

Synthesis and variable coordination modes of a bis-thiophene-appended macrocycle in complex with cobalt(III)

Sharizal Hasan · Paul V. Bernhardt

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Abstract The bis-thiophene appended cyclam derivative L^3 (*trans*-6,13-dimethyl-6,13-bis(thiophene-3'-yl-methylamino)-1,4,8,11-tetraazacyclotetradecane) has been synthesised, characterised and complexed with Co^{III} . The crystal structure of the diprotonated ligand as its cyanoborohydride salt $[H_2L^3][NCBH_3]_2$ is reported. Variable coordination modes to Co^{III} have been identified that find the ligand binding either as a tetradentate (cyclam-like) macrocycle in the structurally characterised complexes *trans*- $[CoL^3Cl_2]Cl$ and *trans*- $[CoL^3(NCBH_3)(OH)]Cl$ or as a hexadentate in $[CoL^3]Cl_3$ where both functionalised exocyclic amines coordinate in *trans* coordination sites. In this case, we have found that the structure of the hexadentate coordinated complex $[CoL^3]^{3+}$ is significantly tetragonally elongated due to steric effects of the thiophene rings and this also leads to a very large 500 mV anodic shift in the $Co^{III/II}$ redox potential relative to the unsubstituted hexaamine complex of Co^{III} .

Keywords Macrocycle · Hexaamine · Thiophene · Cobalt

Introduction

Polythiophene based materials due to their high conductivity have been found to possess a wide range of

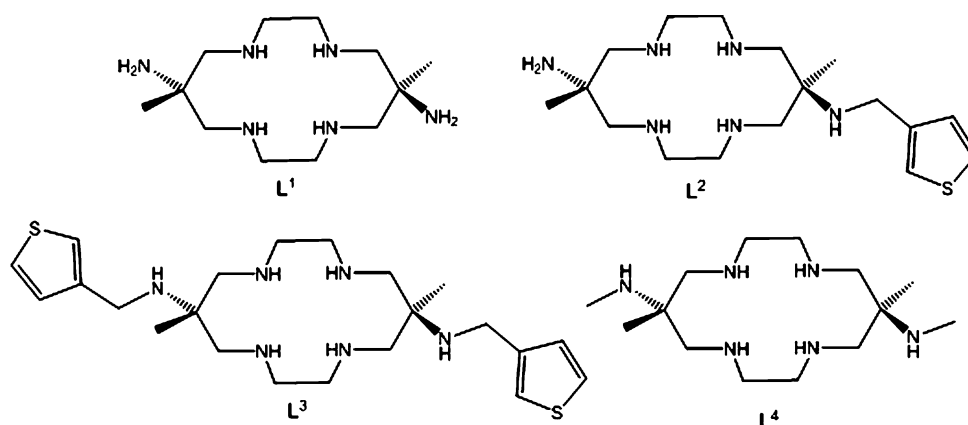
remarkable and useful properties [1–5]. The construction of hybrid polythiophene materials that incorporate redox active transition metal ions add an extra dimension to their electronic properties [6–10] but this demands appropriately constructed bifunctional ligands which can bind a metal ion tightly whilst also bearing a thiophene ring (unsubstituted in the 2- and 5-positions) which may be co-polymerised with a thiophene monomer.

Our own efforts to date have been based on derivatives of L^1 (Scheme 1) synthesised by selective reductive alkylation of a single exocyclic primary amine with thiophene-3-carbaldehyde using cyanoborohydride ($NCBH_3^-$) as the reductant to generate the monofunctionalised ligand L^2 [11]. We have employed chemistry of this type in a number of cases (with different aldehydes) to generate selectively functionalised macrocycles in good yield without the need for any protecting group chemistry [12–16]. A key to the success of this reaction is that $NCBH_3^-$ (unlike BH_4^-) is moderately stable in the presence of water and also reduces imines much more rapidly than aldehydes. Therefore, $NCBH_3^-$ may be present from the outset where it will preferentially reduce the intermediate imine formed gradually during the reaction while being much less reactive toward any aldehyde present.

The monosubstituted ligand L^2 , its Co^{III} coordination chemistry and preliminary electropolymerisation results leading to a polythiophene co-polymer have been published [11]. The focus of this paper is the di-substituted ligand L^3 and we will show that it is rather unusual in favouring either tetradentate or hexadentate coordination which is in contrast to L^2 which exclusively binds as a pentadentate ligand, with the substituted exocyclic amine remaining uncoordinated.

S. Hasan · P. V. Bernhardt (✉)
School of Chemistry and Molecular Biosciences, University of
Queensland, Brisbane 4072, Australia
e-mail: p.bernhardt@uq.edu.au

Scheme 1 Line drawings of macrocyclic ligands in this work



Experimental section

Safety note

Na(NCBH₃) liberates HCN upon acidification and so its reactions must be conducted in a well ventilated fume hood.

Syntheses

The parent ligand *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine hexahydrochloride (L¹·6HCl) was synthesised as described previously [17]. The Co precursor Na₃[Co(CO₃)₃]·3H₂O was prepared according to a literature synthesis [18]. All other reagents were obtained commercially.

Metal free ligands

[H₂L³][NCBH₃]₂

The hexamine L¹·6HCl (4.77 g) was suspended in EtOH:H₂O (9:1 v/v, 300 mL) and the apparent pH was adjusted to 5.5 with NaOH (3 M) to give a clear solution. Solid Na(NCBH₃) (1.88 g) was added and the pH was again readjusted to 5.5 with NaOH solution. Thiophene-3-carbaldehyde (0.91 mL) was added with stirring. The apparent pH increased during the course of the reaction and was periodically readjusted to pH 5.5 by addition of aliquots of dilute HCl (1 M) over the first 3 h of the reaction. The mixture was stirred at room temperature for a total of 16 h. A precipitate of crude [H₂L³][NCBH₃]₂ was filtered off (1.01 g). Recrystallisation of a small amount of this compound from hot MeOH produced crystals of [H₂L³][NCBH₃]₂ suitable for X-ray work. The filtrate contained a mixture of L² and other by-products. The isolation and characterisation of L² has been reported elsewhere [11].

Free base L³

A sample of crude [H₂L³][NCBH₃]₂ (2.6 g combined from several syntheses) was dissolved in hot MeOH (20 mL) and diluted to 250 mL with water. The pH of the solution was increased to *ca.* 12 with NaOH solution (3 M). Methanol was removed by rotary evaporation and the alkaline solution was extracted with CH₂Cl₂ (3 × 75 mL). The combined extracts were dried and evaporated at reduced pressure to leave an oil (1.05 g). The oil was re-dissolved in CH₂Cl₂ (10 mL) and 50 mL MeCN added. The CH₂Cl₂ solvent was evaporated at reduced pressure, and Et₂O (50 mL) was added, resulting in precipitation of the desired product L³ in its free base form. Calcd. for C₂₂H₄₀N₆OS₂ (monohydrate): C 56.4, H 8.6, N 17.9, S 13.7. Found: C 56.8; H 8.3, N 18.3, S 13.4%. ¹H NMR (CDCl₃): δ (ppm) 1.22 (s, 6H), 2.30 (m, 6H), 2.60–2.80 (m, 16H), 3.88 (s, 4H), 7.18 (dd, 2H), 7.32 (dd, 2H), 7.42 (dd, 2H).

Co^{III} complexes

The protonated ligand [H₂L³][NCBH₃]₂ (2.50 g) was dissolved in hot methanol (50 mL). Water (500 mL) was added to the solution and the pH was adjusted to *ca.* 8–9. Solid Na₃[Co(CO₃)₃]·3H₂O (1.80 g) was added and the mixture was stirred at 60 °C for 16 h. The solution was filtered and the filtrate was diluted to approximately 10 L with water and charged on a Sephadex C-25 column (Na⁺ form). Elution with NaCl solution (at the concentrations shown) gave the following 2 bands.

trans-[CoL³(OH)(NCBH₃)]Cl·3H₂O (band 1)

A minor red band eluted with 0.1 M NaCl. After concentration to low volume on a rotary evaporator red crystals of *trans*-[CoL³(OH)(NCBH₃)]Cl·3H₂O suitable for X-ray work formed on standing and were collected by filtration. Further crops were collected from the solution (0.11 g). Calcd. for C₂₃H₅₀BClCoN₇O₅S₂ (tetrahydrate): C 41.0, H

7.5, N 14.6, S 9.5. Found: C 40.3, H 7.2, N 14.4, S 9.3%. ^1H NMR (D_2O): δ (ppm) 1.21 (s, 3H), 1.28 (s, 3H), 2.3–2.7 (m, 16H), 3.85 (s, 2H), 3.90 (s, 2H), 7.18 (d, 1H), 7.30 (d, 1H), 7.40 (d, 1H), 7.47 (m, 2H), 7.49 (d, 1H). Electronic spectrum (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 550 sh (ϵ 45), 486 (ϵ 74), 380 (ϵ 130).

$[\text{CoL}^3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (band 2)

The major orange band from the column eluted with 1.0 M NaCl and upon concentration afforded needle-like orange crystals of $[\text{CoL}^3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ after slow evaporation over several days (0.315 g). Calcd. for $\text{C}_{22}\text{H}_{50}\text{Cl}_3\text{CoN}_6\text{O}_6\text{S}_2$ (hexahydrate): C 36.5, H 7.0, N 11.6, S 8.9. Found: C 36.6, H 7.0, N 11.6, S 8.6%. ^1H NMR (D_2O): δ (ppm) 1.12 (s, 6H), 3.01 (d, 2H), 3.26–3.36 (m, 6H), 3.58–3.61 (m, 4H), 3.88 (s, 4H), 4.15 (d, 4H), 7.39 (dd, 2H), 7.67 (s, 2H), 7.74 (dd, 2H). Electronic spectrum (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 486 (ϵ 120).

trans- $[\text{CoL}^3\text{Cl}_2]\text{Cl} \cdot 1/6\text{H}_2\text{O}$

To a gently warmed solution of $[\text{H}_2\text{L}^3][\text{NCBH}_3]_2$ (0.4 g) in MeOH (60 mL) was added $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 g) with stirring. The mixture turned deep red over the course of 2 min. Concentrated HCl (0.5 mL) was then added and the colour of the solution slowly changed from red to green. Water (1 mL) was added and the solution was to evaporated slowly at room temperature and a green precipitate of the hydrate formed which was filtered off and washed with MeOH and Et_2O . Crystals of *trans*- $[\text{CoL}^3\text{Cl}_2]\text{Cl} \cdot 1/6\text{H}_2\text{O}$ (or alternatively $6\{\textit{trans}\text{-}[\text{CoL}^3\text{Cl}_2]\text{Cl}\} \cdot \text{H}_2\text{O}$) suitable for X-ray work were obtained by recrystallisation from MeOH/MeCN (1:1). Calcd. for $\text{C}_{22}\text{H}_{58}\text{Cl}_3\text{CoN}_6\text{O}_{10}\text{S}_2$ (decahydrate): C 33.2, H 7.3, N 10.6, S 8.1. Found: C 33.5, H 6.7, N 10.6, S 7.7%. ^1H NMR (DMSO- d_6): δ (ppm) 1.70 (s, 6H), 2.86 (m, 4H), 3.04 (m, 4H), 3.20 (m, 4H), 3.42 (m, 4H), 4.34 (s, 4H), 7.56 (m, 2H), 7.68 (m, 2H), 7.95 (m, 2H). Electronic spectrum (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 450 (ϵ 24), 626 (ϵ 26).

Physical methods

Electronic spectra were recorded on an AnalytikJena Specord spectrophotometer. ^1H Nuclear magnetic resonance spectra were measured on a Bruker AC400 spectrometer. Samples run in D_2O were referenced through the addition of sodium(trimethylsilyl)propionate while spectra run in CDCl_3 or DMSO- d_6 were referenced to residual undeuterated solvent peaks and cited versus TMS. Cyclic voltammetry was performed with a BAS100B/W potentiostat utilising a Pt auxiliary electrode, Ag/AgCl reference

electrode (+196 mV vs. NHE) and a glassy carbon working electrode. Solutions contained approximately millimolar concentrations of analyte and 0.1 M NaNO_3 as supporting electrolyte in $\text{H}_2\text{O}:\text{DMSO}$ (7:3 v/v), and were purged with nitrogen before measurement.

Crystallography

For the crystal structures of $[\text{H}_2\text{L}^3][\text{NCBH}_3]_2$, *trans*- $[\text{CoL}^3\text{Cl}_2]\text{Cl} \cdot 3\text{H}_2\text{O}$ and $[\text{CoL}^3]\text{Cl}_3$, intensity data at 293 K were collected on an Oxford Diffraction Gemini Ultra S CCD diffractometer with Mo- $\text{K}\alpha$ radiation (λ 0.71073 Å) operating in the ω scan mode. For *trans*- $[\text{CoL}^3(\text{NCBH}_3)(\text{OH})]\text{Cl} \cdot 3\text{H}_2\text{O}$ data were collected on the same instrument with the brighter Cu- $\text{K}\alpha$ Enhance Ultra source (λ 1.5418 Å). Data reduction and empirical absorption corrections were performed with the CrysAllis package (Oxford Diffraction, vers. 171.33.34d).

All structures were solved with SHELXS86 and refined by a full-matrix least-squares analysis with SHELXL-97 [19]. All non-hydrogen atoms were modelled with anisotropic thermal parameters except those involved in thiophene ring disorder. Hydrogen atoms were included for non-coordinated water molecules where apparent from the difference map. All other H atoms were included at estimated positions using a riding model. Thermal ellipsoid drawings were prepared with ORTEP3 [20] and conventional plots with PLUTON [21]. The SHELX programs and ORTEP3 were run within the integrated WinGX package [22]. Crystal data have been deposited in CIF format with the Cambridge Crystallographic Data Centre (CCDC Nos. 733640–733643) and may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data

$[\text{H}_2\text{L}^3][\text{NCBH}_3]_2$

($\text{C}_{24}\text{H}_{46}\text{B}_2\text{N}_8\text{S}_2$), $M_r = 532.43\text{ g mol}^{-1}$; colourless, $0.4 \times 0.3 \times 0.2\text{ mm}^3$, monoclinic, $P2_1/n$ (No. 14, variant of $P2_1/c$), $a = 11.4849(8)\text{ Å}$, $b = 8.8858(6)\text{ Å}$, $c = 15.478(1)\text{ Å}$, $\beta = 105.172(7)^\circ$, $V = 1524.5(2)\text{ Å}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.16\text{ g cm}^{-3}$, $\theta_{\text{max}} = 25^\circ$, λ (Mo $\text{K}\alpha$) = 0.71073 Å, $T = 293\text{ K}$, 2647 independent reflections ($R_{\text{int}} = 0.030$), $R = 0.0580$ (for 1051 observed reflections $I > 2\sigma(I)$) $wR_2 = 0.1626$ (all data). CCDC No. 733640.

trans- $[\text{CoL}^3(\text{NCBH}_3)(\text{OH})]\text{Cl} \cdot 3\text{H}_2\text{O}$

($\text{C}_{23}\text{H}_{48}\text{BClCoN}_7\text{O}_4\text{S}_2$), $M_r = 655.99\text{ g mol}^{-1}$; red, $0.4 \times 0.2 \times 0.05\text{ mm}^3$, orthorhombic, $P2_12_12_1$ (No. 19),

$a = 35.856(3) \text{ \AA}$, $b = 19.333(1) \text{ \AA}$, $c = 9.2791(6) \text{ \AA}$, $V = 6432.4(8) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calc}} = 1.355 \text{ g cm}^{-3}$, $\theta_{\text{max}} = 62^\circ$, $\lambda(\text{Cu K}\alpha) = 1.54180 \text{ \AA}$, $T = 293 \text{ K}$, 8299 independent reflections ($R_{\text{int}} = 0.0935$), $R = 0.0663$ (for 3142 observed reflections $I > 2\sigma(I)$) $wR_2 = 0.1632$ (all data). CCDC No. 733641.

trans-[CoL³Cl₂]Cl·1/6H₂O

(C₂₂H_{38.33}Cl₃CoN₆O_{0.17}S₂), $M_r = 618.99 \text{ g mol}^{-1}$; green, $0.4 \times 0.2 \times 0.1 \text{ mm}^3$, monoclinic, $P2_1/c$ (No. 14), $a = 14.786(1) \text{ \AA}$, $b = 22.939(2) \text{ \AA}$, $c = 24.920(2) \text{ \AA}$, $\beta = 93.936(7)^\circ$, $V = 8432(1) \text{ \AA}^3$, $Z = 12$, $\rho_{\text{calc}} = 1.463 \text{ g cm}^{-3}$, $\theta_{\text{max}} = 25^\circ$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $T = 293 \text{ K}$, 14 234 independent reflections ($R_{\text{int}} = 0.1199$), $R = 0.0832$ (for 3860 observed reflections $I > 2\sigma(I)$) $wR_2 = 0.2041$ (all data). CCDC No. 733642.

[CoL³]Cl₃·4H₂O

(C₂₂H₄₆Cl₃CoN₆O₄S₂), $M_r = 688.05 \text{ g mol}^{-1}$; orange, $0.3 \times 0.3 \times 0.2 \text{ mm}^3$, triclinic, $P\bar{1}$ (No. 2), $a = 8.5582(6) \text{ \AA}$, $b = 9.0480(5) \text{ \AA}$, $c = 11.6054(6) \text{ \AA}$, $\alpha = 104.073(5)^\circ$, $\beta = 102.418(5)^\circ$, $\gamma = 108.825(6)^\circ$, $V = 781.76(8) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calc}} = 1.461 \text{ g cm}^{-3}$, $\theta_{\text{max}} = 25^\circ$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $T = 293 \text{ K}$, 2750 independent reflections ($R_{\text{int}} = 0.0254$), $R = 0.0566$ (for 2156 observed reflections $I > 2\sigma(I)$) $wR_2 = 0.1941$ (all data). CCDC No. 733643.

Results and discussion

Synthesis and characterisation

The hexaamine macrocycle L¹ underwent reductive alkylation in the presence of 3-thiophenecarbaldehyde and sodium cyanoborohydride in aqueous EtOH to give both the mono- (L²) and bis-thiophenemethyl substituted (L³) macrocycles. The Co^{III} coordination chemistry of L² has been reported elsewhere [11]. Although the ratio of the parent hexamine L¹ to 3-thiophenecarbaldehyde was 1:1, the disubstituted ligand L³ was still produced in significant quantities due to its limited solubility relative to L². This facilitated separation of L² and L³ during the synthesis and L³ was obtained directly as its diprotonated cyanoborohydride salt [H₂L³][NCBH₃]₂. The free base L³ was readily obtained by extracting the ligand from alkaline solution into CH₂Cl₂. The synthesis of L³ has not been optimised further as both ligands L² and L³ may be easily isolated from one another and each are useful for different purposes.

The Co^{III} complexes were synthesised by simple substitution reactions with either the Co^{III} precursor [Co(CO₃)₃]³⁻ or Co^{II} in the presence of excess chloride to

preferentially form the compound *trans*-[CoL³Cl₂]⁺; a synthesis derived from that published for *trans*-[Co(cyclam)Cl₂]Cl [23]. The *trans* geometric isomers were found in all cases as is typical of Co^{III} cyclam chemistry. All *cis*-[Co^{III}(cyclam)(X)(Y)] complexes slowly isomerise to the *trans* isomer [24, 25] unless this is prevented by a chelating co-ligand occupying a *cis* pair of coordination sites [26] or pendent arms attached to the cyclam core [27]. The electronic spectra of Co^{III} complexes are very sensitive to variations in donor atoms and the energies of the visible *d-d* maxima and ligand field splitting varied accordingly. As expected, splitting of the lowest energy ¹T_{1g} ← ¹A_{1g} (O_h) band under the influence of a tetragonal distortion of the ligand field is greatest when weak field ligands such as Cl⁻ occupy the axial coordination sites juxtaposed with the strong field equatorially coordinated amines. As an example, the spectrum of *trans*-[CoL³Cl₂]⁺ (a *trans*-Co^{III}N₄Cl₂ chromophore) in DMSO revealed a large splitting of the ¹T_{1g} state (giving transitions to the ¹A_{2g} and ¹E_g states) whilst this splitting was diminished in *trans*-[CoL³(NCBH₃)(OH)]⁺ (Co^{III}N₅Cl) and unresolved in the Co^{III}N₆ complex [CoL³]³⁺.

Crystal structures

The crystal structure of [H₂L³][NCBH₃]₂ was determined. The diprotonated free ligand is situated on a centre of symmetry and the two anions occupy symmetry related positions above and below the macrocyclic plane. A view of the cation alone is shown in Fig. 1 (left). The sites of protonation are N2 and its inversion related N2' (symmetry operation $-x + 1, -y + 1, -z$) and these NH₂⁺ groups donate H-bonds to two other atoms within the macrocyclic ring, namely N1, N1'. A similar protonation scheme has been found in the crystal structure of the diprotonated parent hexaamine [H₂L¹][ClO₄]₂ [28]. A weaker H-bonding contact is made to the pendent amine N3. All of these non-covalent forces stabilise the conformation of the macrocyclic ring and also define the disposition of the exocyclic amine. The NCBH₃⁻ anions have no significant H-bonding contacts with the macrocycle.

A feature of the structure is disorder of the 3-thiophenylmethyl group. Two orientations were identified and refined with complementary occupancies (78:22%; Fig. 1, right). They are related by a 180° about the C7–C8 bond and also two different locations were resolved for the methylene groups (C7 and C7'). The disorder extends no further than this methylene group and the rest of the macrocyclic ring is ordered.

The crystal structure of *trans*-[CoL³(OH)(NCBH₃)]Cl·3H₂O was determined. The structure comprises two independent cations on general sites in addition to chloride and water molecules. A view of one of the Co complex cations is

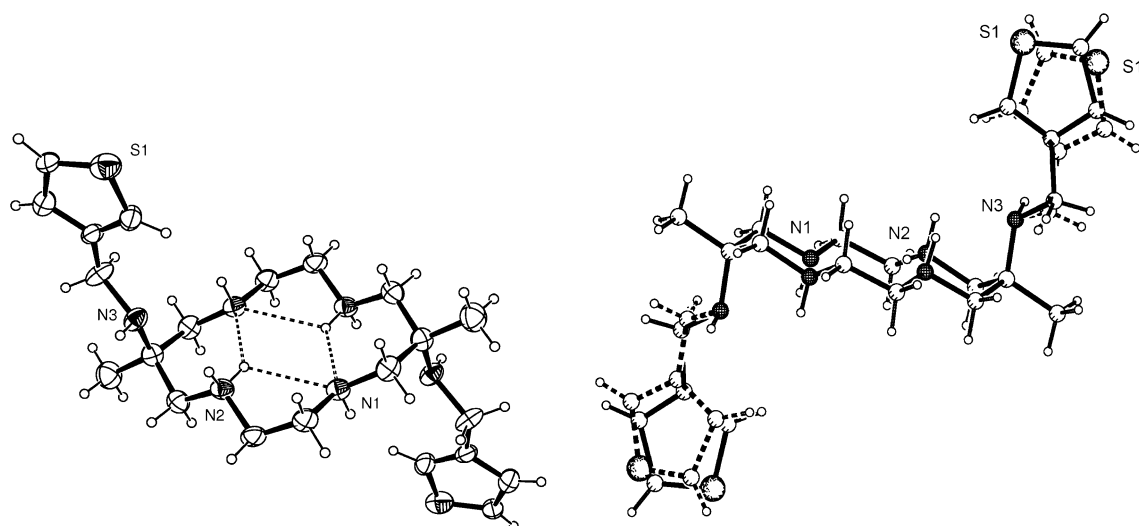


Fig. 1 ORTEP3 view of the $[\text{H}_2\text{L}^3]^{2+}$ cation (*left*; 30% probability ellipsoids) showing intramolecular H-bonding (*right*) PLUTON view showing thiophene disorder

shown in Fig. 2. The novel N-bound cyanoborohydride ligand is apparent and coordinates in an axial coordination site *trans* to the hydroxo ligand. The macrocycle coordinates in a tetradentate mode and the exocyclic amines occupy axial positions, which is the so-called α -isomeric form (see Scheme 2). The conformation of the macrocycle is very similar to that found in the protonated free ligand $[\text{H}_2\text{L}^3][\text{NCBH}_3]$ (Fig. 1).

No other N-bound cyanoborohydride complexes of Co^{III} have been structurally characterised and few have even been synthesised. Those extant comprise the series $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{NCBH}_2\text{R})]^{2+}$ (where $\text{R} = \text{PPh}_3, \text{py}$ and NEt_3) [29]. The only crystallographically characterised cyanoborohydride

complexes of Co are $[\text{Co}^{\text{II}}(\text{DMF})_4(\text{NCBH}_3)_2]$ [30] and $[\text{HCo}^{\text{II}}(\text{PPh}_3)_3(\text{NCBH}_3)]$ [31]. The cyanoborohydride ligand is isoelectronic with MeCN and indeed the Co-N7A/B coordinate bonds (1.91(1) and 1.92(1) Å) are similar to those found in N-bound MeCN complexes of Co^{III} [32–34]. The macrocyclic Co-N bonds (1.93(1)–1.97(1) Å) are typical of Co^{III} cyclam complexes in a *trans* isomeric form [35–37]. The shortest coordinate bond is to the hydroxo ligand (~ 1.88 Å). H-bonds abound in the structure involving the water molecules, amine H-atoms and Cl^- anions. As seen in the structure of $[\text{H}_2\text{L}^3][\text{NCBH}_3]_2$, the relatively non-polar B–H bonds are not involved in any H-bonding contacts.

The related compound *trans*- $[\text{CoL}^3\text{Cl}_2]\text{Cl}\cdot 1/6\text{H}_2\text{O}$ was also structurally characterised. The structure comprises four crystallographically independent complex cations in the asymmetric unit; two on centres of inversion and two on general sites. In each independent complex, the ligand binds as a tetradentate and chloro ligands occupy the axial coordination sites. Thiophene disorder is again present. The Co-N (1.91–1.97 Å) and Co-Cl (2.25–2.27 Å) coordinate bonds span a range of values due to the number of independent molecules in the asymmetric unit and perhaps also an affect of disorder in the coordinated ligands, but these bonds are comparable with those found in the crystal structure of *trans*- $[\text{Co}(\text{cyclam})\text{Cl}_2]\text{Cl}$ [35]. In all complex cations, the pendent amines are axially disposed (α -isomeric form). The conformations of the 3-thiophenylmethyl groups vary. The complex cations labelled ‘A’ (shown in Fig. 3, left) and B, which reside on general positions, share an identical asymmetric conformation where one thiophene ring is orthogonal to the CoN_4 plane while the other is almost parallel with the plane. In contrast, the two centrosymmetric cations ‘C’ (Fig. 3, right) and ‘D’ find both

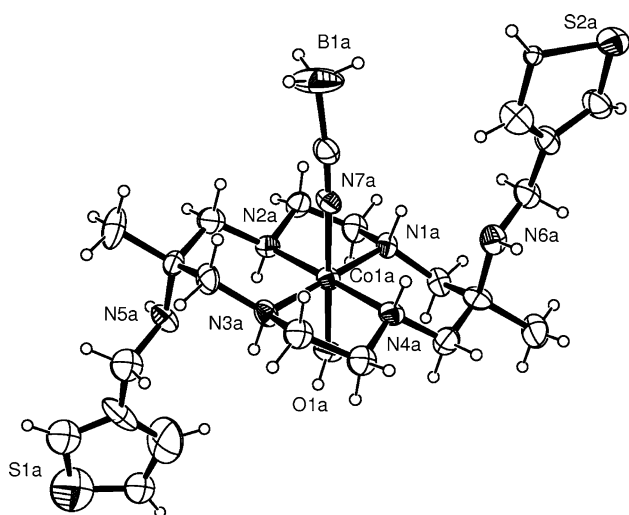


Fig. 2 ORTEP3 view of one of the two independent *trans*- $[\text{CoL}^3(\text{NCBH}_3)(\text{OH})]^+$ cations (30% probability ellipsoids). Thiophene disorder not shown for clarity. The α -isomeric form is present

Scheme 2 The N-based isomeric forms of a tetradentate coordinated disubstituted macrocycle

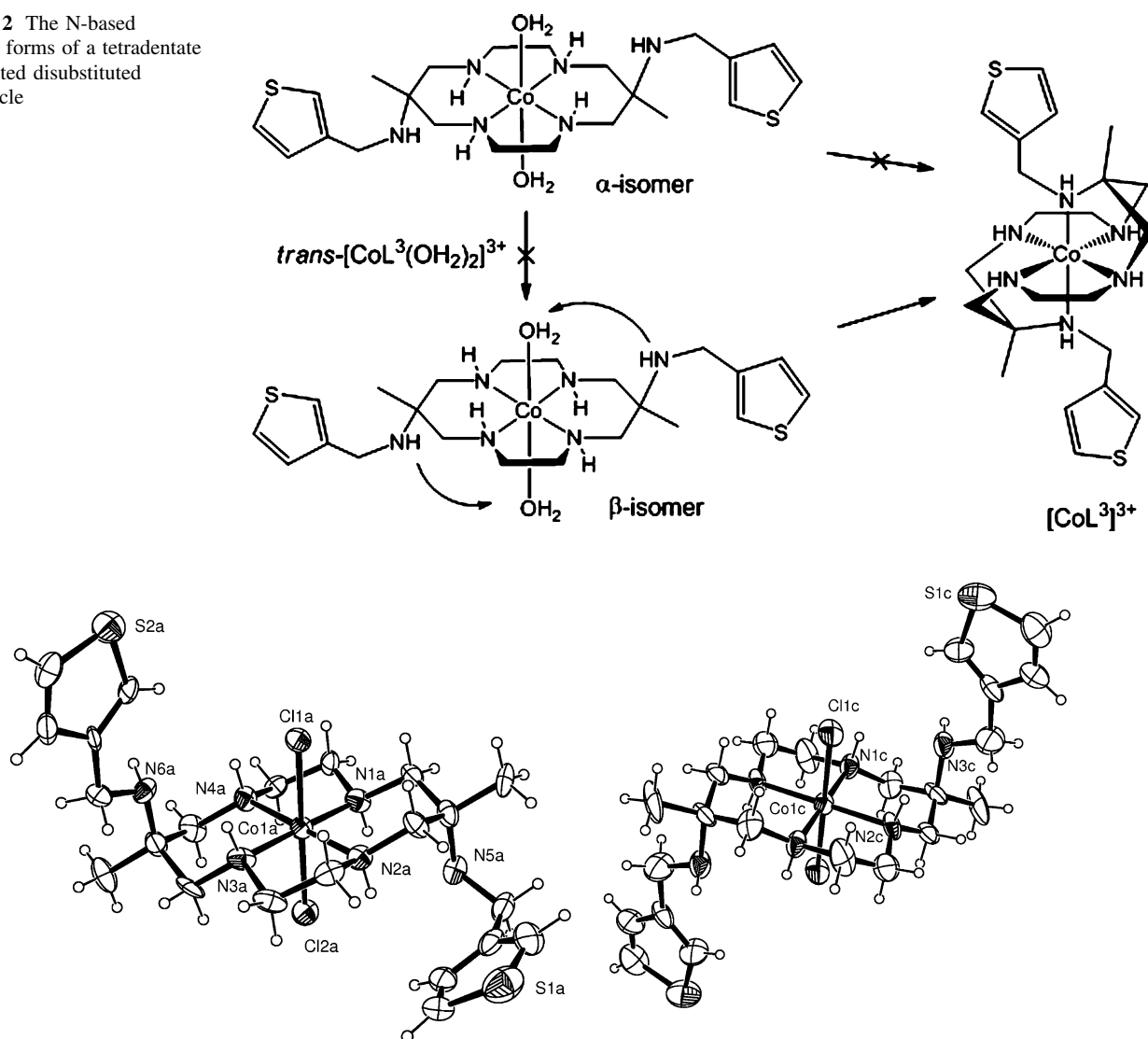


Fig. 3 ORTEP3 views of two (from four) independent $trans\text{-}[\text{CoL}^3\text{Cl}_2]^+$ cations (30% probability ellipsoids). The molecule on the right occupies a centre of symmetry while that on the left is on a general site (note different orientations of the thiophene groups)

thiophene rings orthogonal to the macrocyclic plane. The Co–N coordinate bonds do not differ significantly from those found in the structure of $trans\text{-}[\text{CoL}^3(\text{NCBH}_3)(\text{OH})]\text{Cl}\cdot 3\text{H}_2\text{O}$.

The complex $[\text{CoL}^3]\text{Cl}_3$ exhibits a distinctly different structure to the tetradentate coordinated complexes discussed above. The complex cation is situated on a centre of inversion and one chloride ion is disordered over two sites. As shown in Fig. 4 all six N-donors are coordinated and the centrosymmetric *meso* isomer is found where the coordinated pendent secondary amines have the same chirality. The coordination sphere exhibits a marked tetragonal elongation. The equatorial Co–N bonds (Co–N1 1.927(4) and Co–N2 1.942(4) Å) are much shorter than the axial coordinate bonds (Co–N3 2.030(3) Å) despite the fact that all are secondary amines. We attribute this to steric

influences of the thiophene ring that draw the axially coordinated amine away from the metal. The Co–N bond lengths of the parent complex $[\text{CoL}^1]^{3+}$ (characterized as its chloride/perchlorate [17] and perchlorate salts [38]) are all in the range 1.94–1.95 Å. The pendent N-methylated analog L^4 provides a useful comparison and the crystal structure of *meso*- $[\text{CoL}^4](\text{ClO}_4)_3$ revealed a less pronounced axial elongation (Co–N_{eq} 1.93–1.95 Å and Co–N_{ax} 1.98–2.00 Å) [38].

Electrochemistry

A key property of the thiophene-appended complexes is their $\text{Co}^{\text{III/II}}$ redox potential if ultimately these compounds are to be incorporated into redox active polythiophene films. Cyclic voltammetry in 50% aqueous DMSO was

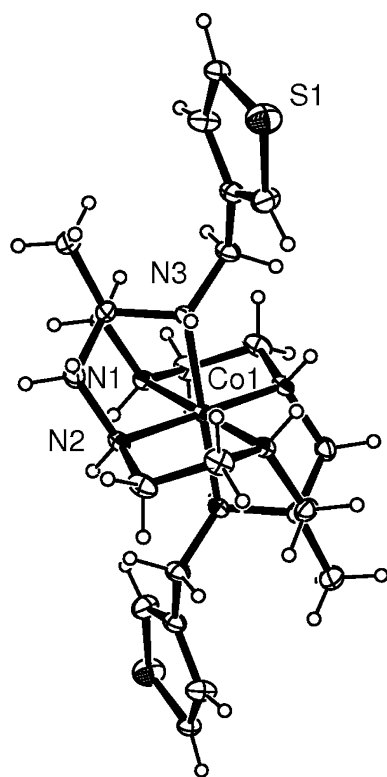


Fig. 4 ORTEP3 view of $[\text{CoL}^3]^{3+}$ cation (30% probability ellipsoids). Hexadentate coordination of the ligand is apparent

undertaken with the Co complexes reported herein. The monodentate chloro and cyanoborohydride ligands in $\text{trans-}[\text{CoL}^3\text{Cl}_2]^+$ and $\text{trans-}[\text{CoL}^3(\text{NCBH}_3)(\text{OH})]^+$ dissociate upon reduction to Co^{II} and their $\text{Co}^{\text{III/II}}$ redox couples were consequently irreversible. Cyclic voltammetry was performed on the hexaamine $[\text{CoL}^3]^{3+}$ and compared with that of the parent hexaamine $[\text{CoL}^1]^{3+}$. A most remarkable result was obtained from the hexaamine complex $[\text{CoL}^3]^{3+}$ which exhibited a totally reversible $\text{Co}^{\text{III/II}}$ couple at an unusually high formal potential of -211 mV versus Ag/AgCl (Fig. 5). By comparison, the redox potential of the parent unsubstituted complex $[\text{CoL}^1]^{3+/2+}$ measured under the same conditions (50% aqueous DMSO) was -730 mV versus Ag/AgCl; a value that is similar to that reported previously in water in the presence of various supporting electrolytes [17, 38–40]. The approximately 500 mV anodic shift in redox potential is truly remarkable given the structural similarities of $[\text{CoL}^1]^{3+}$ and $[\text{CoL}^3]^{3+}$.

A clue to the different redox potentials lies in the marked axial elongation of the Co–N coordinate bonds identified in the structure of $[\text{CoL}^3]^{3+}$ (Co–N3 2.03 Å *cf.* Co–N1/2 1.93 Å) whereas the Co–N bonds in the parent $[\text{CoL}^1]^{3+}$ are essentially the same (Co–N_{ax} 1.95 Å *cf.* Co–N_{eq} 1.94 Å) [17, 38]. This weakening of the axially coordinated donor atoms in $[\text{CoL}^3]^{3+}$ is also reflected in

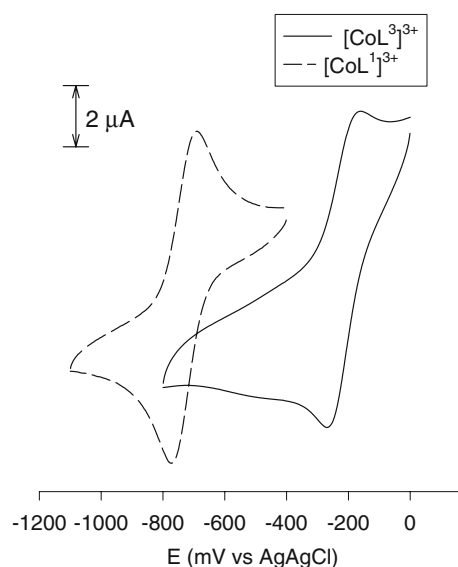


Fig. 5 Cyclic voltammograms of $[\text{CoL}^1]^{3+}$ (broken curve) and $[\text{CoL}^3]^{3+}$ (solid curve). Experimental conditions: sweep rate 100 mV s^{-1} , 1 mM analyte in 50% aqueous DMSO and 0.1 M NaNO_3 as supporting electrolyte

the $d-d$ electronic maximum of $[\text{CoL}^3]^{3+}$ (486 nm) compared with that of $[\text{CoL}^1]^{3+}$ (447 nm) [17]. These properties show that the preferred metal ion size of L^3 coordinated as a hexadentate is much greater than that of L^1 particularly along the axial coordination sites. Put another way, the larger Co^{II} ion is better accommodated within the expanded cavity size of L^3 and this leads to a more positive $\text{Co}^{\text{III/II}}$ redox potential.

Conclusions

The hexaamine ligand L^3 has been isolated and characterized for the first time. We have shown that it is capable of acting as either a tetradentate or hexadentate ligand in complex with Co^{III} although no pentadentate coordinated complexes were observed in this case. The hexadentate $[\text{CoL}^3]^{3+}$ is the first example of a hexaamine complex resulting from complexation of an N-functionalised derivative of L^1 . All other examples we have studied to date (including mono-substituted ligands like L^2 or disubstituted ligands like L^3) have precluded coordination of the substituted exocyclic amine.

It is not obvious why L^3 is able to bind as a hexadentate as opposed to other benzylic-functionalised analogues but the thiophenylmethyl ring is seemingly less sterically demanding and the substituted amine is still able to coordinate in the axial coordination site of Co^{III} . Other derivatives of L^1 where the pendent amine has undergone reductive alkylation (or benzylation) [15, 16] do not coordinate as a hexadentate but instead the substituted amines

remain free from the metal as seen here in the structures of $\text{trans-[CoL}^3\text{Cl}_2\text{]}^+$ and $\text{trans-[CoL}^3\text{(NCBH}_3\text{)(OH)]}^+$.

One important point is that the configuration of the coordinated secondary amines in $\text{trans-[CoL}^3\text{Cl}_2\text{]}^+$ and $\text{trans-[CoL}^3\text{(NCBH}_3\text{)(OH)]}^+$ precludes coordination of the pendent amines. This is illustrated in Scheme 2 where the so-called α - and β -isomers of a tetradentate complex of L^3 are shown. The β -isomer finds the exocyclic amines *anti* to the adjacent macrocyclic amine H-atoms and the pendent amine may coordinate simply by a conformational change to the six-membered chelate ring. This is impossible in the α -isomer where the pendent amine and the two coordinated amine H-atoms are on the same side of the six-membered chelate ring. This isomer is locked into a tetradentate coordination mode unless all macrocyclic secondary amines can invert their configuration (from α - to β -isomer) which is unlikely given the inert nature of the complex.

To the future, we are looking to optimize routes toward polymerizing our thiophene-substituted complexes to generate redox active films that can be switched between two different oxidation states reversibly as indicated by solution cyclic voltammetry of their monomer complexes. These experiments are now underway and the results will be published separately. A key point that has emerged from this study is that the electronic and electrochemical properties of the monomeric complexes may be altered significantly by the attachment of functional groups to the axially coordinating amines. The 500 mV anodic shift in the $\text{Co}^{\text{III/II}}$ redox potential of $[\text{CoL}^3]^{3+}$ relative to $[\text{CoL}^1]^{3+}$ and elongation of the axial Co–N bonds in $[\text{CoL}^3]^{3+}$ highlights the importance of characterizing monomeric precursors of putative polythiophene hybrid materials prior to investigating the properties of the polymer itself.

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