

# Copper(II) template synthesis of a new N<sub>2</sub>S<sub>2</sub>-donor macrocycle incorporating a pendent pyridyl substituent

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**Abstract** The synthesis of the new potentially pentadentate ligand, 2,2'-(2-methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(sulfanediyl)diethanamine (**L**<sup>1</sup>), containing two thioether sulfurs, two –NH<sub>2</sub> amines and a pyridyl nitrogen heteroatom is described. Reaction of **L**<sup>1</sup> with copper(II) chloride and addition of hexafluorophosphate anion has led to isolation of the mixed anion complex Cu<sub>2</sub>(**L**<sup>1</sup>)<sub>2</sub>Cl(PF<sub>6</sub>)<sub>3</sub>. The synthesis and X-ray structure of cobalt(III) species, [Co(**L**<sup>1</sup>)Cl](PF<sub>6</sub>)<sub>2</sub>, is also reported. In situ reaction of **L**<sup>1</sup> with copper(II) as a metal template in the presence of formaldehyde and the carbon acid nitroethane together with triethylamine (as base) led to macrocycle ring closure to yield [Cu(**L**<sup>2</sup>)Cl]PF<sub>6</sub> (where **L**<sup>2</sup> = 6,13-dimethyl-6-nitro-13-(pyridin-2-yl)-1,11-dithia-4,8-diazacyclotetradecane) whose X-ray structure shows that the copper centre has a distorted square pyramidal coordination geometry being

bound by both –NH<sub>2</sub> nitrogens and both sulfurs of **L**<sup>2</sup> while the pyridyl nitrogen remains uncoordinated.

**Keywords** Copper(II) · Cobalt(III) · Template · X-ray · Macrocycle · N<sub>2</sub>S<sub>2</sub>-donor · EPR

## Introduction

The use of metal ion template effects has been a common means for generating new macrocyclic ligand systems since the beginning of synthetic macrocyclic chemistry around 80 years ago. For example, in 1988 the condensation between [Cu(1,2-diaminoethane)<sub>2</sub>]<sup>2+</sup> in methanol with formaldehyde and the carbon acid nitroethane was demonstrated to produce the macrocyclic Cu(II) complex **1** [1] and related in situ reactions of this type were subsequently employed to produce a range of other macrocyclic systems incorporating different metals as well as different backbone substitution patterns (including cyclic ligand systems incorporating potential donor groups appended to their macrocyclic frameworks) [2, 3]. While most of these products incorporated only nitrogens as the heteroatoms, an example of N<sub>2</sub>S<sub>2</sub>-macrocyclic system, 6-methyl-6-nitro-1,11-dithia-4,8-diazacyclotetradecane, isolated as its Cu(II) complex **2** was also characterised [1].

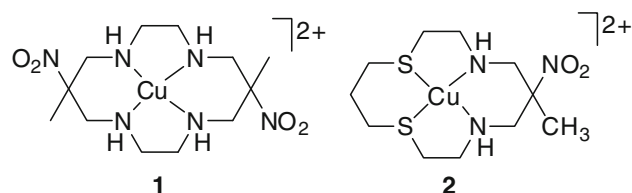
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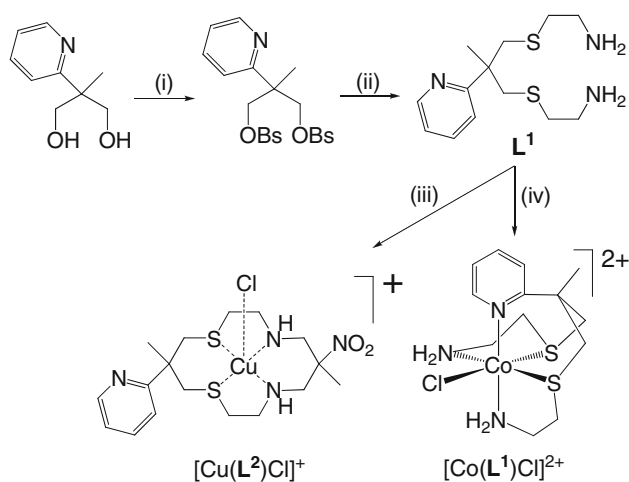


We now report the use of an in situ template reaction of the above type to yield the copper(II) complex of a new

macrocyclic ligand incorporating a macrocyclic  $N_2S_2$ -donor set together with a pendent pyridyl group (see Fig. 1). Relative to tetraaza macrocyclic systems, mixed donor  $N_2S_2$ -donor ring systems have received considerably less attention [2–10]; although it is noted that related mixed N,S-donor systems have been investigated as reagents for metal ion discrimination [11, 12] as well as for the complexation of  $^{111}\text{Ag}$  for use in radiotherapy [13].

## Experimental

Reagents were purchased from Aldrich and used as received. Cation-exchange chromatography employed either Dowex 50WX2 ( $\text{H}^+$  form) or SP-Sephadex C-25 ( $\text{Na}^+$  form) ion exchange resins. Electronic absorption spectra were measured with a SCINCO S-2100 diode array spectrometer, IR spectra on a JASCO S-715 spectrometer, elemental analysis on a Chemtronic TEA-3000 analyser and  $^1\text{H}$  NMR spectra on a Varian 300NB spectrometer operating at 300 MHz. The X-band (9 GHz) EPR spectrum was recorded on a Jeol (Japan) JES-TE300 ESR spectrometer using a 100-kHz field modulation and a Jeol ES-DVT3 variable temperature controller. The spectral simulation was performed using the program Simfonia (v. 1.25, Bruker Instruments Inc.). The EPR measurements employed the following parameters: microwave frequency, 9.212 GHz; microwave power, 1.2 mW; modulation amplitude, 10 G; time constant, 0.3 s; scan speed,  $1,250 \text{ G min}^{-1}$ . Simulation parameters:  $g = [2.030 \ 2.030 \ 2.145]$ ;  $A^{\text{Cu}} = [0 \ 0 \ 510] \text{ MHz}$ ; linewidth =  $[60 \ 60 \ 30] \text{ G}$  along  $g$ -tensor frame. Details of the X-ray structure



**Fig. 1** Ligand and complex synthesis: (i) Benzenesulfonyl chloride, pyridine; (ii) cysteamine, sodium, ethanol; (iii)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol, nitroethane, formaldehyde, triethylamine; (iv)  $\text{Na}_3[\text{Co}(\text{CO})_3]$  in water, HCl

determinations for  $[\text{Co}(\text{L}^1)\text{Cl}](\text{PF}_6)_2$  and  $[\text{Cu}(\text{L}^2)\text{Cl}]\text{PF}_6$  are presented in Table 1.

## 2,2'-(2-Methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(sulfanediy)diethanamine, $\text{L}^1$

Sodium (4.0 g) was dissolved in dry ethanol (200 mL), cysteamine (10.0 g) was added, and the mixture was heated to  $80^\circ\text{C}$  under nitrogen before 2-methyl-2-(pyridin-2-yl)propane-1,3-diyl bis(benzenesulfonate) (29.0 g) was added; heating was continued for 12 h. The solution was cooled to room temperature, evaporated under reduced pressure, and the residue dissolved in chloroform (100 mL) which was washed with water (100 mL  $\times$  3) before drying the separated chloroform phase over  $\text{Na}_2\text{SO}_4$ . The chloroform phase was evaporated under reduced pressure to give a brown oil; yield, 11.0 g. This crude product was further purified via its copper(II) complex; it was dissolved in methanol (200 mL) and to this solution was added  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (11.0 g) in methanol (50 mL) with stirring. The blue solution was evaporated to dryness under reduced pressure and the residue was dissolved in water (300 mL) and the solution was filtered through Celite. The filtrate was adsorbed on SP-Sephadex C-25 ( $\text{Na}^+$  form) and the column was washed with water (300 mL), then eluted with  $0.3 \text{ mol L}^{-1} \text{ NaCl}$ . The first major violet band was collected and its solution was evaporated to dryness under reduced pressure. The resulting blue solid was dissolved in water (200 mL) and  $\text{NaCN}$  (5.0 g) was added; the solution was stirred for 30 min then filtered through Celite. The filtrate was extracted with chloroform (100 mL  $\times$  3), the extracts were washed with water (100 mL  $\times$  3). The chloroform phase was then dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure to give  $\text{L}^1$  as a brown oil; yield, 11.0 g.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}/\text{DCl}$ , 400 MHz):  $\delta$  8.68 (d, 1H,  $\text{ArH}_o$ ,  $J = 5.6$ ), 8.49–8.41 (t, 1H,  $\text{ArH}_p$ ,  $J = 8.0$ ), 8.07 (d, 1H,  $\text{ArH}_m$ ,  $J = 8.4$ ), 7.9–7.86 (t, 1H,  $\text{ArH}_m$ ,  $J = 6.4$ , 7.2), 7.55 (br, 4H,  $\text{NH}_2$ ), 3.15 (s, 2H,  $\text{CCH}_2$ ), 3.05 (s, 2H,  $\text{CCH}_2$ ), 3.02–2.99 (t, 4H,  $\text{CH}_2\text{NH}_2$ ,  $J = 6.8$ , 6.4), 2.62–2.58 (t, 4H,  $\text{SCH}_2$ ,  $J = 6.8$ ), 1.54 (s, 3H,  $\text{CH}_3$ ).

Copper(II) complex of 2,2'-(2-methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(sulfanediy)diethanamine,  $\text{Cu}_2\text{Cl}(\text{L}^1)_2(\text{PF}_6)_3$

$\text{L}^1$  (0.57 g) in methanol (20 mL) was mixed with a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.34 g) in methanol (20 mL);  $\text{NH}_4\text{PF}_6$  was added and the solution was allowed to evaporate slowly to yield blue crystals. Yield, 0.69 g. Anal. Calcd. for  $\text{Cu}_2\text{Cl}(\text{L}^1)(\text{PF}_6)_3$ : C, 26.73; H, 3.97; N, 7.19; S, 10.98. Found: C, 26.91; H, 3.80; N, 7.24; S, 10.86%. MS-ESI, 382.9  $[\text{CuL}^1\text{Cl}]^+$ ; 492.6,  $[\text{CuL}^1(\text{PF}_6)]^+$ . Visible spectrum in water  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon_{\text{max}}$  ( $\text{M}^{-1} \text{ cm}^{-1}$ )) = 565 (2.43). IR

**Table 1** Crystal data and structure refinement details for [Co(L<sup>1</sup>)Cl](PF<sub>6</sub>)<sub>2</sub> and [Cu(L<sup>2</sup>)Cl]PF<sub>6</sub>

Compound	[Co(L <sup>1</sup> )Cl](PF <sub>6</sub> ) <sub>2</sub>	[Cu(L <sup>2</sup> )Cl]PF <sub>6</sub>
Chemical formula	C <sub>13</sub> H <sub>23</sub> ClCoF <sub>12</sub> N <sub>3</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>17</sub> H <sub>28</sub> ClCuF <sub>6</sub> N <sub>4</sub> O <sub>2</sub> PS <sub>2</sub>
<i>M</i> (g mol <sup>-1</sup> )	669.78	628.51
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pna</i> 2 <sub>1</sub>
<i>a</i> (Å)	12.249(2)	11.775(2)
<i>b</i> (Å)	13.202(3)	11.304(2)
<i>c</i> (Å)	14.991(3)	18.432(4)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	101.34(3)	90.00
$\gamma$ (°)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	2,376.9(8)	2,453.4(9)
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.872	1.702
<i>Z</i>	4	4
Crystal size (mm)	0.15 × 0.1 × 0.1	0.6 × 0.5 × 0.2
<i>T</i> (K)	293(2)	293(2)
$\lambda$ (MoK $\alpha$ ) (Å)	0.69996	0.77
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	1.247	1.304
2 $\theta$ <sub>max</sub> (°)	60.72	60.72
<i>hkl</i> range	0 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 19, -21 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 14, -24 ≤ <i>l</i> ≤ 23
<i>N</i>	12,728	5,650
<i>N</i> <sub>ind</sub> ( <i>R</i> <sub>merge</sub> )	7,277 (0.0367)	5,650 (0)
<i>N</i> <sub>obs</sub> ( <i>I</i> > 2 <i>s</i> ( <i>I</i> ))	5,477	5,421
<i>N</i> <sub>var</sub>	308	309
<i>R</i> 1 ( <i>F</i> )	0.0524	0.0469
<i>wR</i> 2 ( <i>F</i> <sup>2</sup> )	0.1606	0.1271
GoF (all)	1.049	0.947
$\Delta\rho$ <sub>min</sub> (eÅ <sup>3</sup> )	-0.816	-0.732
$\Delta\rho$ <sub>max</sub> (eÅ <sup>3</sup> )	1.006	1.044

spectrum (KBr disc, selected peaks, cm<sup>-1</sup>): 3,348; 3,293( $\nu_{\text{NH}}$ ); 3,140; 3,107( $\nu_{\text{C=C}}$ ); 2,992; 2,965( $\nu_{\text{C-C}}$ ); 838( $\nu_{\text{PF}}$ ); 557( $\delta_{\text{FPF}}$ ). Crystals from this preparation were twinned and proved not suitable for crystal structure analysis.

[Chloro[2,2'-(2-methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(sulfanediyl)diethanamine]-cobalt(III) hexafluorophosphate, [Co(L<sup>1</sup>)Cl](PF<sub>6</sub>)<sub>2</sub>

L<sup>1</sup> (1.2 g) was dissolved in 1 mol L<sup>-1</sup> HCl (15 mL) and the solution evaporated to dryness under reduced pressure. The residue was dissolved in water (100 mL) and Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] (1.7 g) was added; the resulting solution was stirred for 24 h followed by addition of 2 mol L<sup>-1</sup> HCl (10 mL). It was then taken to dryness under reduced pressure. The solid residue was dissolved in water (200 mL) and adsorbed onto a SP-Sephadex C-25 (Na<sup>+</sup> form) column. The column was washed with (200 mL)

water and eluted with 0.3 mol L<sup>-1</sup> NaCl to give two bands. The first pink band (F1) was Co<sub>aq</sub><sup>2+</sup> and discarded. The second red component (F2) was collected, adsorbed onto Dowex 50WX2 (H<sup>+</sup> form), washed with 0.5 mol L<sup>-1</sup> HCl (500 mL) and eluted with 3 mol L<sup>-1</sup> HCl. The eluate was evaporated to dryness under reduced pressure. Red crystals suitable for structure determination were obtained by slow evaporation of an aqueous solution of the complex containing excess NH<sub>4</sub>PF<sub>6</sub>. Yield, 0.80 g. Anal. Calcd. for [Co(L<sup>1</sup>)Cl](PF<sub>6</sub>)<sub>2</sub>: C, 23.31; H, 3.46; N, 6.27. Found: C, 23.1; H, 3.60; N, 6.22%. Visible spectrum in water,  $\lambda_{\text{max}}$  (nm) (log  $\epsilon_{\text{max}}$  (M<sup>-1</sup> cm<sup>-1</sup>)) = 527 (2.39), 370 (sh, 2.66). IR spectrum (KBr disc, selected peaks, cm<sup>-1</sup>): 3,327; 3,269 ( $\nu_{\text{NH}}$ ); 3,144( $\nu_{\text{C=C}}$ ); and 2,997( $\nu_{\text{C-C}}$ ); 834( $\nu_{\text{PF}}$ ); 558 ( $\delta_{\text{FPF}}$ ). <sup>1</sup>H NMR (D<sub>2</sub>O/DCl, 400 MHz):  $\delta$  9.27 (d, 1H, ArH<sub>o</sub>, *J* = 6.0), 8.12–8.09 (t, 1H, ArH<sub>p</sub>, *J* = 7.6), 7.78 (d, 1H, ArH<sub>m</sub>, *J* = 8.4), 7.65–7.62 (t, 1H, ArH<sub>m</sub>, *J* = 6.0, 7.6), 3.29–3.24 (m, 2H, CCH<sub>2</sub>), 3.17–3.10 (m, 8H, SCH<sub>2</sub> and CH<sub>2</sub>NH<sub>2</sub>), 2.99–2.97 (m, 2H, CCH<sub>2</sub>), 1.82 (s, 3H, CH<sub>3</sub>).

Chloro[6,13-dimethyl-6-nitro-13-(pyridin-2-yl)-1,11-dithia-4,8-diazacyclotetradecane]-copper(II), hexafluorophosphate,  $[\text{Cu}(\text{L}^2)\text{Cl}]\text{PF}_6$

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.5 g) in methanol (20 mL) was added to  $\text{L}^1$  (2.44 g) in methanol (100 mL) with stirring which was continued for 30 min to give a blue-violet solution. Formaldehyde (37%, 15 g), nitroethane (3.2 g) and triethylamine (7.0 g) were added and the solution was heated at 70 °C for 24 h. The solution was allowed to cool to room temperature, 2 mol  $\text{L}^{-1}$  HCl (20 mL) added and the solution was evaporated to dryness under reduced pressure. The residue was dissolved in water and adsorbed onto Dowex 50WX2 ( $\text{H}^+$  form) in a column. The column was washed with water (200 mL) and 0.5 mol  $\text{L}^{-1}$  HCl (200 mL) then eluted with 3 mol  $\text{L}^{-1}$  HCl to give a single purple band. The eluate was evaporated to dryness under reduced pressure and the residue was dissolved in water. Purple crystals suitable for a structure determination were obtained by slow evaporation of this solution after the addition of excess  $\text{NH}_4\text{PF}_6$ . Yield, 2.6 g. Anal. Calcd. for  $[\text{Cu}(\text{L}^2)\text{Cl}]\text{PF}_6 = \text{C}_{17}\text{H}_{28}\text{ClCuF}_6\text{N}_4\text{O}_2\text{PS}_2$ : C, 32.49; H, 4.49; N, 8.91. Found: C, 33.0; H, 4.6; N, 8.8%. Visible spectrum in water,  $\lambda_{\text{max}}$  (nm) ( $\log \varepsilon_{\text{max}}$  ( $\text{M}^{-1} \text{cm}^{-1}$ )) = 533 (2.37), 625 (sh, 2.00). IR spectrum (KBr disc, selected peaks,  $\text{cm}^{-1}$ ): 3,204 ( $\nu_{\text{NH}}$ ); 3,027 ( $\nu_{\text{C}=\text{C}}$ ); 2,936 ( $\nu_{\text{C}-\text{C}}$ ); and 1,559; 1,464 ( $\nu_{\text{NO}_2}$ ); 840 ( $\nu_{\text{PF}_6}$ ); 558 ( $\delta_{\text{PF}_6}$ ).

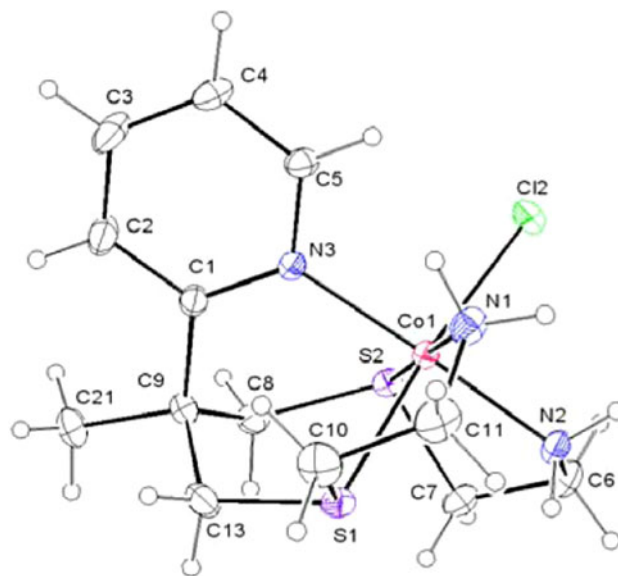
## Results and discussion

In the present study, the sodium salt of cysteamine was reacted with previously reported 2-methyl-2-(pyridin-2-yl)propane-1,3-diyl bis(benzenesulfonate) [14] to yield the new  $\text{N}_3\text{S}_2$  open-chain ligand  $\text{L}^1$  (Fig. 1). Reaction of copper(II) chloride with  $\text{L}^1$  in methanol followed by addition of hexafluorophosphate anion resulted in blue crystals whose visible and infrared spectrum indicated that complexation had occurred. Microanalysis confirmed the expected 1:1 ( $\text{Cu}:\text{L}^1$ ) stoichiometry of this product and, interestingly, indicated that it existed as a mixed anion species of composition  $\text{Cu}_2(\text{L}^1)_2\text{Cl}(\text{PF}_6)_3$ . Unfortunately, the crystals were found to be twinned and unsuitable for an X-ray diffraction study. While this solid complex may possibly exist as a chloro bridged species (or perhaps a cocrystal of two related complexes), in the absence of structural data it appears inappropriate to speculate further about its nature.

In the absence of an X-ray structure of the above copper(II) complex, an attempt was made to obtain a crystalline cobalt(III) complex of  $\text{L}^1$  in order to confirm the structure of  $\text{L}^1$  (which was isolated as a brown oil). Interaction of an aqueous solution of the hydrochloride salt

of  $\text{L}^1$  with  $\text{Na}_3[\text{Co}(\text{CO}_3)_3]$  in the presence of excess HCl yielded red crystals (following chromatography and the addition of ammonium hexafluorophosphate to the eluent). The visible and infrared spectra for this product confirmed the occurrence of complexation and the microanalytical data were in accord with the formation of a complex of type  $[\text{Co}(\text{L}^1)\text{Cl}](\text{PF}_6)_2$ ; the latter was confirmed by an X-ray structure determination (Table 1; Fig. 2). The X-ray analysis also served to confirm the expected structure of  $\text{L}^1$  and showed that all five donor atoms of  $\text{L}^1$  bind to the cobalt(III) centre. The octahedral coordination sphere consists of a chloro ligand and a  $-\text{NH}_2$  group from  $\text{L}^1$  bound in *cis*-positions in the equatorial plane with the remaining two equatorial sites occupied by thioether sulfurs; the axial sites are filled by the pyridyl nitrogen and the remaining  $-\text{NH}_2$  group from  $\text{L}^1$ . All metal-donor bond lengths and angles are unremarkable (see caption in Fig. 2).

In the crystal hydrogen bonding interactions occur between the cationic complexes and the  $\text{PF}_6$  anions (see Table S1 and Fig. S1 in the Supplementary Material for further details of the crystal packing). The coordinated primary amines act as hydrogen-bond donors with the anions bridging adjacent complexes and forming infinite



**Fig. 2** X-ray structure of the octahedral cation in  $[\text{Co}(\text{L}^1)\text{Cl}](\text{PF}_6)_2$ . Selected bond distances (Å) and angles (°): Co(1)–N(3), 1.978(2); Co(1)–N(2), 1.986(2); Co(1)–N(1), 1.994(3); Co(1)–S(2), 2.2011(8); Co(1)–S(1), 2.2223(9); Co(1)–Cl(2), 2.2505(9); N(3)–Co–N(2), 175.66(10); N(3)–Co–N(1), 93.08(10); N(2)–Co–N(1), 91.21(11); N(3)–Co–S(2), 88.08(7); N(2)–Co–S(2), 87.64(8); N(1)–Co–S(2), 178.46(9); N(3)–Co–S(1), 1.95(7); N(2)–Co–S(1), 87.68(8); N(1)–Co–S(1), 86.05(9); S(2)–Co–S(1), 94.93(4); N(3)–Co–Cl(2), 93.84(7); N(2)–Co–Cl(2), 86.72(8); N(1)–Co–Cl(2), 91.22(9); S(2)–Co–Cl(2), 87.68(4); and S(1)–Co–Cl(2), 173.72(3)

undulating two-dimensional layers that extend nearly parallel to the crystallographic *bc*-plane.

Reaction of  $L^1$  with copper(II) as the templating metal ion in the presence of nitroethane, formaldehyde and trimethylamine (as base) under related conditions to those employed previously for macrocycle ring closure [15] yielded  $L^2$  as its copper complex which was isolated after addition of hexafluorophosphate anion to the reaction solution. The visible and infrared spectra of the blue product once again confirmed the occurrence of complexation and the microanalysis was in accord with a complex of type  $[Cu(L^2)Cl]PF_6$ .

The X-ray structure of the complex cation in  $[Cu(L^2)Cl]PF_6$  (Fig. 3) shows that the copper ion is bound by both  $-NH$  nitrogens and both sulfurs of  $L^2$  while the pyridyl nitrogen remains uncoordinated. While pyridyl binding appears possible in this complex (as occurs in the above Co(III) complex), five coordination is instead achieved through the binding of a chloro ligand. Overall, the coordination geometry may be described as distorted square pyramidal, with all metal-donor atom bond lengths (see caption to Fig. 3) being again unremarkable. A combination of both intramolecular and intermolecular hydrogen bonding is present in the crystal (See Table S2 in the Supplementary Material). The coordinated secondary amine hydrogens bond to both the nitro-oxygens in the same complex and to the chloro-ligand in adjacent complexes. The intramolecular interactions result in the formation of infinite one-dimensional chains that extend along the crystallographic *a*-axis (see Fig. S2 in the Supplementary Material).

The visible spectrum of this complex in the d-d region consists of a broad envelope of bands with  $\lambda_{max} = 527$  nm and is typical of other copper(II) complexes with related mixed donor sets [16]. The spectrum is also quite similar to

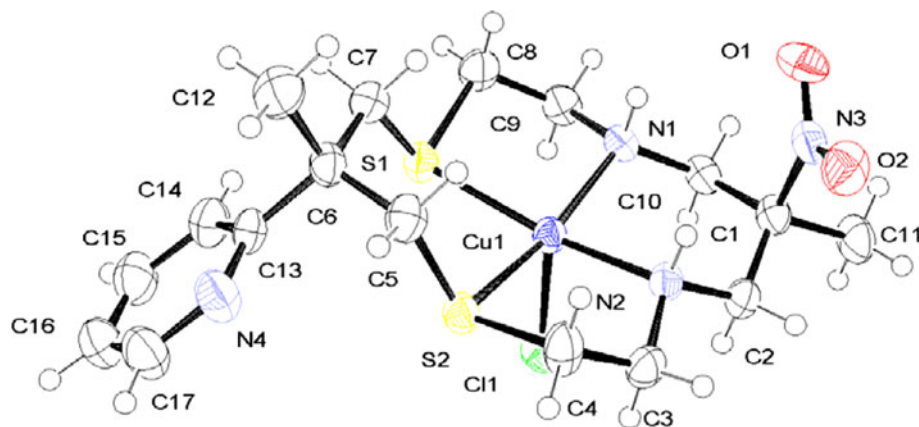
that of  $Cu_2(L^1)_2Cl(PF_6)_3$  (whose maximum occurs at 565 nm).

The EPR spectrum of a frozen solution of  $[Cu(L^2)Cl]PF_6$  in DMF at 110 K is shown in Fig. 4 along with its numerical simulation. The spectrum is well resolved with the axial *g*-tensor ( $S = 1/2$ ,  $g_{\parallel} = 2.145$ ,  $g_{\perp} = 2.030$ ) and the axial copper nuclear hyperfine tensor ( $I = 3/2$ ,  $A_{\parallel} = 510$  MHz =  $170 \times 10^{-4}$  cm $^{-1}$ ), indicating that the ground state is predominantly  $d_{x^2-y^2}$ . For copper(II) complexes with  $N_2S_2$  ligands it is known that the  $g_{\parallel}$  value increases while the  $A_{\parallel}$  value decreases when the twist angle of  $N_2S_2$  increases, such as occurs in type I copper protein [17–19]. However, in the present case the *g* and *A* values are in the range observed for other Cu(II) $N_2S_2$  complexes with square-plane-based geometries (in accord with the crystal structure discussed above for  $[Cu(L^2)Cl]PF_6$ ) [19–22].

In summary, in the present study we present a facile in situ template synthesis of a new  $N_2S_2$ -macrocyclic derivative bearing a pendent pyridyl group which was isolated as its distorted square pyramidal Cu(II) complex. Cu(II) and Co(III) complexes of the related  $N_2S_2$ , open chain, ligand precursor are also reported.

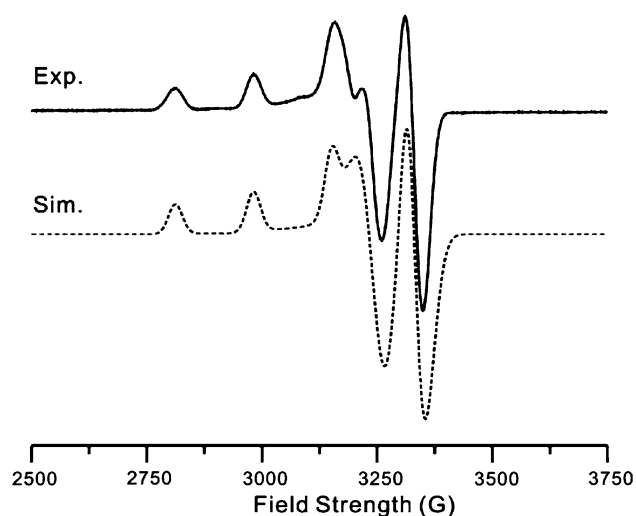
### Supplementary material

Crystallographic data for compounds  $[Co(L^1)Cl](PF_6)_2$  and  $[Cu(L^2)Cl]PF_6$  have been deposited with CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and are identified by deposition numbers of CCDC 782282 and 782283. 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>.



**Fig. 3** X-ray structure of the cation in  $[Cu(L^2)Cl]PF_6$ . Selected bond distances (Å) and angles ( $^{\circ}$ ): Cu–N(2), 2.030(3); Cu–N(1), 2.044(3); Cu–S(1), 2.2981(11); Cu–S(2), 2.3275(12); Cu–Cl(1), 2.5490(11); N(2)–Cu(1)–N(1), 91.72(13); N(2)–Cu(1)–S(1), 166.62(10); N(1)–

Cu(1)–S(1), 88.01(9); N(2)–Cu(1)–S(2), 87.88(10); N(1)–Cu(1)–S(2), 164.39(10); S(1)–Cu(1)–S(2), 88.80(4); N(2)–Cu(1)–Cl(1), 98.21(9); N(1)–Cu(1)–Cl(1), 97.86(10); S(1)–Cu(1)–Cl(1), 95.07(4); and S(2)–Cu(1)–Cl(1), 97.64(4)



**Fig. 4** EPR spectrum (*solid line*) obtained from a frozen solution of  $[\text{Cu}(\text{L}^2)\text{Cl}]\text{PF}_6$  (1.0 mM) in DMF at 110 K and the corresponding simulation (*dotted line*)

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