonance at δ 2.47 appeared as a doublet (<sup>4</sup>J 6.0 Hz) and NH resonances are seen at δ 6.8, 7.2 and 7.4.

***meso* and *rac-trans*-(6,13-Dimethyl-6,13-bis-methylamino-1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride, *meso*- and *rac*-[CoL<sup>5</sup>]Cl<sub>3</sub>.** This mixture of isomers did not separate on a Sephadex C-25 column (80 × 2 cm, Na<sup>+</sup> form) using either 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> or 0.1 mol dm<sup>-3</sup> trisodium citrate as eluent. The *meso* isomer of [CoL<sup>5</sup>]Cl<sub>3</sub> is partially soluble in EtOH, which allowed its isolation by suspension of the solid residue (*ca.* 0.5 g) in EtOH (*ca.* 100 cm<sup>3</sup>), filtration and evaporation of the filtrate to dryness to yield *meso*-[CoL<sup>5</sup>]Cl<sub>3</sub> in an isomerically pure form. <sup>1</sup>H NMR (D<sub>2</sub>O, pD 7): δ 1.24 (s, 6 H), 2.42 (s, 6 H), 2.75 and 3.40 (AB q, br), <sup>3</sup>J = 12.5 Hz, 8 H), 3.00 and 3.60 (m, 8 H). In acidified D<sub>2</sub>O the resonance at δ 2.42 appeared as a doublet (<sup>4</sup>J 5.9 Hz) and NH resonances were seen at δ 7.1 and 7.5. Recrystallisation from dilute HClO<sub>4</sub> gave crystals of *meso*-[CoL<sup>5</sup>][ClO<sub>4</sub>]<sub>3</sub> suitable for X-ray work. The solid that remained in the EtOH suspension contained both *meso*- and *rac*-[CoL<sup>5</sup>]Cl<sub>3</sub>, so purification of the latter isomer was not achieved.

#### Physical methods

Solution UV/VIS spectra were measured on a Perkin-Elmer Lambda 12 spectrophotometer. Cyclic voltammetry was performed with a BAS 100B/W analyser employing an EG&G PARC model 303 static mercury-drop working electrode, an Ag–AgCl reference electrode and a platinum auxiliary electrode. All solutions for electrochemistry were *ca.* 5 × 10<sup>-3</sup> mol dm<sup>-3</sup> in analyte and 0.1 mol dm<sup>-3</sup> in NaClO<sub>4</sub>, and were purged with N<sub>2</sub> before measurement. Infrared spectra of compounds dispersed as KBr discs were measured on a Perkin-Elmer series 1600 FT-IR instrument, NMR spectra on a Bruker AC200 FT instrument. All chemical shifts are cited *versus* the methyl resonance of sodium 3-(trimethylsilyl)propanesulfonate.

#### Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) and operating in the ω–2θ scan mode. Data reduction and empirical absorption corrections (ψ scans) were performed with the XTAL<sup>10</sup> package, except for the structure of *meso*-[CoL<sup>5</sup>][ClO<sub>4</sub>]<sub>3</sub> where no absorption correction was applied.

**Structure solutions.** Structures were solved by heavy-atom methods with SHELXS 86<sup>11</sup> and refined by full-matrix least-squares analysis with SHELXL 93.<sup>12</sup> All non-H atoms were

**Table 1**  $^{13}\text{C}$  NMR Assignments (chemical shift *versus* sodium 3-(trimethylsilyl)propanesulfonate

	C-methyl	N-methyl	[5]-CH <sub>2</sub> <sup>a</sup>	[6]-CH <sub>2</sub> <sup>b</sup>	Tertiary C	Imine CH <sub>2</sub>
[CoL <sup>1</sup> ] <sup>3+</sup>	21.3	—	56.1	62.5	67.4	—
[CoL <sup>3</sup> ] <sup>3+</sup>	17.4	—	56.4	62.1	81.7	174.0
[CoL <sup>4</sup> ] <sup>3+</sup>	17.6, 21.7	—	56.3 <sup>c</sup>	62.0, 62.1	68.0, 81.2	173.3
<i>meso</i> -[CoL <sup>5</sup> ] <sup>3+</sup>	17.5	33.1	56.1, 57.9	60.2, 63.0	72.5	—
<i>rac</i> -[CoL <sup>5</sup> ] <sup>3+</sup>	17.4	33.8	56.4, 57.8	60.3, 64.0	72.6	—
[CoL <sup>6</sup> ] <sup>3+</sup>	17.2, 21.7	33.7	55.4, 56.8, 57.0, 57.1	59.7, 62.9, <sup>c</sup> 63.4	67.2, 72.9	—

<sup>a</sup> Methylene in five-membered chelate ring. <sup>b</sup> Methylene in six-membered chelate ring. <sup>c</sup> Accidentally degenerate.

refined with anisotropic thermal parameters except minor contributors to perchlorate O-atom disorder. Alkyl H atoms were included at estimated positions. Selected bond lengths and angles are presented in Table 2, and the atomic nomenclature is defined in Figs. 1–3 drawn with PLATON.<sup>13</sup>

**Crystal data.** [CoL<sup>1</sup>][ClO<sub>4</sub>]<sub>3</sub>, C<sub>12</sub>H<sub>30</sub>Cl<sub>3</sub>CoN<sub>6</sub>O<sub>12</sub>, *M* = 615.7, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 16.631(3), *b* = 8.631(3), *c* = 17.915(3) Å, β = 114.664(8)°, *U* = 2337(1) Å<sup>3</sup>, *D<sub>c</sub>* (*Z* = 4) = 1.759 g cm<sup>-3</sup>, μ(Mo-Kα) = 11.48 cm<sup>-1</sup>, *F*(000) = 1272, *T* = 293 K. Specimen: yellow prism 0.6 × 0.6 × 0.6 mm, *T*<sub>max,min</sub> 1.00, 0.88; *N* = 4106, *N*<sub>o</sub> = 3194 [*F*<sub>o</sub>] > 2σ(*F*<sub>o</sub>), 2.2 < θ < 25°, *hkl* 0 to 19, 0 to 10, -21 to 21. Final *R*1 = 0.0393, *wR*2 = 0.1068, *w*<sup>-1</sup> = σ(*F*<sub>o</sub>)<sup>2</sup> + (0.0639*P*)<sup>2</sup> + 3.56*P* where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, number of parameters = 340, goodness of fit = 1.020. Residual extrema +0.6, -0.4 e Å<sup>-3</sup>.

[CoL<sup>3</sup>][ClO<sub>4</sub>]<sub>3</sub>, C<sub>14</sub>H<sub>30</sub>Cl<sub>3</sub>CoN<sub>6</sub>O<sub>12</sub>, *M* = 639.72, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 17.084(8), *b* = 8.887(2), *c* = 17.996(8) Å, β = 114.63(2)°, *U* = 2483(1) Å<sup>3</sup>, *D<sub>c</sub>* (*Z* = 4) = 1.711 g cm<sup>-3</sup>, μ(Mo-Kα) = 10.84 cm<sup>-1</sup>, *F*(000) = 1320, *T* = 293 K. Specimen: yellow prism 0.3 × 0.3 × 0.2 mm, *T*<sub>max,min</sub> 1.00, 0.84; *N* = 4363, *N*<sub>o</sub> = 2470 [*F*<sub>o</sub>] > 2σ(*F*<sub>o</sub>), 2.2 < θ < 25°, *hkl* 0 to 20, 0 to 10, -21 to 21. Final *R*1 = 0.0526, *wR*2 = 0.1383, *w*<sup>-1</sup> = σ(*F*<sub>o</sub>)<sup>2</sup> + (0.0842*P*)<sup>2</sup> + 3.10*P* where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, number of parameters = 340, goodness of fit = 1.020. Residual extrema +0.6, -0.4 e Å<sup>-3</sup>.

*meso*-[CoL<sup>5</sup>][ClO<sub>4</sub>]<sub>3</sub>·2H<sub>2</sub>O, C<sub>14</sub>H<sub>38</sub>Cl<sub>3</sub>CoN<sub>6</sub>O<sub>14</sub>, *M* = 679.78, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.938(4), *b* = 13.210(2), *c* = 15.714(5) Å, β = 90.94(2)°, *U* = 2685(1) Å<sup>3</sup>, *D<sub>c</sub>* (*Z* = 4) = 1.681 g cm<sup>-3</sup>, μ(Mo-Kα) = 10.13 cm<sup>-1</sup>, *F*(000) = 1416, *T* = 293 K. Specimen: yellow prism 0.5 × 0.5 × 0.2 mm, *N* = 4727, *N*<sub>o</sub> = 1918 [*F*<sub>o</sub>] > 2σ(*F*<sub>o</sub>), 1.5 < θ < 25°, *hkl* 0 to 15, 0 to 15, -18 to 18. Final *R*1 = 0.0856, *wR*2 = 0.2240, *w*<sup>-1</sup> = σ(*F*<sub>o</sub>)<sup>2</sup> + (0.1679*P*)<sup>2</sup> where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, number of parameters = 386, goodness of fit = 1.020. Residual extrema +1.1, -0.5 e Å<sup>-3</sup>.

CCDC reference number 186/960.

See <http://www.rsc.org/suppdata/dt/1998/1757/> for crystallographic files in .cif format.

## Results and Discussion

The reactivity of the co-ordinated pendant primary amines of [CoL<sup>1</sup>]<sup>3+</sup> was established by condensation with formaldehyde. The resulting mixture of [CoL<sup>3</sup>]<sup>3+</sup> and [CoL<sup>4</sup>]<sup>3+</sup> and starting material could only be partially separated on a cation-exchange column. However, the diimine [CoL<sup>3</sup>]<sup>3+</sup>, which eluted first, was obtained in a pure form. The infrared spectrum of [CoL<sup>3</sup>][ClO<sub>4</sub>]<sub>3</sub> exhibits sharp peaks at 1628 and 1659 cm<sup>-1</sup> (C=N str) in contrast to the spectrum of the starting material [CoL<sup>1</sup>][ClO<sub>4</sub>]<sub>3</sub> which displays a single peak in this region at 1601 cm<sup>-1</sup> [δ(HNH)]. Complete hydrolysis of [CoL<sup>3</sup>]<sup>3+</sup> to regenerate the starting material [CoL<sup>1</sup>]<sup>3+</sup> occurs rapidly (less than 2 min) at pH 11 as shown by NMR spectroscopy. At pH 6 the hydrolysis of one imine to form [CoL<sup>4</sup>]<sup>3+</sup> occurs within 5 min, but the second hydrolysis step is somewhat slower, which is indicative of a significant *trans* influence of the co-ordinated imines. At pH < 5 the hydrolysis reaction is sufficiently slowed that spectroscopic and electrochemical measurements could be made

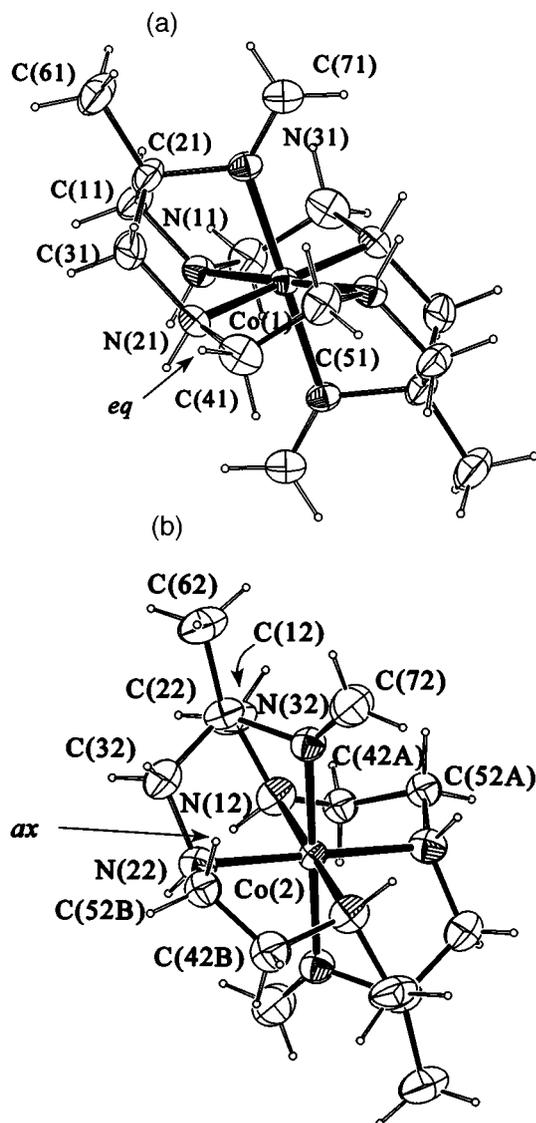
without any detectable changes. We have not pursued a quantitative kinetic analysis of this system. The instability of [CoL<sup>3</sup>]<sup>3+</sup> and [CoL<sup>4</sup>]<sup>3+</sup> to hydrolysis in basic solution rules out chromatography using neutral or weakly basic eluents such as citrate or HPO<sub>4</sub><sup>2-</sup>, so the choice of separation conditions was somewhat limited. It has been found that similar condensation reactions between formaldehyde and acyclic hexaamminecobalt(III) ions<sup>6</sup> proceed to completion, but we have not been able to achieve quantitative yields of the diimine complex [CoL<sup>3</sup>]<sup>3+</sup>. The observed *trans* influence of the co-ordinated imines may be an important factor in this regard. Reduction of the co-ordinated imines of [CoL<sup>3</sup>]<sup>3+</sup> and [CoL<sup>4</sup>]<sup>3+</sup> produced stable N-methylated analogues [CoL<sup>5</sup>]<sup>3+</sup> and [CoL<sup>6</sup>]<sup>3+</sup>, and separation of this mixture, although not straightforward, was greatly facilitated. The asymmetric [CoL<sup>6</sup>]<sup>3+</sup> complex, derived from the monoimine [CoL<sup>4</sup>]<sup>3+</sup>, was the major species present from the reduction.

The most sensitive technique for determining the composition of each reaction mixture was NMR spectroscopy. Table 1 summarises the  $^{13}\text{C}$  NMR resonances of all reactants and products described in this work. The high symmetry (*C*<sub>2h</sub>) of [CoL<sup>1</sup>]<sup>3+</sup> and [CoL<sup>3</sup>]<sup>3+</sup> results in only four and five  $^{13}\text{C}$  resonances respectively. The monoimine [CoL<sup>4</sup>]<sup>3+</sup> possesses a mirror plane, so nine resonances were anticipated, but two were accidentally degenerate. The isomeric, dimethylated [CoL<sup>5</sup>]<sup>3+</sup> complexes both exhibit seven resonances as a result of their *S*<sub>2</sub> (*meso*) and *C*<sub>2</sub> (*rac*) symmetries. The monomethylated complex [CoL<sup>6</sup>]<sup>3+</sup> is asymmetric, but two resonances were accidentally degenerate so only twelve peaks were identified. The resonances most sensitive to reactions at the pendant amine sites originated from the C-methyl and tertiary C atoms. The imine substituents caused a 14 ppm downfield shift in the tertiary C atom resonance, relative to [CoL<sup>1</sup>]<sup>3+</sup>, and a 4 ppm upfield shift in the C-methyl resonance. Reduction of the imine to an N-methyl had little effect on the C-methyl resonance but the tertiary C atom was shifted *ca.* 9 ppm upfield relative to the imine. Proton NMR spectroscopy was more useful in quantifying the relative proportions of the components of each reaction mixture through integration, but the spectra were generally rather complicated, particularly in the methylene region. The most easily interpretable spectrum was due to the diimine [CoL<sup>3</sup>]<sup>3+</sup>, which displayed an AA'BB' pattern corresponding to the macrocyclic five-membered chelate ring protons in addition to an AB spin system for the methylene protons attached to the six-membered chelate rings. More comprehensive discussions of the  $^1\text{H}$  NMR spectra of complexes of L<sup>1</sup> and close analogues can be found elsewhere.<sup>14,15</sup>

The crystal structure of [CoL<sup>3</sup>][ClO<sub>4</sub>]<sub>3</sub> comprises two independent complex cations on centres of symmetry and perchlorate anions on general sites. The two cations are not the same, with the most apparent difference being the conformations of the macrocyclic five-membered chelate rings. In cation 1 [Fig. 1(a)] the five-membered chelate rings are eclipsed. In previous work<sup>15</sup> we have employed the nomenclature *eq,eq* to describe the type of conformation found in cation 1, where the methylene H atom *trans* to its adjacent amine H atom is in an equatorial disposition. This proton is highlighted in Fig. 1(a). However, in cation 2 [Fig. 1(b)] the five-membered chelate rings

**Table 2** Selected bond lengths (Å) and angles (°)

	[CoL <sup>3+</sup> ][ClO <sub>4</sub> ] <sub>3</sub>		[CoL <sup>1+</sup> ][ClO <sub>4</sub> ] <sub>3</sub>		<i>meso</i> -[CoL <sup>5+</sup> ][ClO <sub>4</sub> ] <sub>3</sub>	
	Cation 1 <i>n</i> = 1 ( <i>eq,eq</i> )	Cation 2 <i>n</i> = 2 ( <i>eq,ax</i> )	Cation 1 <i>n</i> = 1 ( <i>eq,eq</i> )	Cation 2 <i>n</i> = 2 ( <i>eq,eq</i> )	Cation 1 <i>n</i> = 1 ( <i>eq,eq</i> )	Cation 2 <i>n</i> = 2 ( <i>eq,ax</i> )
Co–N(1 <i>n</i> )	1.944(4)	1.973(5)	1.941(3)	1.941(3)	1.945(8)	1.932(9)
Co–N(2 <i>n</i> )	1.942(4)	1.952(5)	1.936(3)	1.944(3)	1.943(8)	1.945(8)
Co–N(3 <i>n</i> )	1.918(4)	1.939(5)	1.953(3)	1.955(3)	1.999(8)	1.977(9)
N(1 <i>n</i> )–Co–N(2 <i>n</i> )	91.1(2)	93.0(2)	90.9(1)	90.8(1)	91.9(3)	91.3(4)
N(1 <i>n</i> )–Co–N(3 <i>n</i> )	84.1(2)	83.5(2)	85.0(1)	84.8(1)	85.3(3)	83.2(4)
N(3 <i>n</i> )–Co–N(2 <i>n</i> )	84.6(2)	83.5(2)	85.1(1)	84.8(1)	83.6(4)	85.3(4)

**Fig. 1** Views of the two independent [CoL<sup>3+</sup>]<sup>3+</sup> cations showing 30% probability ellipsoids: (a) cation 1 (*eq,eq* conformer) and (b) cation 2 (*eq,ax* conformer). The H atom defining the *eq* or *ax* conformation of the five-membered chelate ring is indicated

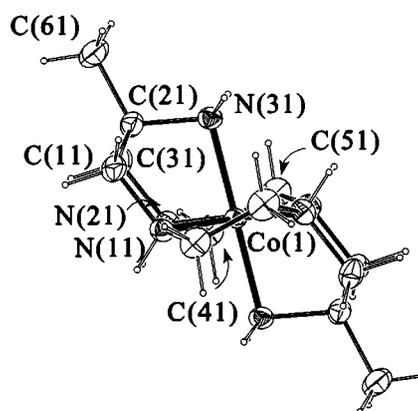
are evenly disordered between their two puckered conformations. We have observed similar disorder in the past and have shown<sup>16</sup> that it corresponds to a racemic mixture of two chiral conformers *eq,ax* and *ax,eq*, i.e. the five-membered chelate rings are staggered. The conformational differences result in slight variations in the co-ordinate bond lengths of the two cations (Table 2). In cation 1, there is a significant tetragonal compression, whereas the geometry of cation 2 is more symmetrical.

For comparison, the starting material was crystallised as its triperchlorate salt [CoL<sup>1+</sup>][ClO<sub>4</sub>]<sub>3</sub>. The crystal structure of the

**Table 3** Physical properties

	$\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$E/V$ vs. Ag–AgCl	Co–N <sub>mac</sub> , Co–N <sub>pend</sub> */Å
[CoL <sup>1+</sup> ] <sup>3+</sup>	447 (73), 328 (76)	–0.79	1.94, 1.95
[CoL <sup>3+</sup> ] <sup>3+</sup>	436 (78), 324 (92)	–0.71	1.95, 1.93
<i>meso</i> -[CoL <sup>5+</sup> ] <sup>3+</sup>	462 (77), 332 (90)	–0.63	1.94, 1.99
[CoL <sup>6+</sup> ] <sup>3+</sup>	454 (73), 326 (90)	–0.71	

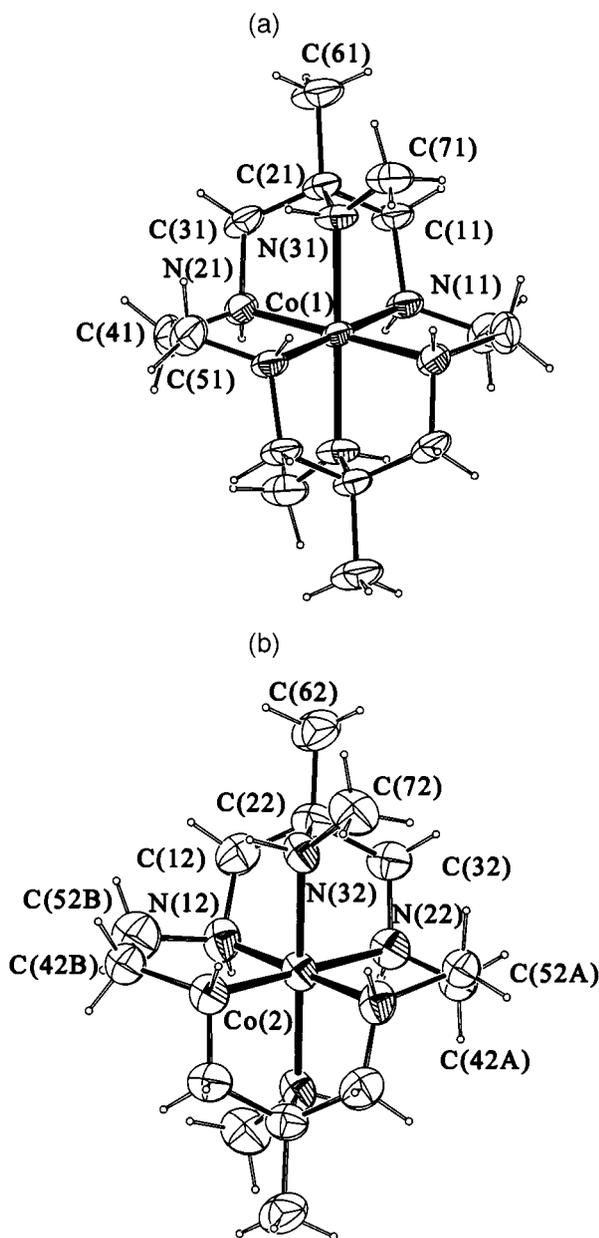
\* Averaged over both independent cations.

**Fig. 2** View of one of the two independent [CoL<sup>1+</sup>]<sup>3+</sup> cations showing 30% probability ellipsoids

mixed salt [CoL<sup>1+</sup>Cl<sub>2</sub>(ClO<sub>4</sub>) is known,<sup>2</sup> and in the present structure the complex cation exhibits essentially the same geometry (Fig. 2). The Co–N bond lengths in the two independent centrosymmetric cations (Table 2) are quite short by comparison with other hexaamminecobalt(III) ions. The crystal structure of this complex is isomorphous with those of other trivalent analogues: [ML<sup>1+</sup>][ClO<sub>4</sub>]<sub>3</sub> (M = Fe<sup>III</sup>,<sup>17</sup> Cr<sup>III</sup><sup>18</sup> or Rh<sup>III</sup>),<sup>19</sup> and also with the diimine [CoL<sup>3+</sup>][ClO<sub>4</sub>]<sub>3</sub>. Interestingly, no disorder of the five-membered chelate rings was found in the structure of [CoL<sup>1+</sup>][ClO<sub>4</sub>]<sub>3</sub> whereas all of the isomorphous trivalent analogues exhibited disorder. This illustrates that disorder of the chelate rings is not directed by lattice forces, but has its origins in the local co-ordination geometry. This supports earlier molecular mechanics predictions<sup>16</sup> that small metal ions such as Co<sup>III</sup> will prefer the *eq,eq* conformation, whereas larger ions such as Cr<sup>III</sup> and Rh<sup>III</sup> will favour the staggered *eq,ax* (*ax,eq*) conformation.

The crystal structure of *meso* [CoL<sup>5+</sup>][ClO<sub>4</sub>]<sub>3</sub>·2H<sub>2</sub>O again reveals two independent centrosymmetric complex cations with anions and water molecules on general sites. Cation 1 is found in the *eq,eq* conformation [Fig. 3(a)], and a significant tetragonal elongation is seen. By contrast, disorder in the macrocyclic five-membered chelate rings of cation 2 [Fig. 3(b)] is again indicative of a racemic mixture of the *eq,ax* and *ax,eq* conformers as discussed above. No significant elongation or compression is seen in cation 2.

Cyclic voltammetry of [CoL<sup>3+</sup>]<sup>3+</sup>, *meso*-[CoL<sup>5+</sup>]<sup>3+</sup> and [CoL<sup>6+</sup>]<sup>3+</sup> revealed totally reversible Co<sup>III/II</sup> redox couples (Table 3). An



**Fig. 3** Views of the two independent  $meso$ -[CoL<sup>3</sup>]<sup>3+</sup> cations showing 30% probability ellipsoids: (a) cation 1 (*eq,eq* conformer) and (b) cation 2 (*eq,ax* conformer)

anodic shift of *ca.* 80 mV in the redox potentials occurs with the addition of each successive N-methyl group to the parent [CoL<sup>1</sup>]<sup>3+</sup> complex. This was expected, as the inductive and steric effects of N-methyl groups are known to stabilise lower oxidation states. The [CoL<sup>3</sup>]<sup>3+/2+</sup> redox couple was also anodically shifted relative to [CoL<sup>1</sup>]<sup>3+/2+</sup> by *ca.* 100 mV. In this case we suggest that electronic effects are the dominant factor. By analogy with the electrochemistry of pyridine or bipyridine complexes of Co<sup>III</sup>, considerable stabilisation of the divalent state is found relative to saturated amines {*E*<sub>2</sub> [Co(bipy)<sub>3</sub>]<sup>3+/2+</sup> = +0.09 V vs Ag–AgCl},<sup>20</sup> and the observed anodic shift in the redox potential of [CoL<sup>3</sup>]<sup>3+</sup> relative to [CoL<sup>1</sup>]<sup>3+</sup> is consistent with this. As mentioned above, the diimine [CoL<sup>3</sup>]<sup>3+</sup> is susceptible to base-catalysed hydrolysis, so electrochemistry was performed at pH 5. However, below pH 4 all reversibility is lost as the transient [CoL<sup>3</sup>]<sup>2+</sup> ion (a labile species) is rapidly protonated. Therefore, one must work in a relatively narrow pH window in order to achieve both reversible electrochemistry and a stable imine complex.

The UV/VIS electronic spectra of [CoL<sup>1</sup>]<sup>3+</sup>, [CoL<sup>6</sup>]<sup>3+</sup> and *meso*-[CoL<sup>5</sup>]<sup>3+</sup> (Table 3) were only moderately sensitive to N-methylation of the primary amines. Nevertheless, successive red-shifts in the two maxima were found with increasing N-methylation. The spectrum of the diimine [CoL<sup>3</sup>]<sup>3+</sup> exhibited maxima at significantly higher energy than those of the starting material, and this reflects the stronger ligand field strength of imine donors relative to amines.

## Conclusion

The potential of [CoL<sup>3</sup>]<sup>3+</sup> as an electrophilic precursor to more intricate macrocyclic species is apparent. Although we have only investigated its reaction with hydride as the nucleophile in this work, a number of other reagents might be expected to add to the imine C atom of [CoL<sup>3</sup>]<sup>3+</sup>, such as anions of 'carbon acids' such as nitroalkanes and malonic esters. We have demonstrated that the physical properties of the N-methylated complexes *meso*-[CoL<sup>5</sup>]<sup>3+</sup> and [CoL<sup>6</sup>]<sup>3+</sup> are perturbed from those of the parent hexaamine [CoL<sup>1</sup>]<sup>3+</sup>. That is, the unusual physical and structural properties exhibited by [CoL<sup>1</sup>]<sup>3+</sup> (high energy electronic maxima, short Co–N bond lengths, large negative redox potential)<sup>2</sup> are tempered somewhat by alkylation of the co-ordinated amines. The synthetic utility of this method promises to be a useful tool in the further elaboration of pendant arm macrocycles and their complexes.

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## References

- 1 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
- 2 P. V. Bernhardt, T. W. Hambley and G. A. Lawrance, *J. Chem. Soc., Dalton Trans.*, 1989, 1059.
- 3 M. Tobe, C. K. Poon and B. Bosnich, *Inorg. Chem.*, 1965, **4**, 1102.
- 4 P. V. Bernhardt, L. A. Jones and P. C. Sharpe, *J. Chem. Soc., Dalton Trans.*, 1997, 1169.
- 5 N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3.
- 6 A. Höhn, R. J. Geue, A. M. Sargeson and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1989, 1648.
- 7 L. Fabbri, M. Licchelli, A. M. Manotti Lanfredi, O. Vassalli and F. Ugozzoli, *Inorg. Chem.*, 1996, **35**, 1582.
- 8 P. V. Bernhardt, *J. Chem. Soc., Dalton Trans.*, 1996, 4319.
- 9 P. V. Bernhardt, J. C. Hetherington and L. A. Jones, *J. Chem. Soc., Dalton Trans.*, 1996, 4325.
- 10 S. R. Hall, H. D. Flack and J. M. Stewart (Editors), *The XTAL3.2 User's Manual*, Universities of Western Australia, Geneva, and Maryland, 1992.
- 11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 12 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Göttingen, 1993.
- 13 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 14 P. V. Bernhardt, P. Comba and T. W. Hambley, *Inorg. Chem.*, 1993, **32**, 2804.
- 15 P. V. Bernhardt, K. A. Byriel, C. H. L. Kennard and P. C. Sharpe, *Inorg. Chem.*, 1996, **35**, 2045.
- 16 P. V. Bernhardt and P. Comba, *Helv. Chim. Acta*, 1991, **74**, 1834.
- 17 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Chem. Commun.*, 1989, 553.
- 18 P. V. Bernhardt, P. Comba, N. F. Curtis, T. W. Hambley, G. A. Lawrance, M. Maeder and A. Siriwardena, *Inorg. Chem.*, 1990, **29**, 3208.
- 19 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1990, 983.
- 20 M. J. Weaver and S. M. Nettles, *Inorg. Chem.*, 1980, **19**, 1641.

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