

# An unexpected mixed-valence cobalt(II)/cobalt(III) complex of a pyrrole-containing tridentate Schiff-base ligand

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**Abstract** The synthesis and characterisation of an unexpected mixed-valence complex  $[\text{Co}^{\text{III}}(\text{L}^1)(\text{aep})(\text{NCS})]_2 [\text{Co}^{\text{II}}(\text{NCS})_4]$  **1**, of the deprotonated tridentate Schiff-base ligand  $(\text{L}^1)^-$  [where  $\text{HL}^1$  is *N*-(1*H*-pyrrol-2-ylmethylene)-2-pyridineethanamine], is reported. This complex was synthesised by both non-stoichiometric and stoichiometric one pot procedures, by mixing 2-formylpyrrole, 2-(2-aminoethyl)pyridine (aep), cobalt(II) acetate and sodium thiocyanate at room temperature. The crystal structure of **1**·Et<sub>2</sub>O confirmed that two, almost identical, mixed ligand octahedral cobalt(III) monocationic complexes crystallise with a tetrahedral cobalt(II) tetra-thiocyanato dianionic counter ion.

**Keywords** Tridentate ligands · Pyrrole · Schiff-bases · Cobalt

**Dedication** This article is dedicated to Professor Len Lindoy on the occasion of his 75th birthday.

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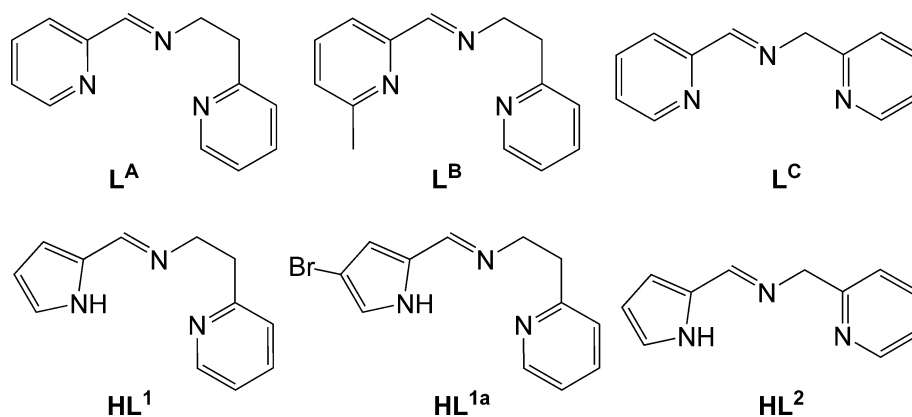
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## Introduction

Over the years much effort has gone into the investigation of complexes of a wide range of acyclic Schiff-base ligands, in particular into pyridine containing systems [1–7]. Much less is known about complexes of pyrrole-analogues of such ligands, despite the potentially interesting similarities to porphyrins. Recently, our focus has been on the copper(II) chemistry of N<sub>3</sub> tridentate Schiff-base ligands, in particular the mixed pyrrole-pyridine ligands  $\text{HL}^1$  and  $\text{HL}^2$  (Fig. 1) [8, 9]. These ligands have allowed us to generate a series of copper(II) complexes, of  $(\text{L}^1)^-$  in the form of  $[\text{Cu}_2(\text{L}^1)_2(\mu\text{-Cl})_2]$  (**2**),  $[\text{Cu}_2(\text{L}^1)_2(\mu\text{-Br})_2]$  (**3**),  $[\text{Cu}_2(\text{L}^1)_2(\mu_{1,1}\text{-N}_3)_2]$  (**4**) and  $[\text{Cu}_2(\text{L}^1)_2(\mu_{1,3}\text{-NCS})_2]$  (**5**); of  $(\text{L}^2)^-$  in the form of  $[\text{Cu}(\text{L}^2)\text{Cl}]$  (**6**),  $[\text{Cu}(\text{L}^2)\text{Br}]$  (**7**) and  $[\text{Cu}_2(\text{L}^2)_2(\mu_{1,3}\text{-NCS})_2]$  (**8**); and of  $\text{HL}^2$  in the form of  $[\text{Cu}(\text{HL}^2)\text{Cl}_2]$  (**9**) and  $[\text{Cu}(\text{HL}^2)\text{Br}_2]$  (**10**), together with an unusual bromo-bridged 1D polymeric copper(II) complex of the serendipitously brominated pyrrole derivative  $(\text{L}^{1a})^-$ ,  $[\text{CuL}^{1a}(\mu\text{-Br})]_\infty$  (**11**) [8, 9]. The deprotonated forms of ligands  $\text{HL}^1$  and  $\text{HL}^2$ ,  $(\text{L}^1)^-$  and  $(\text{L}^2)^-$ , are closely related to the neutral pyridine-pyridine ligands,  $\text{L}^A$ ,  $\text{L}^B$  and  $\text{L}^C$  (Fig. 1) which have been well studied [1–7], and summarised in our recent publication [9]. The structures of the complexes of  $\text{L}^A$ ,  $\text{L}^B$ ,  $\text{L}^C$  and of  $(\text{L}^1)^-$  and  $(\text{L}^2)^-$ , taken together with those obtained with other closely related tridentate Schiff-base ligands [10–24], indicate that the use of less flexible tridentate ligands tends to result in the formation of monomeric and dimeric complexes while the use of more flexible tridentate ligands tends to give rise to dimeric or polymeric complexes.

The copper(II) complexes of  $(\text{L}^1)^-$  and  $(\text{L}^2)^-$  mentioned above were all prepared using preformed ligands,  $\text{HL}^1$  and  $\text{HL}^2$ , derived from 2-formylpyrrole and 2-(2-aminoethyl)pyridine (aep) or 2-aminomethylpyridine (amp),

**Fig. 1** Selection of tridentate N<sub>3</sub> Schiff-base ligands, including the ligand used in this research, HL<sup>1</sup>



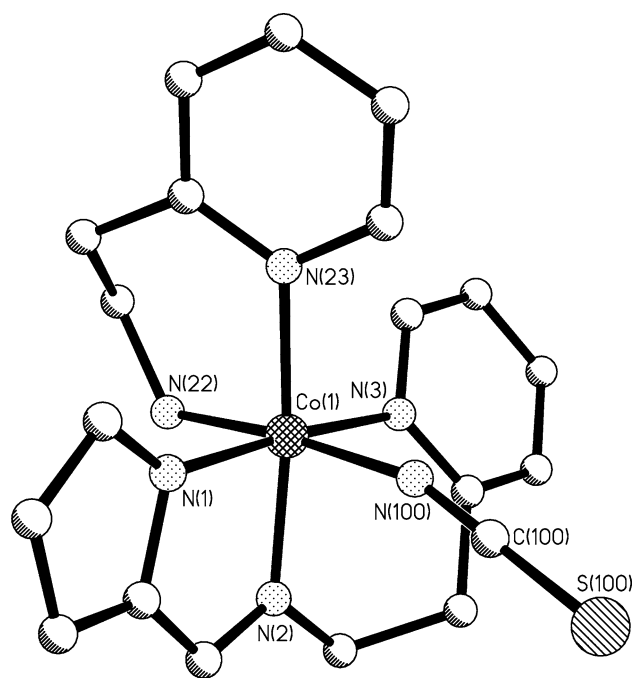
respectively. However, in initial attempts to prepare other first row transition metal complexes of (L<sup>1</sup>)<sup>-</sup> and (L<sup>2</sup>)<sup>-</sup>, one pot reactions were attempted. The first complex targeted was a thiocyanate-bridged dimeric cobalt complex of (L<sup>1</sup>)<sup>-</sup> analogous to the copper complexes of (L<sup>1</sup>)<sup>-</sup>, [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(μ<sub>1,3</sub>-NCS)<sub>2</sub>] (**5**), and of (L<sup>2</sup>)<sup>-</sup>, [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>(μ<sub>1,3</sub>-NCS)<sub>2</sub>] (**8**). However, rather than a dimeric cobalt complex, instead an unexpected mixed-valence cobalt complex, [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>] (**1**), was obtained. Here we report the fortuitous and then the deliberate preparation of **1**, along with the crystal structure of this mixed-valence cobalt complex.

## Results and discussion

### One pot synthesis and characterisation

The dark green mixed valent complex [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>] (**1**), was initially obtained by mixing 2-formylpyrrole, 2-(2-aminoethyl)pyridine (aep), cobalt(II) acetate and two equivalents of sodium thiocyanate in methanol at room temperature (isolated in 60% yield based on aep). The microanalysis data showed the stoichiometry of the crude product to be consistent with the formula Co<sup>III</sup>Co<sup>II</sup>(L<sup>1</sup>)<sub>2</sub>(aep)<sub>2</sub>(NCS)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>, **1**·2H<sub>2</sub>O. The slow diffusion of diethyl ether into an acetonitrile solution of the complex gave single crystals of **1**·Et<sub>2</sub>O. An X-ray structure determination was carried out, confirming the formation of this unexpected mixed-valence cobalt complex (Figs. 2, 3).

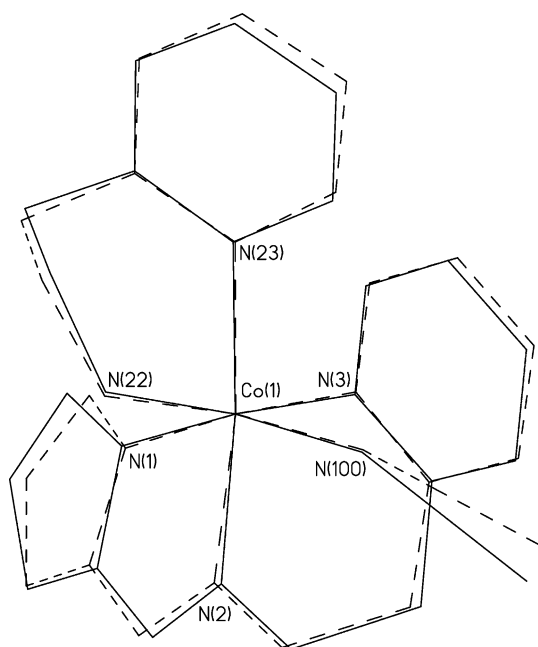
For completeness, stoichiometric synthesis of **1** was attempted. Different reaction times, 6 and 9 days, were tried at room temperature, in methanol in an open flask. The products from both reactions were both impure but that from the longer reaction time was the better of the two, indicating that a longer reaction time was required. When an even longer reaction time, 18 days, was used analytically pure product was obtained (in 50% yield). The longer reaction time, as compared to the overnight reaction for the



**Fig. 2** Perspective view of one of the two cations of the mixed-valence cobalt complex [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>]·Et<sub>2</sub>O (1·Et<sub>2</sub>O). Hydrogen atoms have been omitted for clarity

non-stoichiometric preparation, is possibly due to oxidation of the cobalt(II) to cobalt(III) being less favourable.

The infrared spectrum of [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>] (**1**) shows two distinctive strong sharp bands at 2110 and 2073 cm<sup>-1</sup>, which are attributed to the C≡N stretches of the two different types of thiocyanate ions present [25]. Thiocyanate is an ambidentate ligand which can bind in a variety of modes [26]. In this case the observed bands are consistent with both of the thiocyanate ions being bound as terminal ions through the nitrogen donor atoms, but to cobalt ions in two different oxidation states and coordination environments, in agreement with the X-ray structure determination. The strong and somewhat broad signal at 1590 cm<sup>-1</sup> is assigned as being due



**Fig. 3** Perspective view of a least squares fit of the nitrogen donor atoms and cobalt atom in one cation containing Co(1), with the equivalent atoms in the other crystallographically independent cation, containing Co(2), in the mixed-valence cobalt complex **1**·Et<sub>2</sub>O. Hydrogen atoms have been omitted for clarity

primarily to the C=N stretch of the imine bond. This compares well to position of the imine band (at *ca.* 1590 cm<sup>-1</sup>) in the dimeric copper(II) complexes of (L<sup>1</sup>)<sup>-</sup>, [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(μ-X)<sub>2</sub>] (X = Cl, Br, N<sub>3</sub>, NCS) (**2–5**) [8], and in another related copper(II) complex (at 1588 cm<sup>-1</sup>) [27].

The electrospray mass spectrum of **1** exhibits two significant fragments: C<sub>20</sub>H<sub>22</sub>N<sub>6</sub>SCo at 437 corresponds to [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sup>+</sup>; and C<sub>19</sub>H<sub>22</sub>N<sub>5</sub>Co at 379 to [Co<sup>III</sup>(L<sup>1</sup>)(aep)]<sup>+</sup>. Both fragments confirm the presence of both the ligand (L<sup>1</sup>)<sup>-</sup> and aep.

The complex has a molar conductivity value in acetonitrile which is very close to the literature range for 2:1 electrolytes [28], consistent with the thiocyanate ions remaining bound in acetonitrile solution.

Complex **1** contains two diamagnetic cobalt(III) centres (d<sup>6</sup>) and a single cobalt(II) centre so is therefore paramagnetic. The effective magnetic moment was found to be 4.4 BM per compound (which contains three cobalt ions). This is within the expected range, 4.4–4.8 BM [29], for tetrahedral cobalt(II) complexes.

Tetrahedral cobalt(II) complexes usually show <sup>4</sup>T<sub>1</sub>(F) ← <sup>4</sup>A<sub>2</sub>(F) and <sup>4</sup>T<sub>1</sub>(P) ← <sup>4</sup>A<sub>2</sub>(F) d–d transitions as complex envelopes in the near infrared and visible regions respectively [30, 31]. The extinction coefficients of these absorptions are generally 10–100 for the former and 100–2000 dm<sup>3</sup> mol cm<sup>-1</sup> for the latter. For six coordinate low spin cobalt(III) complexes two absorption bands are generally observed due to the d–d transitions <sup>1</sup>T<sub>1g</sub> ← <sup>1</sup>A<sub>1g</sub>

and <sup>1</sup>T<sub>2g</sub> ← <sup>1</sup>A<sub>1g</sub>. A weak band corresponding to the spin-forbidden <sup>3</sup>T<sub>1g</sub> ← <sup>1</sup>A<sub>1g</sub> transition is sometimes observed in the region of 715–910 nm [30, 31]. The UV–Vis spectrum of dark green **1** in CH<sub>3</sub>CN exhibits a complex envelope with a maximum at 624 nm ( $\epsilon = 1.61 \times 10^3$  dm<sup>3</sup> mol cm<sup>-1</sup> per **1**) and a feature at 588 nm ( $\epsilon = 1.02 \times 10^3$  dm<sup>3</sup> mol cm<sup>-1</sup> per **1**), and a band at 347 nm ( $\epsilon = 2.68 \times 10^4$  dm<sup>3</sup> mol cm<sup>-1</sup> per **1**) with a shoulder at 465 nm ( $\epsilon = 1.3 \times 10^3$  dm<sup>3</sup> mol cm<sup>-1</sup> per **1**). The band centred at 624 nm is likely to be the <sup>4</sup>T<sub>1</sub>(P) ← <sup>4</sup>A<sub>2</sub>(F) transition of Co<sup>2+</sup> and the strong band at 347 nm is due to either a charge transfer or  $\pi$ – $\pi^*$  transition.

### X-ray crystal structure

Dark green plate crystals [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>]·Et<sub>2</sub>O were obtained by the slow diffusion of diethyl ether vapour into an acetonitrile solution of the crude product, 1·2H<sub>2</sub>O, and the X-ray crystal structure determined (Figs. 2, 3; Table 1). This confirmed that it consists of discrete [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sup>+</sup> cations and [Co<sup>II</sup>(NCS)<sub>4</sub>]<sup>2-</sup> anions in a 2:1 molar ratio, and hence that it is indeed an unexpected mixed-valence cobalt complex.

The cobalt(II) ion, Co(3), is coordinated by four terminal N-bound thiocyanate ligands in a slightly distorted tetrahedral arrangement, forming the counter anion, [Co<sup>II</sup>(NCS)<sub>4</sub>]<sup>2-</sup>. The N–Co(3)–N angles range from 105.2(3)° to 113.4(3)° (average 109.4°) and the Co(3)–N bond distances range from 1.917(7) to 1.963(7) Å (average 1.939 Å) (Table 1). These parameters are in the normal range quoted for this anion in the literature [32–35]. As expected, the Co(3)–N–C(thiocyanate) angles deviate from linearity by only 7° [173.1(7)–178.5(8)°] and the N–C–S angles are essentially linear [177.7(8)–179.4(9)°] (Table 1).

Two crystallographically independent [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sup>+</sup> cations, containing Co(1) and Co(2), respectively, are present in the unit cell. The geometries of these cations are fairly similar to one another (Fig. 3; Table 1). One cation, that containing Co(1), is therefore taken as representative in the following discussion. The cobalt(III) ion is coordinated to six nitrogen donor atoms in an octahedral environment: three from a deprotonated tridentate (L<sup>1</sup>)<sup>-</sup> ligand, two from an aep ligand and one from a thiocyanato anion. Of the six Co(1)–N bonds, the longest bonds form between Co(1) and the nitrogen donors of the two pyridine rings [Co(1)–N(3) 2.004(6) Å, Co(1)–N(23) 1.990(6) Å; Co(2)–N(43) 1.971(7) Å, Co(2)–N(63) 1.978(6) Å]. These values are similar to those observed in closely related octahedral cobalt(III) complexes containing two aep moieties [1.983(5)–2.045(5) Å] [36, 37]. The bond formed between Co(1) and the deprotonated negatively charged pyrrole nitrogen atom, Co(1)–N(pyrrole) [1.927(7) Å for

**Table 1** Selected bond lengths (Å) and angles (°) for complex **1**·Et<sub>2</sub>O

Co(1)–N(100)	1.912 (7)	N(100)–Co(1)–N(3)	90.3 (3)
Co(1)–N(2)	1.922 (6)	N(2)–Co(1)–N(3)	92.3 (3)
Co(1)–N(1)	1.927 (7)	N(1)–Co(1)–N(3)	175.5 (3)
Co(1)–N(22)	1.941 (6)	N(22)–Co(1)–N(3)	89.7 (2)
Co(1)–N(23)	1.990 (6)	N(23)–Co(1)–N(3)	96.1 (3)
Co(1)–N(3)	2.004 (6)	N(41)–Co(2)–N(110)	87.5 (3)
Co(2)–N(41)	1.912 (6)	N(41)–Co(2)–N(42)	82.1 (3)
Co(2)–N(110)	1.918 (7)	N(110)–Co(2)–N(42)	90.3 (3)
Co(2)–N(42)	1.928 (6)	N(41)–Co(2)–N(62)	91.6 (3)
Co(2)–N(62)	1.951 (6)	N(110)–Co(2)–N(62)	173.8 (3)
Co(2)–N(43)	1.971 (7)	N(42)–Co(2)–N(62)	83.4 (3)
Co(2)–N(63)	1.978 (6)	N(41)–Co(2)–N(43)	175.1 (3)
Co(3)–N(150)	1.917 (7)	N(110)–Co(2)–N(43)	89.4 (3)
Co(3)–N(120)	1.935 (8)	N(42)–Co(2)–N(43)	94.1 (3)
Co(3)–N(130)	1.941 (7)	N(62)–Co(2)–N(43)	91.1 (3)
Co(3)–N(140)	1.963 (7)	N(41)–Co(2)–N(63)	90.0 (3)
N(100)–Co(1)–N(2)	86.9 (3)	N(110)–Co(2)–N(63)	92.2 (3)
N(100)–Co(1)–N(1)	88.7 (3)	N(42)–Co(2)–N(63)	171.5 (3)
N(2)–Co(1)–N(1)	83.3 (3)	N(62)–Co(2)–N(63)	94.0 (3)
N(100)–Co(1)–N(22)	174.4 (3)	N(43)–Co(2)–N(63)	94.0 (3)
N(2)–Co(1)–N(22)	87.5 (2)	N(150)–Co(3)–N(120)	112.3 (3)
N(1)–Co(1)–N(22)	90.9 (3)	N(150)–Co(3)–N(130)	113.4 (3)
N(100)–Co(1)–N(23)	92.8 (3)	N(120)–Co(3)–N(130)	109.7 (3)
N(2)–Co(1)–N(23)	171.6 (3)	N(150)–Co(3)–N(140)	109.6 (3)
N(1)–Co(1)–N(23)	88.3 (3)	N(120)–Co(3)–N(140)	106.1 (3)
N(22)–Co(1)–N(23)	92.8 (3)	N(130)–Co(3)–N(140)	105.2 (3)

Co(1)–N(pyrrole) and 1.912(6) Å for Co(2)–N(pyrrole)] is shorter than the Co(1)–N(pyridine) bond but is close to that found in related octahedral cobalt(III) complexes of pyrrole containing ligands [38, 39]. The thiocyanate ion is bound to Co(1) [or Co(2)] through the nitrogen atom N(100) [or N(110)] and is *trans* to the amine nitrogen atom N(22) [or N(62)] from aep. Both of the thiocyanate ions in the independent cations are essentially linear, and the bond distance Co(1)–N(100) at 1.912(7) Å [1.918(7) Å for Co(2)–N(110)] is similar to those reported for related octahedral cobalt(III) complexes [34, 40]. The pyrrole and pyridine rings within the ligand (L<sup>1</sup>)<sup>−</sup> are not coplanar [dihedral angles are 25.7(4)° in the cation containing Co(1) and 35.2(3)° in the cation containing Co(2)]. The pyridine ring of aep makes angles with the pyrrole and pyridine rings from the (L<sup>1</sup>)<sup>−</sup> ligand of 75.5° [71.7° in the Co(2) cation] and 75.4(2)° [65.3(3)° in the Co(2) cation], respectively.

The four hydrogen atoms of the two primary amines in the two cations are involved in hydrogen-bonding with an oxygen atom of a solvent diethyl ether molecule and three of the four sulphur atoms of the [Co<sup>II</sup>(NCS)<sub>4</sub>]<sup>2−</sup> anions.

These hydrogen bonds link the cations and anions of **1** together in three dimensions.

## Conclusion

The reproducible preparation and characterisation of an unexpected mixed-valence cobalt(II)/cobalt(III) complex of (L<sup>1</sup>)<sup>−</sup>, **1**, has been described. This dark green complex can be synthesised from both non-stoichiometric and stoichiometric one pot procedures, by mixing 2-formylpyrrole, aep, cobalt(II) acetate and sodium thiocyanate at room temperature. The X-ray crystal structure determination carried out on **1**·Et<sub>2</sub>O confirms that it is the mixed-valence cobalt complex [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>]·Et<sub>2</sub>O, **1**·Et<sub>2</sub>O.

## Experimental

### General information

Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR System as pressed KBr discs. MS spectra were collected on an EI/CI/FAB Kratos MS80RFA. UV–Vis spectra were obtained on a Varian 500 Scan UV–Vis–NIR spectrophotometer. Molar conductivity measurements were carried out on a Suntext SC-170 conductivity meter. Elemental analyses were carried out by the Campbell Micro-analytical Laboratory at the University of Otago. All chemicals and solvents were of reagent grade and were used as received.

### Synthesis of [Co<sup>III</sup>(L<sup>1</sup>)(aep)(NCS)]<sub>2</sub>[Co<sup>II</sup>(NCS)<sub>4</sub>] (**1**)

#### Method A

To a stirred pink solution of cobalt(II) acetate tetrahydrate (0.596 g, 2.39 mmol) in methanol (80 mL) was added slowly a solution of 2-formylpyrrole (0.227 g, 2.39 mmol) in methanol (20 mL). After 5 min stirring a solution of 2-(2-aminoethyl)pyridine (aep) (0.292 g, 2.39 mmol) in methanol (5 mL) was added slowly to the resulting red solution. After stirring for 20 min addition of sodium thiocyanate (0.388 g, 4.78 mmol) in methanol (10 mL) gave a dark red solution which was stirred overnight, resulting in a dark brown solution. The solution was then evaporated to ca. 30 mL, giving a dark green precipitate and the resulting mixture was allowed to stand overnight. The dark green powder was filtered off and dried in vacuo (0.433 g, 60% based on aep). Elemental analysis: Calcd. (%) for C<sub>44</sub>H<sub>44</sub>N<sub>16</sub>S<sub>6</sub>Co<sub>3</sub>·(H<sub>2</sub>O)<sub>2</sub>: C: 43.96; H: 4.02; N: 18.64; S: 16.00. Found: C: 44.02; H: 3.82; N: 18.32; S:

15.72. Subsequent recrystallisation from acetonitrile by the slow diffusion of diethyl ether vapour produced a dark green crystalline solid. Elemental analysis: Calcd. (%) for  $C_{44}H_{44}N_{16}S_6Co_3$ : C: 45.32; H: 3.80; N: 19.22; S: 16.50. Found: C: 45.51; H: 3.74; N: 19.30; S: 16.12. IR (KBr disc)  $\nu_{max}/cm^{-1}$ : 3188, 3111, 2928, 2851, 2110, 2073, 1590, 1481, 1442, 1391, 1337, 1317, 1229, 1183, 1041, 762. Room temperature magnetic moment  $\mu = 4.4$  BM per complex (which contains three cobalt ions).  $\Lambda_m(CH_3CN) = 205 \Omega^{-1} cm^2 mol^{-1}$  (c.f. 220–300  $\Omega^{-1} cm^2 mol^{-1}$  for a 2:1 electrolyte in  $CH_3CN$  [28]).  $\lambda_{max}/nm(CH_3CN)$  [ $\epsilon/dm^3 mol^{-1} cm^{-1}$  per complex]: 347 ( $2.68 \times 10^4$ ), 465 (shoulder,  $1.3 \times 10^3$ ), 588 ( $1.02 \times 10^3$ ), 624 ( $1.61 \times 10^3$ ). ESI-MS:  $m/z$  437 [ $Co^{III}(L^1)(aep)(NCS)$ , i.e.  $C_{20}H_{22}N_6SCo]^+$ , 379 [ $Co^{III}(L^1)(aep)$ , i.e.  $C_{19}H_{22}N_5Co]^+$ .

#### Method B: stoichiometric

To a stirred pink solution of cobalt(II) acetate tetrahydrate (0.1868 g, 0.75 mmol) in methanol (40 mL) was added dropwise a solution of 2-formylpyrrole (0.0476 g, 0.50 mmol) in methanol (10 mL). After 5 min stirring a solution of aep (0.1222 g, 1.00 mmol) in methanol (5 mL) was added slowly to the resulting intense pink solution, resulting in a red solution which changed to dark red in colour after 7 h stirring. Then sodium thiocyanate (0.1216 g, 1.50 mmol) in methanol (10 mL) was added and the resulting solution was stirred in an open flask for 18 days. The solution was then reduced in vacuo to ca. 10 mL, giving a dark green precipitate and the resulting mixture was allowed to stand overnight. The dark green powder was filtered off and dried in vacuo (0.1488 g, 50%). Elemental analysis: Calcd. (%) for  $C_{44}H_{44}N_{16}S_6Co_3 \cdot (H_2O)_2$ : C: 43.96; H: 4.02; N: 18.64; S: 16.00. Found: C: 44.17; H: 3.92; N: 18.42; S: 15.69. Subsequent recrystallisation by the slow diffusion of diethyl ether vapour into a solution of this crude product yielded dark green crystals. Elemental analysis: Calcd. (%) for  $C_{44}H_{44}N_{16}S_6Co_3 \cdot (Et_2O)$ : C: 46.49; H: 4.39; N: 18.07; S: 15.51. Found: C: 46.30; H: 4.42; N: 18.40; S: 15.42. IR (KBr disc)  $\nu_{max}/cm^{-1}$ : 3175, 3103, 2966, 2923, 2852, 2090, 2074, 1590, 1481, 1441, 1393, 1320, 1162, 1041, 761.

#### X-ray crystallography

All data were collected on a Bruker SMART diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were corrected for Lorentz and polarization effects and semi-empirical absorption corrections (SADABS) were applied. The structure was solved by direct methods (SHELXS-97) [41], and refined against  $F^2$  using all data by full matrix least-squares techniques

**Table 2** Crystallographic data for complex **1**·Et<sub>2</sub>O

	Complex <b>1</b> ·Et <sub>2</sub> O
Empirical formula	$C_{48}H_{54}N_{16}OS_6Co_3$
Formula mass	1240.22
Crystal colour, habit	Dark green, plate
Crystal size (mm)	0.40 × 0.20 × 0.02
Temperature (K)	186 (2) K
Crystal system	Monoclinic
Space group	$P2(1)/n$
$a$ (Å)	21.617 (12)
$b$ (Å)	10.472 (5)
$c$ (Å)	24.530 (13)
$\alpha$ (°)	90
$\beta$ (°)	97.492 (8)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	5505 (5)
$Z$	4
$D_c$ (g/cm <sup>3</sup> )	1.496
$\mu$ (mm <sup>-1</sup> )	1.174
$F(000)$	2556
$\theta$ range for data collection (°)	1.67–26.45
Reflections collected	69346
Independent reflections	11144
$R(int)$	0.3497
Max/Min transmission	1.00/0.74
Data/restraints/parameters	11144/0/669
Goof ( $F^2$ )	0.915
$R_1$ [ $I > 2\sigma(I)$ ]	0.0711
$wR_2$ (all data)	0.1734
Largest peak and hole ( $e$ Å <sup>-3</sup> )	0.482 and -0.525

(SHELXL-97) [41]. All non-hydrogen atoms were made anisotropic. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they are attached (including their isotropic thermal parameters which were equal to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom). A summary of the crystallographic data and refinement parameters is given in Table 2. CCDC 820990 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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