Full Paper

Synthesis and Characterisation of $[(en)_2Co]^{3+}$ Complexes Coordinated by Substituted Thiourea Ligands

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Substituted thiourea ligands bind in a bidentate manner forming a four-membered ring through the sulfur atom and a deprotonated thiourea nitrogen atom when reacted with $[(en)_2Co(OSO_2CF_3)_2]^+$ in tetramethylene sulfone. Reaction of unsymmetrical ligands results in the formation of coordination isomers, some of which can be separated by column chromatography using Sephadex SPC-25. Coordination isomers are easily distinguishable based on visible and ¹H NMR spectroscopy . Twelve *para*-substituted and one *meta*-substituted ligands were studied: *N,N'*-dibenzylthiourea (**1a**); *N*-(R)phenyl-*N'*-benzylthiourea {R = H (**2a**), NO₂ (**2b**), CH₃ (**2c**)}; *N*-(R)phenyl-*N'*-(R')phenylthiourea {R, R': H, H (**3a**), H, CH₃ (**3b**), OCH₃, NO₂ (**3c**), CH₃, NO₂ (**3d**)}; *N*-methyl-*N'*-(R)phenylthiourea {R = H (**4a**), CH₃ (**4b**), OCH₃ (**4c**), NO₂ (**4d**), 3-CH₃ (**4e**)}. The solid state structure (X-ray) of one isomer of **Co-4a** as its perchlorate salt confirms the coordination mode suggested by ¹H NMR spectroscopy and shows that the Co–N bond *trans* to the coordinated thiourea sulfur induces a structural *trans* effect of 0.019 Å.

Introduction

The interaction of substituted thiourea ligands with metal ions has been of interest for several reasons. *N*-alkyl- and *N*-dialkyl-*N'*-acyl(aroyl)thioureas have been evaluated as monitoring ligands for platinum group metals in waste effluent streams.[1] Thiourea derivatives of acridine complexed to Au[I] show activity against *Mycobacterium* tuberculosis[2] and possess antitumour activity when complexed to Pt[II][3–5] and Rh[III].[6] The antifungal properties of *N*-benzoyl-*N'*-dialkylthiourea derivatives complexed to Co[III] have been evaluated[7,8] and *N*-(antipyridinyl)-*N'*-(2-methoxyphenyl)thiourea has been fabricated into a sensor that detects Co[II].[9] In addition, the coordination chemistry of urea,[10–12] thiourea,[13] and substituted urea ligands[14–16] has been of general interest over many years. Continuing our interest in the coordination of sulfur-containing ligands to Co[III][17–19] we examined the coordination of the *N,N'*-substituted thiourea ligands shown in Fig. 1 to the robust $[(en)_2Co]^{3+}$ fragment. All of the ligands bond to Co[III] in a bidentate manner through the thiourea sulfur and a deprotonated nitrogen atom forming a four-membered ring. Two coordination isomers are formed from the reaction of unsymmetrical ligands. Reported here are details of the reaction of thirteen ligands and characterisation of their cobalt adducts by NMR spectroscopy and electrospray mass spectrometry. Results from single-crystal X-ray diffraction

on one complex confirms the binding mode and shows that the Co–N bond *trans* to the coordinated thiourea sulfur atom is lengthened.

Results and Discussion

Synthesis

Syntheses of the complexes were accomplished by the reaction of substituted thiourea ligands with *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$ in tetramethylenesulfone as illustrated in Scheme 1. The triflato ion is readily substituted under mild conditions and these preparations are another example of the synthetic versatility of labile trifluoromethanesulfonato complexes.[6,16,19–24] Isolated product yields ranged from 15 to 50 % and are significantly lower than the nearly quantitative yields often reported for similar reactions. The most prevalent side product is *cis*-$[(en)_2Co(H_2O)_2]^{3+}$ which forms when unreacted *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$ is exposed to water before and during chromatography. The yields, however, are similar to those reported for the reaction of *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$ with substituted urea ligands[16] and are probably low due to the need to deprotonate the ligand.

Symmetrical thiourea ligands (**1** and **3a**) react with *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$ to produce a single thiourea-containing

product while unsymmetrical ligands have the potential to produce coordination isomers. Isomers of the benzyl (**2**) and methyl derivatives (**4**) are separable on Sephadex SPC-25 with 0.2 M NaClO₄ while those of the diphenyl derivatives (**3**) are not. When isomers can be separated, the first 2+ band to elute is coordinated through the thiourea sulfur and the deprotonated urea nitrogen next to the phenyl ring (*endo* isomer) while the second 2+ band removed is coordinated through the thiourea sulfur and the deprotonated urea nitrogen adjacent to the benzyl or methyl group (*exo* isomer) (Fig. 2).

When the phenyl substituent is a nitro group (**2b, 3c, 3d, 4d**) more of the *endo* isomer is usually formed as might be expected from the increased acidity of the –NH closest to the nitro group. Aside from this, product distributions are variable and appear to depend on reaction time. In one investigation four identical experiments were set up with **4b** and analysed after 2, 3, 14, and 21 days of stirring. Short reaction times (2 and 3 days) favoured the *endo* isomer while the *exo* isomer predominated at longer reaction times (14 and 21 days) suggesting that the *exo* isomer is formed from the isomerisation of the *endo* isomer in tetramethylene sulfone. There is no evidence of isomerisation, however, in aqueous solution or in the solid state for the *para*-substituted

derivatives. Visible spectra of sealed aqueous solutions of **Co-4b** (both isomers) are unchanged after sitting for one year in the dark and NMR spectra of several different solid samples (both isomers) after seven years of storage are identical to those originally obtained. Isomerisation was observed with the 3-methyl derivative (**4e**). After cleanly separating the isomers by chromatography, NMR spectra of the isolated crystals of the *exo* isomer (filtered two weeks after chromatography) were clearly contaminated with a small amount of the *endo* isomer (Fig. 3).

In addition to their elution characteristics on Sephadex SPC-25, the 2+ charge of the complexes is confirmed by elemental analysis and electrospray mass spectrometry. Nine complexes were examined using the electrospray technique. All show the presence of [(en)₂Co(thiourea)]ClO₄⁺, [(en)₂Co(thiourea)]²⁺, and [(en)Co(thiourea)]ClO₄⁺. For **1** the masses of these complexes appear at 533, 217, and 473, respectively. Results were identical for pairs of isomers run separately (**Co-4a** and **Co-4c**) and are not complicated by the presence of two isomers in a single sample (**Co-3c**). Finally, single-crystal X-ray crystallography of the *endo* isomer of **Co-4a** confirms the structure illustrated in Fig. 2.
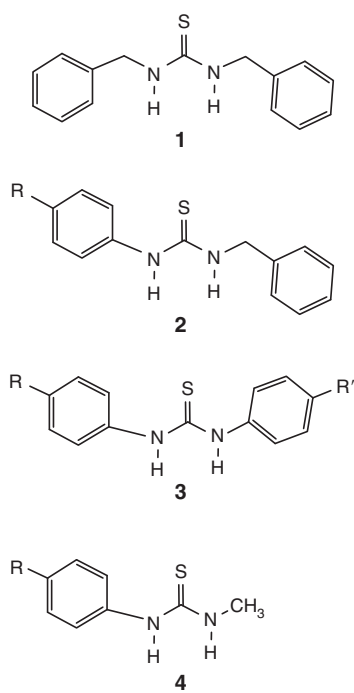

Fig. 1. Ligands in this study. The substituents (R, R′) are as follows: **2**: **2a** H, **2b** NO₂, **2c** CH₃; **3**: **3a** H, H, **3b** H, CH₃, **3c** OCH₃, NO₂, **3d** CH₃, NO₂; **4**: **4a** H, **4b** CH₃, **4c** OCH₃, **4d** NO₂, and **4e** CH₃ (meta).

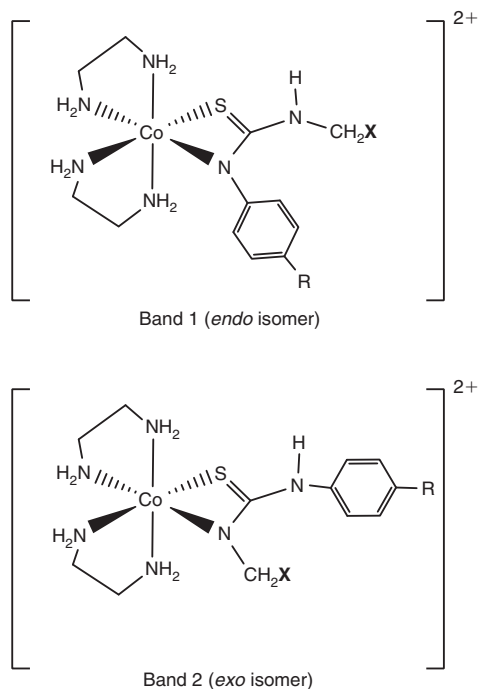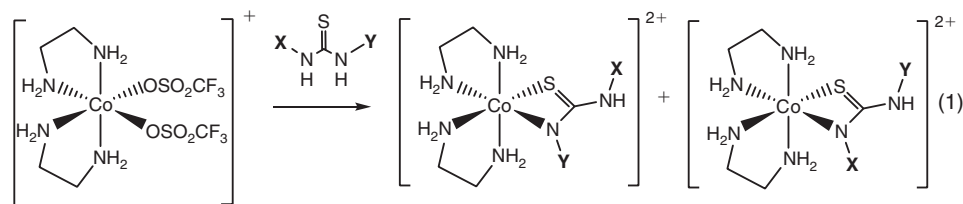Band 1 (*endo* isomer)

Band 2 (*exo* isomer)

Fig. 2. Structures of the coordination isomers illustrated for ligands **2** (X = C₆H₅) and **4** (X = H).

Scheme 1.

Spectroscopic Characterisation

Visible Spectroscopy

Fig. 4 illustrates the visible spectra of the isomers of **Co-4a** in water; these are representative of all complexes examined.
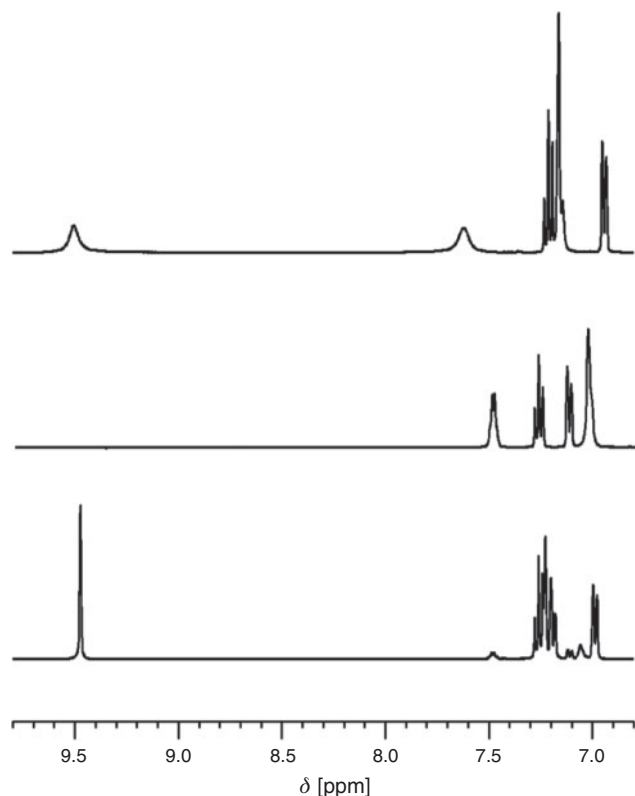

Fig. 3. ^{1}H NMR spectra of **4e** (upper) and its coordination isomers when bonded to the $[(en)_2Co]^{3+}$ fragment: the *endo* isomer of **Co-4e** (middle) and the *exo* isomer of **Co-4e** (lower) in d_6-DMSO.
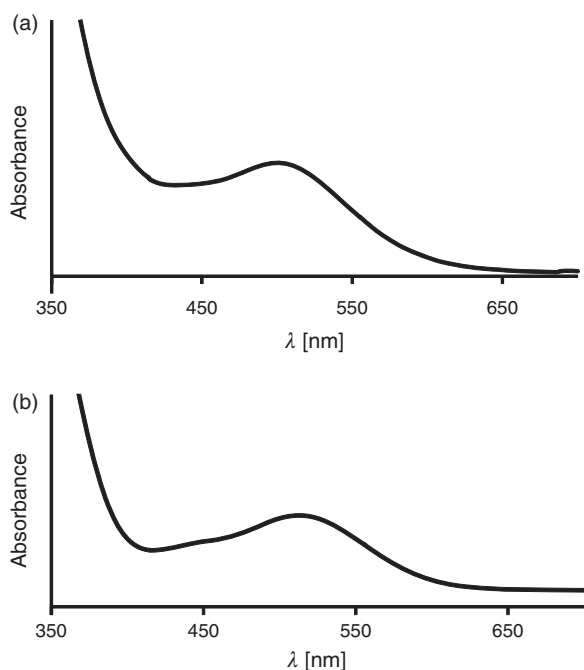

Fig. 4. Visible spectra of the complexes of **4a** in water. (a) Band 1: *endo* isomer. (b) Band 2: *exo* isomer.

Isomers are easily distinguishable with the visible spectrum of the *endo* isomer showing a λ_{max} at 513 nm followed by a higher energy shoulder at 450 nm before rising into the UV region. Complexes of the *exo* isomer rise to the UV region more quickly and have no shoulder at 450 nm and the lower energy transition is closer to 503 nm. Solutions of the *endo* isomers are maroon in colour while solutions of the *exo* isomers, while still maroon, have a purplish cast.

NMR Spectroscopy

^{1}H NMR spectroscopy clearly identifies the mode of thiourea coordination to the $[(en)_2Co]^{3+}$ fragment due to the disappearance of the appropriate –NH resonance of the free ligand upon coordination. Fig. 3 presents the ^{1}H NMR spectra for **4e** and its coordination isomers from 6.8 to 9.8 ppm. The –NH resonances in the uncoordinated ligand (upper spectrum) appear as broad singlets with the thiourea hydrogen adjacent to the aromatic ring being more downfield at 9.5 ppm. In the *endo* isomer (middle spectrum) coordination through the deprotonated urea nitrogen adjacent to the phenyl ring is indicated by the disappearance of the –NH resonance at 9.5 ppm and the sharpening of the signal arising from the –NH adjacent to the methyl group into a quartet at 7.5 ppm. In the *exo* isomer (lower spectrum) the broad signal at 7.5 ppm is absent consistent with coordination through –NCH$_3$ while the resonance at 9.5 ppm is now a sharp singlet. As mentioned earlier, the *exo* isomer of **Co-4e** undergoes a small amount of isomerisation into the *endo* isomer – this is evidenced in Fig. 3 by the residual quartet at 7.5 ppm in the spectrum of the *exo* isomer. The portion of each spectrum below 7 ppm (not shown) is consistent with the discussion that follows regarding Fig. 5.

The ^{1}H NMR spectra for **Co-1** and **Co-3a** in Fig. 5 illustrate additional features that were consistently observed in all complexes. The $-CH_2NH_2$ resonances of the coordinated ethylenediamine ligands appear as a group of overlying signals centred at $\sim$2.5 ppm, but when the ligand is coordinated though a nitrogen adjacent to a phenyl group as in **Co-3a** (middle spectrum) one of the hydrogen signals shifts upfield to 1.5 ppm. COSY and HMQC experiments clearly show that this signal is due to a –CH of an ethylenediamine ligand. Location of the $-CH_2NH_2$ resonances of the coordinated ethylenediamines also vary depending on the coordination mode of the ligand. When the deprotonated urea nitrogen adjacent to a phenyl group is coordinated as in **Co-3a**, the eight amine hydrogens appear over a range of 3 to 6 ppm, but when the coordinated N is not adjacent to a phenyl group as in **Co-1** (lower spectrum) the signals are bunched closer together over a range of only 1.2 ppm. The sharp singlet observed in all spectra at 3.4 ppm is due to water. The four benzylic hydrogens in **Co-1** are also found in the amine hydrogen region. Those adjacent to the coordinated, deprotonated urea nitrogen appear as an AB quartet at 4.1 ppm while those next to the non-coordinated, protonated urea nitrogen appear as a doublet at 4.5 ppm. The hydrogen attached to the uncoordinated urea nitrogen appears downfield from the aromatic hydrogens of the phenyl or benzyl rings. In **Co-1** this resonance appears as a triplet at 8.3 ppm while in **Co-3a** it appears as a sharp singlet at 9.8 ppm – each of these signals integrate as a single hydrogen and are shifted only slightly from their location in the non-coordinated ligand.

The upper spectrum in Fig. 5 is that of the main product produced from the reaction of the unsymmetrical ligand **2b**. Coordination through the *endo* position is indicated in three
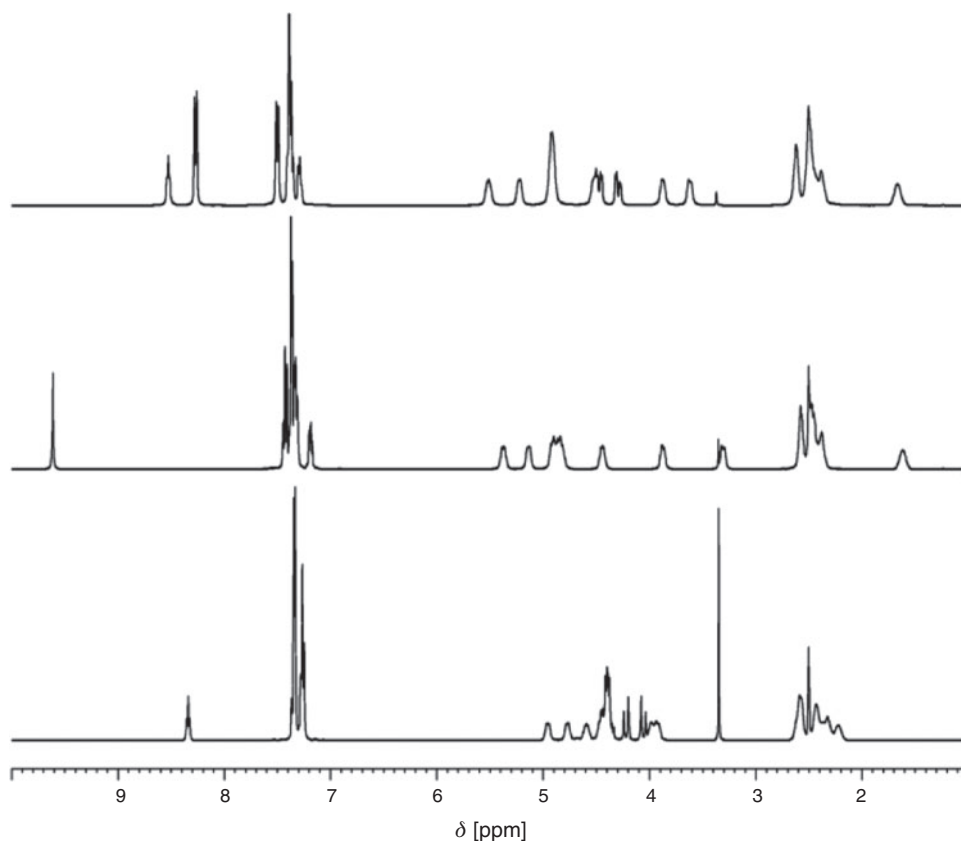
Fig. 5. ^{1}H NMR spectra of **Co-1** (lower), **Co-3a** (middle), and **Co-2b** (upper) in d_6-DMSO.

ways. First, the –NH(C$_6$H$_5$) resonance present in the free ligand is gone while the –NHCH_2(C$_6$H$_5$) resonance remains as a triplet at 8.5 ppm. Second, the amine hydrogens are spread over the region from 6.0 to 3.5 ppm and this total area integrates as 10 hydrogens – eight due to –NH_2CH$_2$ and two due to –CH_2(C$_6$H$_5$) which appear as an AB quartet at 4.4 ppm. Third, a single –CH_2NH$_2$ appears at 1.6 ppm and the remaining seven appear in the cluster at 2.5 ppm.

Fig. 6 presents ^{13}C-APT NMR spectra for the same three complexes used to generate Fig. 5. The symmetry present in symmetrical ligands **1** and **3a** is broken upon coordination. For example, the benzylic peak at 47.1 ppm and the quaternary carbon peak at 139.3 ppm in non-coordinated **1** each split into two peaks in **Co-1**: 48.4 and 45.3 ppm and 138.7 and 138.3 ppm, respectively. The three peaks due to aromatic –CHs in **3a** (124 to 129 ppm) appear as six peaks in **Co-3a** over the same region and the single peak due to the quaternary carbon in **3a** at 140.1 ppm appears as two peaks at 136.7 and 141.0. When non-symmetrical ligands coordinate (**Co-2b**) the same overall pattern of peaks observed for the free ligand is retained, but some peaks are shifted due to interaction with the Co^{III}. In all cases, signals due to –CH_2NH$_2$ appear as three overlapping or as four distinct peaks around 45 ppm, always downfield of the solvent peak (d_6-DMSO) centred at 39.5 ppm.

Isomers formed from reaction of ligands **3b**–**3d** are not separable on Sephadex SPC-25, but do co-crystallise. Peaks are doubled in the ^{13}C NMR and both –NHX resonances are present in the ^{1}H NMR spectra. The single peaks at 21.1 and 180.2 in the ligand **3b** are split into two peaks: 21.1 and 21.2 and 173.5 and 173.8, respectively, in the isolated cobalt product. Also in **3b**, the five CH resonances of the free ligand split into

10 peaks between 122 and 132 ppm while the remaining three quaternary carbon peaks appear as six peaks between 134 and 142 ppm. The same pattern was observed in each of the complexes formed from reaction of four unsymmetrical substituted diphenyl ligands. Integration of the –NHX resonances allows calculation of the isolated amounts of each isomer. In **Co-3b**, for example, the isomers are isolated in roughly a 50:50 distribution while for **Co-3d** the distribution is 60:40 (*endo* –CH$_3$ compared with *endo* –NO$_2$). No additional attempts were made to resolve the isomers.

Crystallographic Investigations

Single-crystal X-ray diffraction analysis of the perchlorate salt of the *endo* isomer of **Co-4a** confirms the bidentate coordination of the ligands to Co^{III} through the thiourea sulfur and a deprotonated thiourea nitrogen atom forming a four-membered ring (Fig. 7). Selected bond lengths and angles are given in Table 1. Coordination of the substituted thiourea to Co^{III} significantly alters bond lengths about the thiourea carbon atom compared with the non-coordinated ligand. The C–S bond length compiled from twenty structures of thiourea ligands[25–28] averages 1.68 (1) Å. Upon coordination of **4a** to Co^{III} the C–S bond lengthens to 1.740 (3) Å. In Co^{III} complexes coordinated by thioether ligands[17,29] the average C–S distance is 1.82 (1) Å; thus the C–S bond length found here of 1.740 (3) Å is about halfway between that of a C–S double and a C–S single bond length. As the C–S bond lengthens, the C–N bonds decrease to 1.317 (4) (*endo*) Å and 1.329 (4) (*exo*) Å from an average of 1.36 (1) Å in the free ligands due to delocalisation arising from deprotonation of the ligand. Structural determinations have also
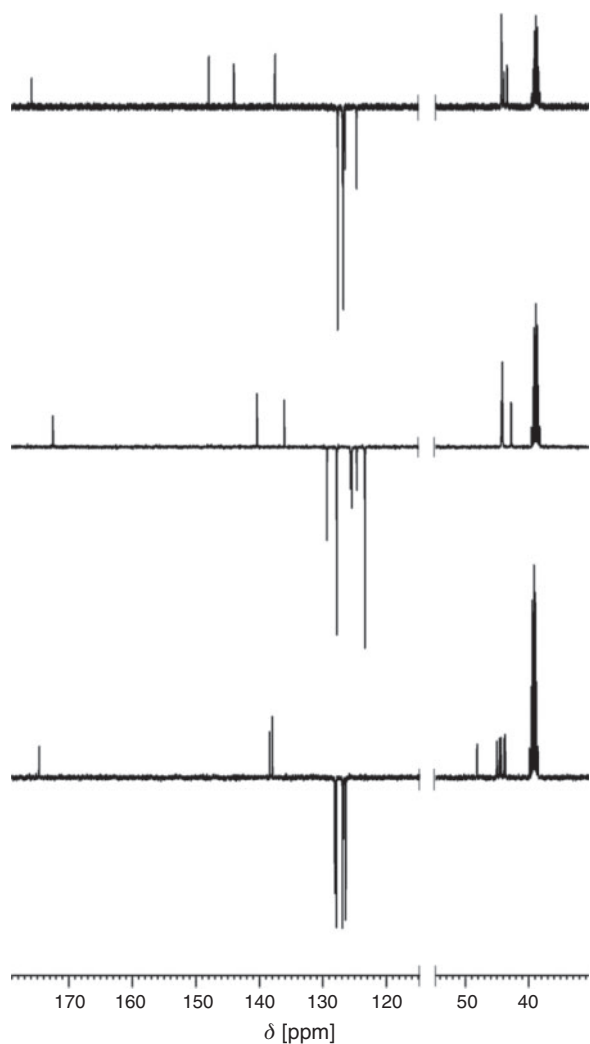
Fig. 6. ^{13}C-APT NMR spectra of **Co-1** (lower), **Co-3a** (middle) and **Co-2b** (upper) in d_6-DMSO.
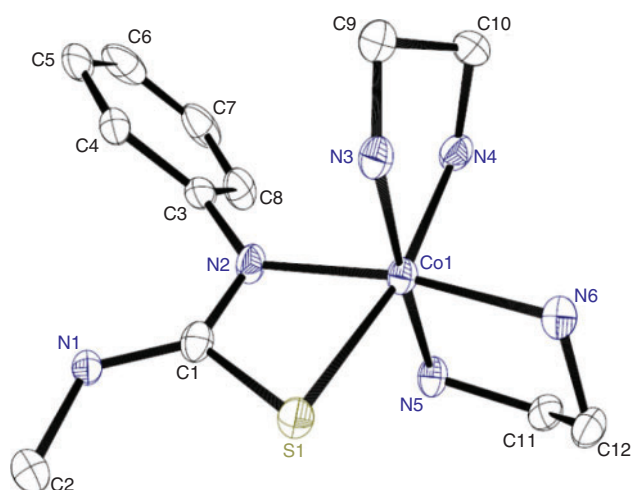

Fig. 7. Ellipsoid plot of a cation of **Co-4a** (*endo* isomer). Hydrogen atoms have been omitted for clarity.

been reported with disubstituted thiourea ligands bonded to Pt[II,[1,3,5]] Rh[III,[1,6]] Rh[I,[30]] Co[III,[8]] Zn[II,[31]] Hg[II,[32]] and Cu[I,[33]] The mode of coordination observed here has been reported previously – twice in complexes of Pt[II[1,5]] and once with Rh[I,[30]]

Table 1. Selected bond lengths [Å] and angles [deg.] for the cation [Co-4a][2+] (*endo* isomer)

Standard deviations are in parentheses; refer to Fig. 7 for the numbering scheme

Bond lengths			
Co(1)–N(2)	1.934(3)	Co(1)–N(5)	1.957(2)
Co(1)–N(3)	1.957(3)	Co(1)–N(6)	1.962(2)
Co(1)–N(4)	1.976(3)	Co(1)–S(1)	2.2848(10)
S(1)–C(1)	1.740(3)	N(1)–C(1)	1.329(4)
N(1)–C(2)	1.453(4)	N(2)–C(1)	1.317(4)

Bond angles			
N(5)–Co(1)–N(3)	177.15(11)	N(2)–Co(1)–N(6)	169.44(11)
N(2)–Co(1)–S(1)	72.26(8)	N(4)–Co(1)–S(1)	168.28(8)
C(1)–S(1)–Co(1)	77.14(12)	C(1)–N(1)–C(2)	122.7(3)
C(1)–N(2)–C(3)	124.5(3)	C(1)–N(2)–Co(1)	101.4(2)
C(3)–N(2)–Co(1)	133.8(2)	N(2)–C(1)–N(1)	127.0(3)
N(2)–C(1)–S(1)	109.2(2)	N(1)–C(1)–S(1)	123.8(3)

The common binding mode of *N*-benzoyl-*N′*-alkylthiouruea ligands is coordination through the acyl oxygen atom and thiourea sulfur to form a six-membered ring while substituted thiourea ligands lacking an acyl group generally bind to the metal in a monodentate manner through the thiourea sulfur atom. The average C–S distance in the structures referenced above is 1.74 (2) Å and is not dependent on the coordination mode or the metal and is identical to that observed in this work. In the cobalt complex, Co(MTCB)$_3$ (MTCB = *N*-(morpholinothiocarbonyl) benzamide)[8] the Co–S distance of 2.213(6) Å is shorter than the 2.285 (1) Å found here. By way of comparison, the range of Co–S(thioether) bond lengths is 2.217 (2) to 2.301 (1) Å.[29] That the bond in the coordinated thiourea complexes studied here is not shorter (expected due to charge delocalisation in the deprotonated ligand compared with neutral thiourea or thioether ligands) could be a consequence of distortions arising from coordination of the four-membered ring.

The four-membered ring has bond angles of 72.26 (8)°, 77.1 (1)°, 109.2 (2)°, and 101.4 (2)°. This arrangement is facilitated by deformation of the trigonal planar environment about the thiourea carbon atom (C1) with bond angles of 109.2 (2)°, 127.0 (3)°, and 124.8 (3)° and lengthening of the bond between the S and C1. The bite angle of the coordinated thiourea ligand, 72.26 (8)°, is smaller than the bite angle of 85.4 (4)° generated by the coordinated ethylenediamines which form five-membered rings. The small bite angle contributes to the overall distorted octahedral geometry about the Co.

The Co–N(en) bond distance *trans* to the thiourea sulfur, 1.976 (3) Å, is longer than those of the Co–N(en) bonds which are *trans* to each other, 1.957 (3) Å. Thus, there is a small, but observable structural *trans* effect (STE) induced by the thiourea sulfur of 0.019 Å. S-bonded thiourea ligands coordinated to Ru[III[6]] and thioether ligands coordinated to Co[III[29]] both induce a STE of 0.02 Å. Greater effects are induced by coordinated sulfur atoms possessing a negative formal charge as in thiolato complexes of Co[III] where an average STE of 0.044 (2) Å was found.[34,35] A more significant STE would be expected in the complex examined given the negative formal charge the thiourea sulfur develops due to delocalisation in the deprotonated, coordinated ligand. The lack of a significant STE induced by the deprotonated N atom of the thiourea ligand is also unexpected given that effects as large as 0.03 Å have been observed in two structures containing deprotonated urea ligands.[16,36]

Unpublished work on related structures (J. Krause and L. Roecker, unpubl. data) suggests that the STE induced by deprotonated, coordinated thiourea ligands are much larger than observed in the structure reported here. We are currently obtaining additional crystallographic data to confirm this unpublished work.

Conclusion

The reaction of [(en)₂Co(OSO₂CF₃)₂](CF₃SO₃) with symmetrical thiourea ligands results in the formation of a single cobalt(III) complex while the reaction with unsymmetrical ligands results in the formation of two isomeric complexes. The coordination isomers are easily distinguishable by either visible or ¹H NMR spectroscopy. Using these well characterised complexes as a starting point, understanding more complicated interactions of substituted thiourea ligands that serve as bridging ligands between cobalt(III) ions is possible (L. Roecker et al., unpubl. data).

Experimental

General Data

All chemicals were reagent grade and used as received with the exception of tetramethylene sulfone which was vacuum-distilled before use. Cis-[(en)₂Co(OSO₂CF₃)₂](CF₃SO₃) was prepared following a reported procedure.[24] Visible spectra were obtained with a Perkin–Elmer Lambda 3B spectrophotometer. ¹H and ¹³C NMR spectra were recorded with a JOEL JNM-FX-200 at Berea College or with a Bruker 400 at Bates College in DMSO-d_6 with TMS as an internal reference. Mass spectra were recorded on a Thermo Finnigan LCQ Deca Max. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, USA.

Preparation of Ligands

Ligands were prepared by the reaction of an amine with the appropriate isothiocyanate. A typical preparation is described here for the preparation of **3b**. Methylisothiocyanate (5.0 g, 68 mmole) was slowly added to a stirred solution of p-toluidine (7.3 g, 68 mmol) that had been dissolved in 50 mL of absolute ethanol. The mixture was heated to reflux; cooling to room temperature deposited a white solid that was then isolated by vacuum filtration and recrystallised twice from 150 mL of hot absolute ethanol (9.8 g, 80 % yield). All ligands were characterised by ¹H and ¹³C NMR (APT) spectroscopy; many were also characterised by the 2D experiments HMQC or COSY to help determine which hydrogen atoms were connected to which carbon atoms.

Compound **1**: δ_H (400 MHz, d_6-DMSO) 4.71 (s, 4H), 7.33 (m, 10H), 7.96 (s, 2H). δ_C (400 MHz, d_6-DMSO) 126.2, 127.60, 128.25 (CH, CH₃); 47.07, 139.25 (C, CH₂); C=S not observed.

Compound **2a**: δ_H (300 MHz, d_6-DMSO) 4.80 (d, J 7.5, 2H), 7.14 (t, J 7.5, 1H), 7.42 (m, 9H), 8.25 (s, 1H), 9.69 (s, 1H). δ_C (400 MHz, d_6-DMSO) 123.31, 124.29, 126.87, 127.43, 128.27, 128.64 (CH); 47.22, 139.00, 139.16, 180.78 (C, CH₂).

Compound **3a**: δ_H (300 MHz, d_6-DMSO) 7.14 (t, J 7.5, 2H), 7.37 (t, J 7.5, 4H), 7.49 (d, J 7.5, 4H), 9.81 (s, 2H). δ_C (300 MHz, d_6-DMSO) 124.25, 125.03, 129.05 (CH); 140.09, 180.15 (C).

Compound **3b**: δ_H (300 MHz, d_6-DMSO) 2.29 (s, 3H), 7.14 (m, 3H), 7.35 (m, 5H), 7.50 (d J 8.5, 1H), 9.72 (s, 2H). δ_C (300 MHz, d_6-DMSO) 21.1, 124.2, 124.5, 124.9, 129.0, 129.5 (CH, CH₃); 134.3, 137.4, 140.1, 180.2 (C).

Compound **3c**: δ_C (300 MHz, d_6-DMSO) 20.8, 56.0, 114.1, 124.5, 126.5, 129.5 (CH, CH₃); 132.1, 134.1, 137.2, 156.5, 182.5 (C).

Compound **4a**: δ_H (300 MHz, d_6-DMSO) 2.93 (d, J 4.5, 3H), 7.14 (t, J 6.0, 1H), 7.32 (m, 4H), 7.68 (s, 1H), 9.56 (s, 1H). δ_C (300 MHz, d_6-DMSO) 32.1, 123.1, 124.9, 129.2 (CH, CH₃); 139.1, 181.2 (C).

Compound **4b**: δ_H (300 MHz, d_6-DMSO) 2.28 (s, 3H), 2.91 (d, J 4.5, 3H), 7.14 (d, J 7.8, 2H), 7.23 (d, J 7.8, 2H), 7.55 (s, 1H), 9.45 (s, 1H). δ_C (300 MHz, d_6-DMSO) 21.1, 31.8, 124.3, 129.8 (CH, CH₃); 134.2, 137.0, 181.7 (C).

Compound **4c**: δ_H (300 MHz, d_6-DMSO) 2.88 (d, J 4.5, 3H), 3.75 (s, 3H), 6.90 (d, J 6.9, 2H) 7.19 (d, J 6.9, 2H), 7.44 (s, 1H), 9.33 (s, 1H). δ_C (300 MHz, d_6-DMSO) 31.8, 56.0, 114.6, 126.8 (CH, CH₃); 132.0, 157.2, 182.0 (C).

Compound **4d**: δ_H (300 MHz, d_6-DMSO) 2.97 (d, J 4.5, 3H), 7.81 (d, J 8.7, 2H) 8.18 (d, J 8.7, 2H), 8.24 (s, 1H), 10.21 (s, 1H). δ_C (300 MHz, d_6-DMSO) 31.7, 120.9, 125.1 (CH, CH₃); 142.3, 147.0, 181.4 (C).

Compound **4e**: δ_H (400 MHz, d_6-DMSO) 2.28 (s, 3H), 2.91 (d, J 3.9, 3H), 6.93 (d, J 7.5, 1H) 7.17 (m, 3H), 7.61 (s, 1H), 9.49 (s, 1H). δ_C (400 MHz, d_6-DMSO) 21.05, 31.28, 120.40, 123.78, 125.46, 128.56 (CH, CH₃); 138.04, 138.87, 180.94 (C).

Preparation of Co^{III} Complexes Coordinated by Substituted Thiourea Ligands

All cobalt complexes were prepared by the reaction between the thiourea ligand with cis-[(en)₂Co(OSO₂CF₃)₂](CF₃SO₃) in tetramethylene sulfone. A typical reaction is described here for the reaction with **4e** to produce **Co-4e**. Ligand **4e** (0.30 g, 1.62 mmol) was dissolved in 10 g of tetramethylene sulfone and [(en)₂Co(OSO₂CF₃)₂](CF₃SO₃) (1.00 g, 1.59 mmol) was added. The reaction mixture was sealed and stirred. After 3 days the reaction solution was diluted with 300 mL of water and stirred for 20 min before filtering to remove unreacted ligand. The solution was sorbed onto Sephadex SPC-25 (2 cm ID × 20 cm) and loaded as a dark maroon band. After washing with water, elution with 0.1 M NaClO₄ removed a minor pink band of [(en)₂Co(O₂CO)]⁺. Continued elution with 0.2 M NaClO₄ moved a maroon band that broadened and separated into two distinct bands which were the desired products. These were followed by an orange band of [(en)₂Co(OH₂)₂]³⁺. After removing the first maroon band with 0.2 M NaClO₄, the top of the column containing the diaquo complex was removed and then the second maroon band was removed with 0.5 M Ba(ClO₄)₂. Evaporation and/or refrigeration over several days yielded crystalline samples of each product: Band 1 (*endo* isomer) (0.29 g, 33 % yield), Band 2 (*exo* isomer) (0.16 g, 18 % yield). All complexes were characterised by visible, ¹H NMR, and ¹³C NMR (APT) spectroscopy; many were also characterised by the 2D NMR experiments HMQC or COSY along with electrospray mass spectrometry.

Caution: Although we have not experienced any explosions, perchlorate salts are potentially explosive and should be handled only in very small quantities.

Complex **Co-1**: δ_H (400 MHz, d_6-DMSO) 2.4 (br m, 8 H), 3.90 (br s, 2H), 4.14 (q, J 47.5, 15.5, 2H), 4.40 (m, 5H), 4.59 (s, 1H), 4.75 (s, 1H), 4.95 (s, 1H) 7.30 (m, 10 H), 8.33 (t, J 6.1, 1 H). δ_C (400 MHz, d_6-DMSO) 126.77, 127.04, 127.26, 128.22, 128.43 (CH); 43.99, 44.17, 44.65, 44.91, 45.31, 48.43, 138.29, 138.71, 174.94 (C, CH₂). m/z (z = +1) 533, 473; (z = +2) 217. Anal Calc. for CoSC₁₉H₃₁N₆Cl₂O₈·2H₂O (633.5): Co 8.80, Cl 10.59. Found: Co 8.76, Cl 10.63 %.

Complex **Co-2a** Band 1: δ_H (400 MHz, d_6-DMSO) 1.57 (s, 1H), 2.5 (br, 7 H), 3.30 (s, 1H), 3.90 (s, 1H), 4.35 (q, J 55.5, 14.6, 2H), 4.50 (s, 1H), 4.60 (s, 1H), 4.70 (s, 1H), 4.80 (s, 1H), 5.15 (s, 1H), 5.35 (s, 1H), 7.35 (m, 10 H), 8.20 (t, J 5.4, 1H). δ_C (400 MHz, d_6-DMSO) 126.04, 126.33, 126.99, 127.29, 128.23, 129.95 (CH); 43.36, 44.22, 44.70, 44.80, 45.00, 138.72, 140.86, 174.81 (C, CH_2). m/z ($z = +1$) 519, 459; ($z = +2$) 209. Calc. MW 619.4.

Complex **Co-2b** Band 1: δ_H (400 MHz, d_6-DMSO) 1.67 (s, 1H), 2.5 (m 7 H), 3.61 (s, 1H), 3.85 (s, 1H), 4.38 (q, J 55.5, 14.6, 2H), 4.50 (s, 1H), 4.95 (s, 3H), 5.21 (2, 1H), 5.50 (s, 1H), 7.28 (d J 8.7, 1H), 7.42 (m, 4H), 7.50 (d J 8.7, 2H), 8.27 (d J 8.7, 2H), 8.52 (t, J 5.4, 1H). δ_C (400 MHz, d_6-DMSO) 125.2, 127.15, 127.40, 127.54, 128.29 (CH); 43.97, 44.48, 44.68, 44.88, 138.15, 144.61, 148.56, 176.42 (C, CH_2).

Complex **Co-2c** Band 1: δ_H (400 MHz, d_6-DMSO) 1.61 (s, 1H), 2.25 (s, 3H), 2.5 (br, 7 H), 3.28 (s, 1H), 3.90 (s, 1H), 4.30 (q, J 55.5, 14.6, 2H), 4.45 (s, 1H), 5.10 (s, 1H), 5.30 (s, 1H), 5.50 (s, 1H), 5.70 (s, 1H), 5.80 (s, 1H), 7.30 (m, 9 H), 8.20 (t, J 5.4, 1H). δ_C (400 MHz, d_6-DMSO) 20.65, 126.16, 126.96, 127.27, 128.21, 130.50 (CH, CH_3); 43.37, 44.15, 44.66, 44.80, 44.90, 135.33, 138.02, 138.75, 174.71 (C, CH_2).

Complex **Co-3a**: δ_H (400 MHz, d_6-DMSO) 1.61 (s, 1H), 3.30 (s, 1H), 3.88 (s, 1H), 4.45 (s, 1H), 4.88 (s, 3H), 5.13 (s, 1H), 5.39 (s, 1H), 7. 28 (t, J 6.0, 1H), 7.35 (m, 9H). δ_C (400 MHz, d_6-DMSO) 124.01, 125.25, 126.07, 126.25, 128.43, 129.96 (CH); 43.32, 44.72, 44.90, 136.68, 140.97, 173.07 (C, CH_2). m/z ($z = +1$) 505, 445; ($z = +2$) 203. Calc. MW 605.4.

Complex **Co-3b** (mixture of isomers): δ_C (300 MHz, d_6-DMSO) 21.1, 21.4, 124.3, 124.7, 125.4, 126.2, 126.7, 126.8, 129.0, 129.5, 130.5, 131.0 (CH, CH_3); 43.8, 45.2, 45.4, 133.5, 134.2, 135.3, 136.5, 138.2, 141.2, 173.5, 173.8 (C, CH_2).

Complex **Co-3c** (mixture of isomers): m/z ($z = +1$) 580, 520; ($z = +2$) 241. Calc. MW 680.4.

Complex **Co-4a** Band 1: δ_H (300 MHz, d_6-DMSO) 1.60 (s, 1H), 2.50 (br, 7H), 2.71 (d, 3H), 3.4 (s, 1H), 3.88 (s, 1H), 4.51 (s, 1H), 4.8 (br, 3H), 5.12 (s, 1H), 5.35 (s, 1H), 7.35 (m, 5H), 7.55 (q, J 4.5, 1H). δ_C (300 MHz, d_6-DMSO) 27.8, 126.6, 126.9, 130.6 (CH, CH_3); 44.0, 45.3, 45.5, 141.5 (C, CH_2); C=S not observed. m/z ($z = +1$) 443, 383; ($z = +2$) 172. Calc. MW 543.3.

Complex **Co-4a** Band 2: δ_H (300 MHz, d_6-DMSO) 2.50 (br, 8H), 2.71 (s, 3H), 4.01 (s, 1H), 4.30 (s, 2H), 4.45 (s, 1H), 4.69 (s, 2H), 4.82 (s, 1H), 4.97 (s, 1H), 7.21 (br, 1H), 7.38 (br, 4H), 9.54 (s, 1H). δ_C (300 MHz, d_6-DMSO) 33.2, 123.3, 125.3, 129.2 (CH, CH_3); 44.9, 45.2, 45.3, 46.0, 137.7, 171.2 (C, CH_2). m/z ($z = +1$) 443, 383; ($z = +2$) 172. Anal. Calc. for $CoSC_{12}H_{25}N_6Cl_2O_8 \cdot 2H_2O$ (543.3): Co 10.17, Cl 12.24. Found: Co 10.13, Cl 12.20%.

Complex **Co-4b** Band 1: δ_H (300 MHz, d_6-DMSO) 1.62 (s, 1H), 2.28 (s, 3H), 2.5 (br, 8H), 2.68 (d, J 7.8, 3H), 3.88 (s, 1H), 4.50 (s, 1H), 4.75 (br, 3H), 5.11 (s, 1H), 5.32 (s, 1H), 7.12 (d, J 7.8, 2H), 7.21 (d, J 7.8, 2H), 7.49 (q, J 4.5, 1H). δ_C (300 MHz, d_6-DMSO) 21.3, 27.8, 126.8, 131.1 (CH, CH_3); 44.0, 45.3, 45.5, 135.9, 138.9 (C, CH_2); C=S not observed.

Complex **Co-4b** Band 2: δ_H (300 MHz, d_6-DMSO) 2.30 (s, 3H), 2.5 (br, 8H), 2.70 (s, 3H), 4.00 (s, 1H), 4.35 (br, 3H), 4.61 (s, 1H), 4.70 (s, 1H), 4.80 (s, 1H) 4.95 (s, 1H), 7.19 (d, J 7.8, 2H), 7.28 (d, J 7.8, 2H), 9.48 (s, 1H). δ_C (300 MHz, d_6-DMSO) 21.1, 33.1, 123.6, 129.7 (CH, CH_3); 44.8, 45.2, 45.3, 45.9, 134.5, 135.0 (C, CH_2); C=S not observed. m/z ($z = +1$) 457, 397; ($z = +2$) 179. Calc. MW 557.3.

Complex **Co-4c** Band 1: δ_H (300 MHz, d_6-DMSO) 1.69 (s, 1H), 2.45 (s, 3H), 2.5 (br, 8H), 2.66 (d, J 4.8, 3H), 3.20 (s, 1H), 3.80 (s, 1H), 4.45 (s, 1H), 4.70 (s, 3H), 5.05 (s, 1H), 5.25 (s, 1H), 6.95 (d, J 8.4, 2H), 7.28 (d, J 8.4, 2H), 7.42 (q, J 4.5, 1H). δ_C (300 MHz, d_6-DMSO) 27.1, 55.3, 115.1, 127.6 (CH, CH_3); 43.3, 44.6, 44.7, 44.8, 133.0, 157.2, 175.4 (C, CH_2). m/z ($z = +1$) 473, 413; ($z = +2$) 187. Calc. MW 573.3.

Complex **Co-4c** Band 2: δ_H (300 MHz, d_6-DMSO) 2.50 (br, 8H), 2.68 (s, 3H), 4.00 (s, 1H), 4.30 (s, 3H), 4.58 (s, 1H), 4.78 (s, 2H), 4.76 (s, 1H), 6.96 (d, J 8.4, 2H), 7.27 (d, J 8.4, 2H), 9.42 (s, 1H). δ_C (300 MHz, d_6-DMSO) 33.0, 55.8, 114.2, 126.0 (CH, CH_3); 44.9, 45.2, 45.3, 46.0, 130.1, 157.6, 171.7 (C, CH_2). m/z ($z = +1$) 473, 413; ($z = +2$) 187. Calc. MW 573.3.

Complex **Co-4e** Band 1: δ_H (400 MHz, d_6-DMSO) 1.61 (s, 1H), 2.32 (s, 3H), 2.50 (m, 7H), 2.68 (d, J 4.6, 3H), 3.25 (s, 1H), 3.87 (s, 1H), 4.48 (s, 1H), 4.65 (s, 1H), 4.78 (s, 2H), 5.10 (s, 1H), 5.30 (s, 1H), 7.03 (m, 2H), 7.12 (d, J 7.3, 1H), 7.27 (t, J 7.8, 1H), 7.49 (q, J 4.5, 1H). δ_C (400 MHz, d_6-DMSO) 20.98, 27.22, 123.27, 126.68, 129.73 (CH, CH_3); 43.40, 44.69, 44.93, 139.41, 140.71, 175.21 (C, CH_2).

Complex **Co-4e** Band 2: δ_H (400 MHz, d_6-DMSO) 2.32 (s, 3H), 2.56 (m, 8H), 2.72 (s, 3H), 4.42 (m, 3H), 4.50 (s, 1H), 4.89 (s, 1H), 5.12 (s, 2H), 5.27 (s, 1H), 6.99 (d, J 7.4, 1H), 7.23 (m, 3H), 9.47 (s, 1H). δ_C (400 MHz, d_6-DMSO) 21.05, 32.64, 119.91, 123.22, 125.27, 128.45 (CH, CH_3); 44.22, 44.49, 44.77, 45.35, 137.00, 137.87, 170.49 (C, CH_2).

X-Ray Crystallography

X-ray diffraction data were collected at 90 K on a Nonius kappa CCD diffractometer from a crystal flash-cooled directly into

Table 2. Crystal data and structure refinement for the perchlorate salt of $[\text{Co-4a}]^{2+}$ (*endo* isomer)

Parameter	$[\text{Co-4a}]^{2+}$
Empirical formula	$[C_{12}H_{25}N_6S](ClO_4)_2 \cdot 1.32H_2O$
Formula weight	567.05
Crystal size [mm^3]	$0.25 \times 0.20 \times 0.10$
Temperature [K]	90.0(2)
Wavelength [Å]	0.71073
Crystal system, space group	Triclinic, P −1
Unit cell dimensions	
a [Å]	9.7586(3)
b [Å]	9.8451(3)
c [Å]	12.9448(5)
α [deg.]	75.0898(14)
β [deg.]	89.7522(14)
γ [deg.]	68.5636(16)
Volume [Å^3]	1113.08(6)
Z	2
Calculated density [g cm^{-3}]	1.692
Absorption coefficient [mm^{-1}]	1.163
$F(000)$	586.4
θ range for data collection	1.64° to 27.44°
Limiting indices	$-12 \le h \le 12$, $-12 \le k \le 12$, $-16 \le 1 \le 13$
Reflections collected/unique	13 240/5078 ($R_{int} = 0.0570$)
Completeness to $\theta = 27.44$ [%]	99.7
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.893 and 0.760
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5078/16/313
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	R_1 0.0484, wR_2 0.0885
R indices (all data)	R_1 0.1003, wR_2 0.1031
Largest diff. peak and hole [e Å^{-3}]	0.724 and −0.522

liquid nitrogen.[37] Unit cell parameters were obtained from 10×1 degree frames and were refined using a least-squares scheme based on all data frames (*SCALEPACK*, Denzo-SMN[38]). Lorentz and polarisation corrections were applied during data reduction. The structure was solved by direct methods (*SHELXS97*[39]) and refined against F^2 by weighted full-matrix least-squares (*SHELXL97*[39]). Absorption corrections (*SCALEPACK*[38] and *XABS2*[40]) were applied. Hydrogen atoms were found in difference maps and refined using a combination of riding models and free refinement with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.[41] Final models were checked using Platon[42] and by an R-tensor.[43] Crystal data and relevant details of the structure determination are summarised in Table 2 and selected geometrical parameters are given in Table 1. All bond lengths (Table S1) and angles (Table S2) are provided as Supplementary Material.

Crystallographic information files have been deposited with the Cambridge Crystallographic Data Centre and assigned the deposit codes 931427. These can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Selected bond lengths and bond angles for the cation [**Co-4a**]$^{2+}$ (*endo* isomer) are available on the Journal's website.

Acknowledgements

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