

Reaction of 2-Pyridylmethylthiourea Derivatives with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ Induces Hypodentate Coordination of an Ethylenediamine Ligand

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Pyridylmethylthiourea derivatives coordinate with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ in a tridentate manner resulting in the formation of a hypodentate ethylenediamine ligand. Four ligands were studied: *N*-(*R*)phenyl-*N'*-2-pyridylmethylthiourea (*R* = H (**1a**), CH₃ (**1b**), OCH₃ (**1c**)) and *N*-benzyl-*N'*-2-pyridylmethylthiourea (**2**). These bind through the sulfur, a deprotonated *exo* nitrogen, and the pyridyl nitrogen atoms forming four and five-membered rings, respectively. The ligand also coordinates in a bidentate manner through the sulfur and deprotonated *endo* or *exo* nitrogen atoms, forming two additional coordination isomers. The solid state structure (X-ray) of one of the bidentate isomers of **Co-1b**²⁺ (*endo* isomer) shows that the coordinated thiourea sulfur induces a structural *trans* effect of 0.035 Å on the *trans* Co–N bond while that of the tridentate isomer of **Co-1a**³⁺ confirms the coordination mode of the ligand and the presence of a protonated hypodentate ethylenediamine ligand as suggested by ¹H and ¹³C NMR spectroscopy.

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Introduction

This study examines the products formed from the reaction of four 2-pyridylmethylthiourea derivatives (Fig. 1) with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ in tetramethylene sulfone. Substituted thiourea ligands that do not contain a pyridyl group coordinate to the $[(\text{en})_2\text{Co}]^{3+}$ subunit in a bidentate manner through the thiourea sulfur atom and a deprotonated nitrogen atom (Fig. 2),^[1] while the urea analogues of the ligands illustrated in Fig. 1 coordinate

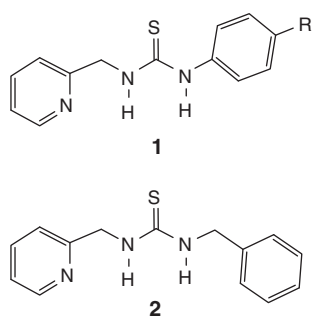


Fig. 1. Structures of the ligands in this study. The substituents, *R*, in **1** are as follows: H (**1a**), CH₃ (**1b**), and OCH₃ (**1c**).

in a bidentate manner through the pyridyl nitrogen and deprotonated *exo* urea nitrogen atom (Fig. 3).^[2] Our original intent in pursuing this work was to prepare the thiourea analogues of the complex illustrated in Fig. 3 to complement our previous study on the acid hydrolysis of the urea analogues.^[2] While each of the previously studied ligands afforded relatively simple chemistry when reacted with the cobalt precursor—forming predominantly two structural isomers upon reaction with non-pyridyl-containing thiourea ligands or the desired urea complex upon reaction with pyridyl urea ligands—reaction with pyridyl-containing thiourea ligands was complicated by the unexpected cleavage of a single Co–N(en) bond in the usually robust $[(\text{en})_2\text{Co}]^{3+}$ fragment, which facilitated tridentate coordination of the hybrid ligand (Fig. 4d) in up to 55 % yield. The reaction of $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ with the pyridylthiourea ligands was also complicated by formation of a black precipitate that accounts for 10–15 % of the starting materials. Smaller amounts of other side products are formed by bidentate chelation through the thiourea moiety. This paper describes the isolation and characterisation of the reaction products (Fig. 4a, b, d) by NMR spectroscopy. Single-crystal X-ray diffraction on two reaction products confirms the bidentate chelation through the thiourea moiety (*endo* coordination) of ligand **1b** in **Co-1b**²⁺ (Fig. 5) and

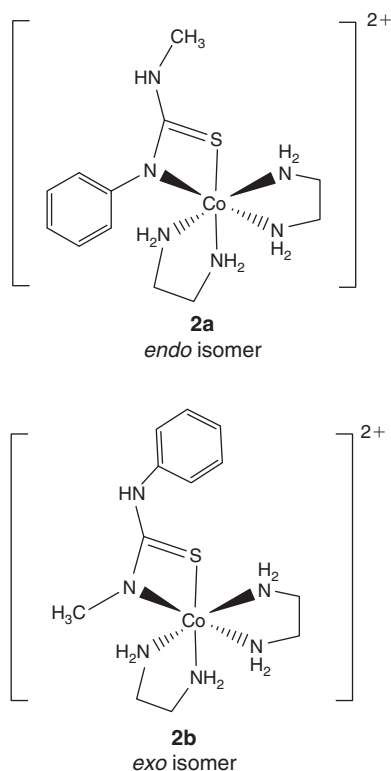


Fig. 2. Substituted thiourea ligands without a pyridyl group form two coordination isomers with $[(\text{en})_2\text{Co}]^{3+}$.

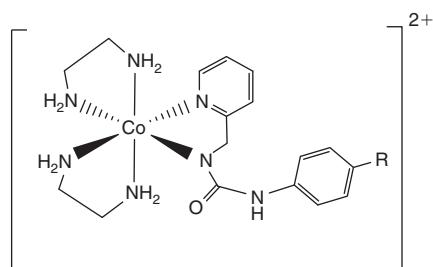


Fig. 3. Known structure of the urea analogues of the thiourea ligands coordinated to the $[(\text{en})_2\text{Co}]^{3+}$ fragment.

the tridentate binding mode of ligand **1a** in **Co-1a**³⁺ (Fig. 6). The X-ray studies suggest that structural *trans* effects contribute to the formation of the hypodentately coordinated ethylenediamine ligand.

Results and Discussion

Synthesis

The reaction of $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2](\text{CF}_3\text{SO}_3)$ in tetramethylenesulfone with thiourea ligands containing a pendant pyridyl moiety was expected to lead to the formation of three structural isomers (Fig. 4a–c) in which the added ligand coordinates in a bidentate manner consistent with the established reactivity of related ligands.^[1,2] The target complex (Fig. 4c), however, was not isolated because the pyridylthiourea ligand bonded in a tridentate manner (Fig. 4d) through the open coordination site arising from cleavage of a Co–N(en) bond. That the ligand is capable of bonding in a tridentate manner is not unexpected as evidenced by coordination of similar ligands

such as thiosemicarbazones^[3] and the ability of the thiourea moiety to form four-membered rings,^[1] but rupture of the Co–N(en) bond, which allowed it to do so, was unexpected. Hypodentate coordination^[4] of ethylenediamine has been documented previously in Co^{III} complexes of $[(\text{en})_2(\text{Cl})\text{CoN}(\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_3)]^{3+}$,^[5,6] $[(\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{4+}$,^[7] and $[(\text{en})_2\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2]^{5+}$,^[8] but they are prepared by a different synthetic route. $[(\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{4+}$, for example, is prepared in 40 % yield from the reaction of ethylenediamine with excess $[(\text{NH}_3)_5\text{CoOSMe}_2]^{3+}$ while $[(\text{en})_2\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2]^{5+}$ is formed in 19 % yield from the reaction of *cis*- $[(\text{en})_2\text{CoCl}_2]^+$ in neat ethylenediamine.^[5,8] The complexes coordinated by a tridentate thiourea ligand along with a hypodentate ethylenediamine ligand (Fig. 4d) are formed in 40–55 % yield with the bidentate thiourea isomers (Fig. 4a, b) each accounting for ~5–10 % of the overall yield. All reactions are accompanied by the rapid formation of a black precipitate upon mixing the ligand with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ —this product accounts for 10–15 % of the total starting materials and remains unidentified. Small amounts of the carbonato complex, $[(\text{en})_2\text{CoO}_2\text{CO}]^+$, are also formed.

The reaction products (after filtration to remove the black product) are easily separated by column chromatography (Sephadex SPC-25) using a gradient of increasing NaClO_4 concentrations. The singly and doubly charged complexes elute as expected with 0.1 and 0.2 M NaClO_4 , respectively, while the tripositive hypodentate complex requires 0.4 M NaClO_4 , higher than expected. This confused initial interpretation of the results as our experience has found that tripositive cations usually elute with 0.3 M salt solutions from Sephadex SPC-25. Elemental analysis and X-ray crystallography, however, confirm the 3+ charge. Dilution and subsequent re-elution of each fraction with 0.5 M $\text{Ba}(\text{ClO}_4)_2$ affords concentrated solutions from which pure products precipitate after cooling and/or evaporation. These complexes were characterised by a variety of NMR experiments in addition to X-ray crystallography of two complexes.

Crystallographic Investigations

Single-crystal X-ray diffraction analysis of the perchlorate salt of the *endo* isomer of **Co-1b**²⁺ confirms one possible hypodentate binding mode for pyridyl-substituted thiourea ligands in which the potentially tridentate ligand is coordinated in a bidentate manner through the thiourea sulfur and a deprotonated thiourea nitrogen atom, forming a four-membered ring (Fig. 5). Selected bond lengths and angles are given in Table 1. Details of how coordination through the thiourea moiety affects bond lengths and angles within the ligand has been recently described and the results obtained here are consistent with those observations.^[1] The four-membered ring has a bite angle of 72.04 (7)° with the Co^{III} centre with the remaining angles of the ring being 76.9(1)°, 109.3(2)°, and 101.6(2)° for the Co–S–C, N–C–S, and Co–N–C angles, respectively. This arrangement is facilitated by deformation of the trigonal planar environment about the thiourea carbon atom with bond angles of 109.3(2)°, 125.7(3)°, and 124.9(2)° along with lengthening of the C–S bond to 1.741(3) Å from the 1.68(1) Å found in non-coordinated thiourea ligands.^[9–12] The Co–S distance is 2.2946(8) Å, similar in length to that observed in Co^{III} complexes bonded to neutral thioether sulfur atoms where Co–S(thioether) bond lengths range from 2.217 to 2.301 Å.^[13] That the bond in the coordinated thiourea complexes studied here is not shorter (expected because of charge delocalisation in the deprotonated ligand

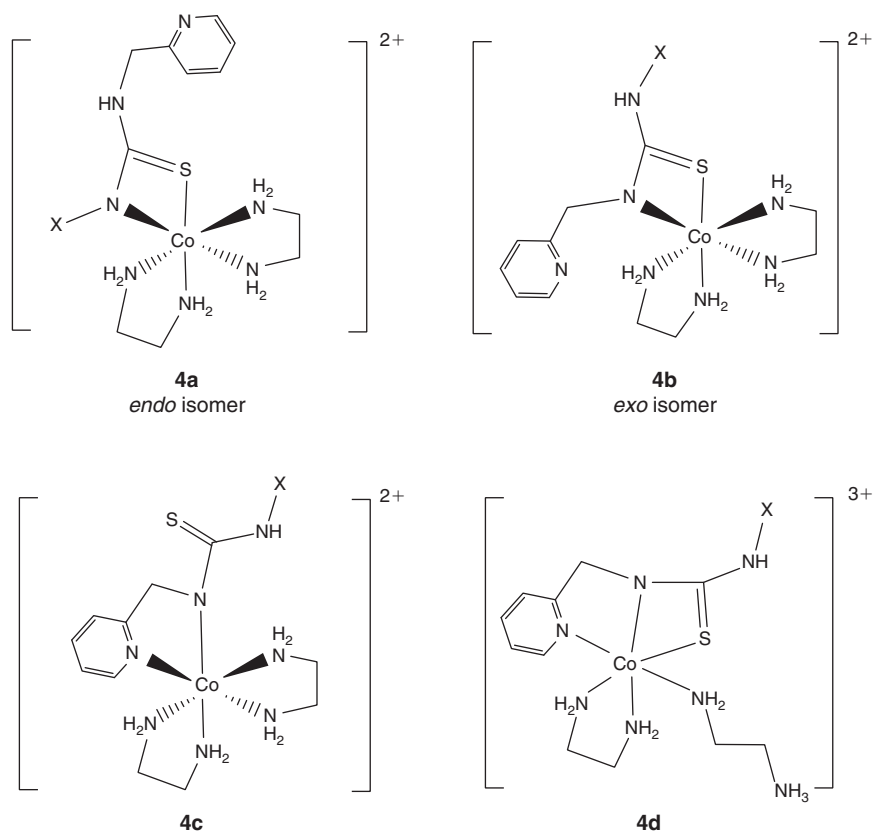


Fig. 4. Four possible coordination isomers of 2-pyridylmethylthiourea ligands with ethylenediamine complexes of Co^{III} .

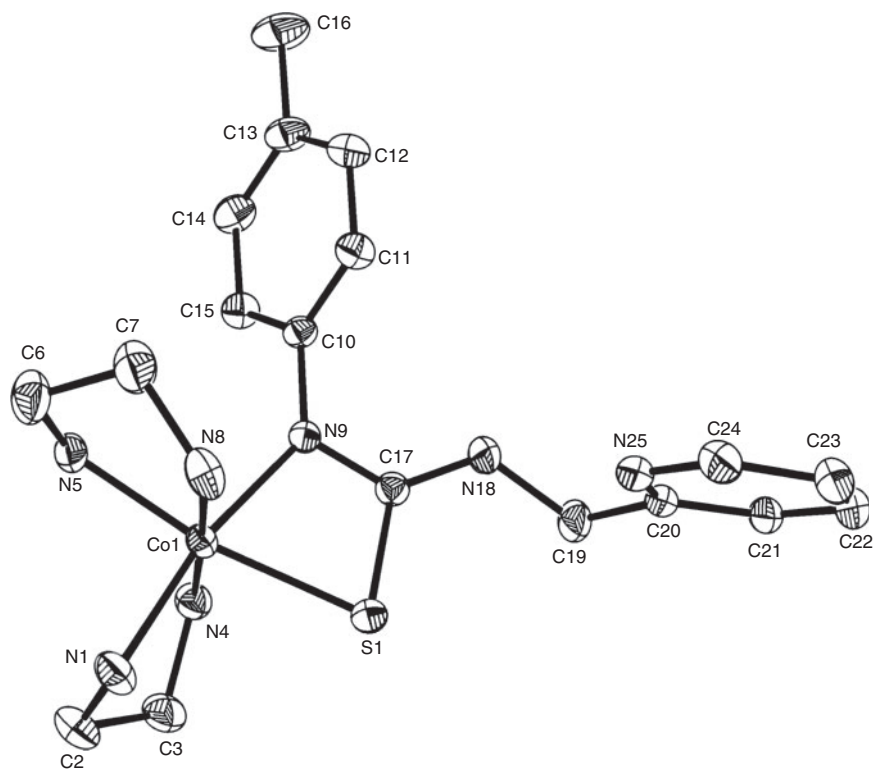


Fig. 5. Ellipsoid plot of one of the cations of Co-1b^{2+} (endo isomer). Hydrogen atoms have been omitted for clarity.

compared with a neutral thioether ligand) could be a consequence of distortions arising from coordination of the four-membered ring.

The Co–N(en) bond distance *trans* to the thiourea sulfur, 1.992(3) Å, is longer than those of the Co–N(en) bonds which are *trans* to each other, 1.957(4) Å. The structural *trans* effect (STE) of 0.035(5) Å induced by the partially negatively charged thiourea sulfur atom is larger than that observed when neutrally charged sulfur atoms coordinate. Thioether ligands coordinated to Co^{III} and S-bonded thiourea ligands coordinated to Ru^{III} both induce a STE of 0.02 Å.^[13,14] A larger STE of 0.044(2) Å has been found in complexes that are

coordinated by atoms possessing a full negative formal charge as in thiolato complexes of Co^{III}.^[15,16] The Co–N(en) bond distance *trans* to the deprotonated thiourea nitrogen also shows a small, but not unexpected, STE of 0.015(3) Å relative to the *trans* Co–N(en) bonds. STEs as large as 0.03 Å have been observed in structures containing deprotonated urea ligands.^[2,17] While the STEs observed here are larger than those observed in our previous report,^[1] they are more consistent with data that we have collected on related structures (J. Krause and L. Roecker, unpubl. data). Thus, it appears that the coordinated thiourea ligand induces lengthening, and presumably weakening, of select Co–N(en) bonds that may help to explain formation of the hypodentate ethylenediamine ligand.

Single-crystal X-ray diffraction analysis of the perchlorate salt of **Co-1a**³⁺ confirms the tridentate binding of the pyridyl-substituted thiourea ligand and the monodentate binding of an ethylenediamine ligand to Co^{III} (Fig. 6). Selected bond lengths and angles are given in Table 2. The ligand binds in a meridional fashion through the pyridyl nitrogen, the deprotonated *exo* thiourea nitrogen, and the thiourea sulfur atoms forming five and four-membered rings, respectively. The coordinated tridentate ligand is planar, with the root mean square deviation from the plane, defined by all ligand atoms except C12–C17, being 0.086 and 0.015 Å for the A and B cations, respectively. Co1A and N4A both lie above the plane at 0.032(3) and 0.126(8) Å; Co1B is above the plane by 0.017(3) Å and N4B below the plane by 0.01(1) Å. The N(py)–Co–S angle observed here is only 153.8°(4), much smaller than that observed in tridentate ligands that form two five-membered rings to Co^{III}. In *mer*-[Co(dien)₂]³⁺, for example, the *trans* N–Co–N bond angles of the tridentate ligands are 171.7° and 170.7°.^[18] The N(en) atom in the plane of the tridentate ligand (N4) splits the difference between the N(py) and S with the N(py)–Co–N(en) and S–Co–N(en) angles being 102° and 104°, respectively.

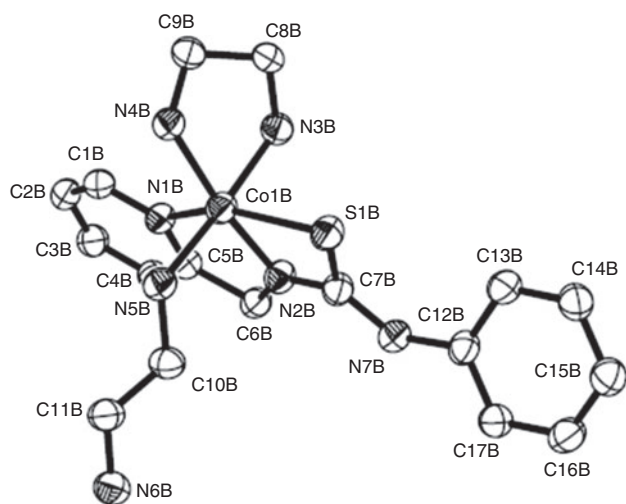


Fig. 6. Ellipsoid plot of one of the cations of **Co-1a**³⁺ (hypodentate). Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg.) for the monomeric cations of [Co-1b]²⁺ (*endo* isomer)

Standard deviations are in parentheses. The unit cell contained two cations unrelated by symmetry. Refer to Fig. 5 for the numbering scheme

Cation 1	Bond length (Å)	Cation 2	Bond length (Å)
Co(1)–S(1)	2.2895(6)	Co(2)–S(2)	2.2996(6)
Co(1)–N(9)	1.9431(16)	Co(2)–N(34)	1.9261(17)
Co(1)–N(4)	1.9545(18)	Co(2)–N(29)	1.963(2)
Co(1)–N(8)	1.9558(19)	Co(2)–N(30)	1.950(2)
Co(1)–N(1)	1.9732(18)	Co(2)–N(26)	1.9704(19)
Co(1)–N(5)	1.9916(18)	Co(2)–N(33)	1.9922(19)
S(1)–C(17)	1.7394(19)	S(2)–C(42)	1.743(2)
N(9)–C(17)	1.315(2)	N(34)–C(42)	1.312(3)
N(9)–C(10)	1.423(2)	N(34)–C(35)	1.425(3)
C(17)–N(18)	1.336(3)	C(42)–N(43)	1.335(3)
Bond angle (deg.)		Bond angle (deg.)	
N(9)–Co(1)–S(1)	72.11(5)	N(34)–Co(2)–N(30)	91.73(8)
N(8)–Co(1)–N(5)	85.39(8)	N(30)–Co(2)–N(33)	85.34(9)
N(4)–Co(1)–N(1)	85.21(8)	N(29)–Co(2)–N(26)	85.23(9)
C(17)–S(1)–Co(1)	77.14(7)	C(42)–S(2)–Co(2)	76.75(7)
C(17)–N(9)–C(10)	123.16(16)	C(42)–N(34)–C(35)	122.06(17)
C(17)–N(9)–Co(1)	101.18(12)	C(42)–N(34)–Co(2)	102.07(13)
C(10)–N(9)–Co(1)	135.38(13)	C(35)–N(34)–Co(2)	135.67(14)
N(9)–C(17)–N(18)	126.03(18)	N(34)–C(42)–N(43)	125.43(19)
N(9)–C(17)–S(1)	109.55(14)	N(34)–C(42)–S(2)	109.10(15)
N(18)–C(17)–S(1)	124.41(15)	N(43)–C(42)–S(2)	125.46(16)

The coordinated atoms perpendicular to the tridentate ligand (atoms N2–N3–N4–N5) are planar with a root mean square deviation of 0.018 Å. Bond lengths and angles within the two subunits of the tridentate ligand are similar to those of bidentate complexes of related ligands.

The structure contains a protonated hypodentate ethylenediamine ligand—all three hydrogen atoms attached to the terminal nitrogen atom were located in the difference map. Protonation is also indicated by the presence of three perchlorate anions for each cation. The average Co–N5 bond length is 1.957 (7) Å, similar to the average of 1.963(6) Å found in four other Co^{III} structures.^[6–8] The coordinating atom of the hypodentate ligand is *trans* to a N(en), 175.3(4)°. The hypodentate ligand on cation A adopts a *gauche* conformation when viewed down the C–C bond while that on cation B adopts an *anti* arrangement, presumably because of different hydrogen bonding environments. In cation B, the dangling hypodentate ligand is well ordered and involved in hydrogen bonding with the water solvate while in cation A the ligand is disordered over two distinct conformations. These two disordered conformations are correlated with the disordered perchlorate anions. Both *gauche* and *anti* conformations have been observed previously.^[6–8]

Spectroscopic Analysis

NMR Spectroscopy

Fig. 7 illustrates the ¹H NMR spectra for the ligand **1b** and the three complexes it forms upon reaction with [(en)₂Co

(OSO₂CF₃)₂]⁺ in tetramethylene sulfone. The upper spectrum is that of the uncoordinated ligand—important signals to note are the singlet attributable to –NH(phenyl) at 9.80 ppm and the triplet attributable to –NHCH₂(py) at 8.13 ppm. The following two spectra are those of the maroon *endo* isomer (Fig. 4a) and of the orange *exo* isomer (Fig. 4b). The most obvious way to distinguish between the *endo* and the *exo* coordination mode is the presence or absence of the signal attributable to the appropriate –NH. The absence of the signal at 9.80 ppm in the second spectrum suggests coordination as the *endo* isomer while the absence of the signal at 8.13 ppm in the one that follows suggests coordination as the *exo* isomer. Consistent with our previous observations, in the *endo* coordination mode, signals attributable to the ethylenediamine hydrogen atoms are spread over the range of 3 to 6 ppm while in the *exo* isomer they are bunched more tightly together from 4 to 5.2 ppm. In addition, the *endo* mode is characterised by a single –CH₂NH₂ signal being shifted upfield to 1.6 ppm.^[1]

The lower spectrum in Fig. 7 is that of the tripositive complex containing the hypodentate, protonated ethylenediamine ligand and the pyridyl thiourea ligand coordinated in a tridentate manner. Coordination of the pyridyl group is indicated by the downfield shifts of the doublet at 8.5 and triplet at 7.4 to 8.8 and 8.1 ppm, respectively. The –NHCH₂(py) signal at 8.14 ppm disappears, while that attributable to –NH(phenyl) shifts from 9.8 to 10.7 ppm. Signals in the region from 2 to 3 ppm are attributable to –CH₂NH₂ and –CH₃ and integrate as eleven protons. The region from 3.7 to 5.7 ppm integrates as eight

Table 2. Selected bond lengths (Å) and angles (deg.) for the monomeric cations of Co-1a³⁺ (hypodentate). Standard deviations are in parentheses. The unit cell contained two cations unrelated by symmetry. Refer to Fig. 6 for the numbering scheme

Cation A	Bond length (Å)	Cation B	Bond length (Å)
Co(1A)–N(2A)	1.850(5)	Co(1B)–N(2B)	1.865(5)
Co(1A)–N(3A)	1.952(5)	Co(1B)–N(3B)	1.959(18)
		Co(1B)–N(3D)	1.91(6)
Co(1A)–N(5A)	1.976(5)	Co(1B)–N(5B)	1.974(5)
Co(1A)–N(4A)	1.983(5)	Co(1B)–N(4B)	2.003(16)
		Co(1B)–N(4D)	1.96(5)
Co(1A)–N(1A)	1.982(5)	Co(1B)–N(1B)	1.958(5)
Co(1A)–S(1A)	2.3224(19)	Co(1B)–S(1B)	2.3002(17)
S(1A)–C(7A)	1.737(7)	S(1B)–C(7B)	1.758(6)
N(1A)–C(5A)	1.359(8)	N(1B)–C(5B)	1.344(7)
C(5A)–C(6A)	1.509(9)	C(5B)–C(6B)	1.517(8)
C(6A)–N(2A)	1.448(8)	C(6B)–N(2B)	1.446(7)
N(2A)–C(7A)	1.291(8)	N(2B)–C(7B)	1.292(7)
C(7A)–N(7A)	1.369(8)	C(7B)–N(7B)	1.346(7)
N(7A)–C(12A)	1.417(8)	N(7B)–C(12B)	1.411(7)
Bond angle (deg.)		Bond angle (deg.)	
N(3A)–Co(1A)–N(5A)	175.3(3)	N(3B)–Co(1B)–N(5B)	175.5(3)
N(2A)–Co(1A)–N(4A)	174.5(2)	N(2B)–Co(1B)–N(4B)	172.7(5)
		N(2B)–Co(1B)–N(4D)	174(2)
N(1A)–Co(1A)–S(1A)	152.77(18)	N(1B)–Co(1B)–S(1B)	154.89(15)
N(2A)–Co(1A)–S(1A)	71.17(17)	N(2B)–Co(1B)–S(1B)	71.54(15)
N(2A)–Co(1A)–N(1A)	81.6(2)	N(2B)–Co(1B)–N(1B)	83.3(2)
N(2A)–C(7A)–S(1A)	107.6(5)	N(2B)–C(7B)–S(1B)	106.5(4)
N(4A)–Co(1A)–N(1A)	102.4(2)	N(1B)–Co(1B)–N(4B)	101.7(7)
		N(1B)–Co(1B)–N(4D)	102(2)
N(4A)–Co(1A)–S(1A)	104.85(16)	N(4B)–Co(1B)–S(1B)	103.3(7)
		N(4D)–Co(1B)–S(1B)	103(2)

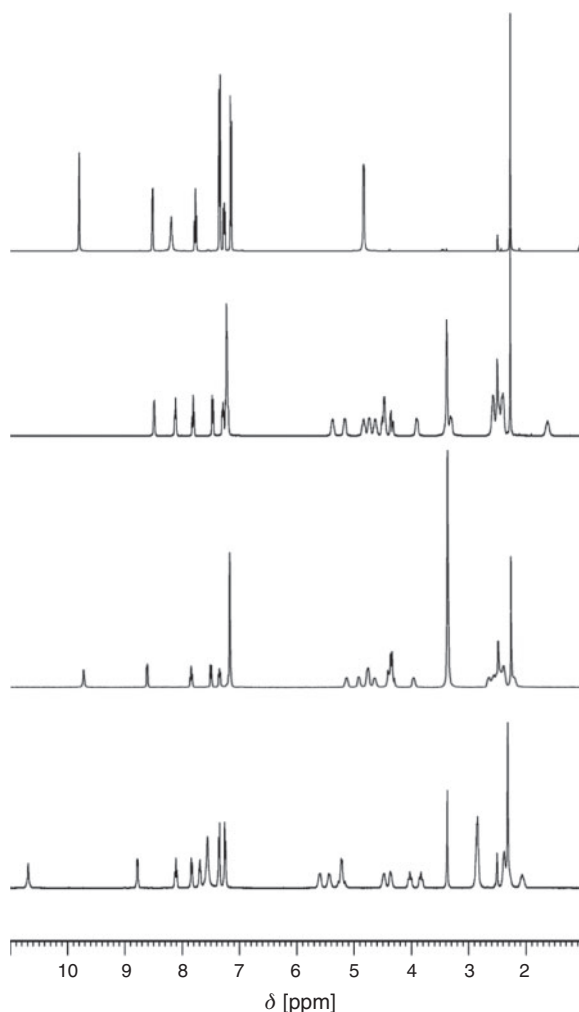


Fig. 7. ^1H NMR spectra of the ligand **1b** (upper) followed by its bidentate complexes *endo* **Co-1b** $^{2+}$, *exo* **Co-1b** $^{2+}$, and its tridentate complex **Co-1b** $^{3+}$ (lower) in d_6 -DMSO.

protons — two are accounted for by the AB quartet attributable to $-\text{CH}_2\text{py}$ centred at 5.3 ppm with the remaining six attributable to $-\text{CH}_2\text{NH}_2$. Between the doublets at 7.4 and 7.3 ppm attributable to the *para*-substituted amine and the four signals arising from the pyridyl hydrogen atoms from 8.8 to 7.7 ppm is a broad singlet at 7.6 ppm that integrates as three hydrogen atoms attributed to the protonated hypodentate ethylenediamine, $-\text{CH}_2\text{NH}_3^+$. Isolation of the protonated complex from aqueous solution is not unexpected given the $\text{p}K_a$ values of related complexes (7.36 and 7.96 for $[(\text{en})_2\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2]^{5+}$, for example) $^{[8]}$ and the higher charged, protonated complex apparently precipitates first.

Fig. 8 illustrates the ^1H NMR region from 7 to 11 ppm for the phenyl, 4-methyl, and benzyl tridentate complexes (bottom to top). Each has a broad singlet at 7.6 ppm, which integrates as three hydrogens. When a drop of D_2O is added the resonances attributed to $-\text{NH}$ and $-\text{CH}_2\text{NH}_3^+$ quickly disappear (upper spectrum). The spectra also illustrate the consistency of the pyridyl portion of the ^1H NMR spectrum and how the location of the $-\text{NH}(\text{phenyl})$ or $-\text{NH}(\text{benzyl})$ peak shifts depending on the substituent. The large shifts in the location of these resonances compared with the uncoordinated ligand is not observed in the *exo* isomers of complexes that coordinate in a bidentate manner

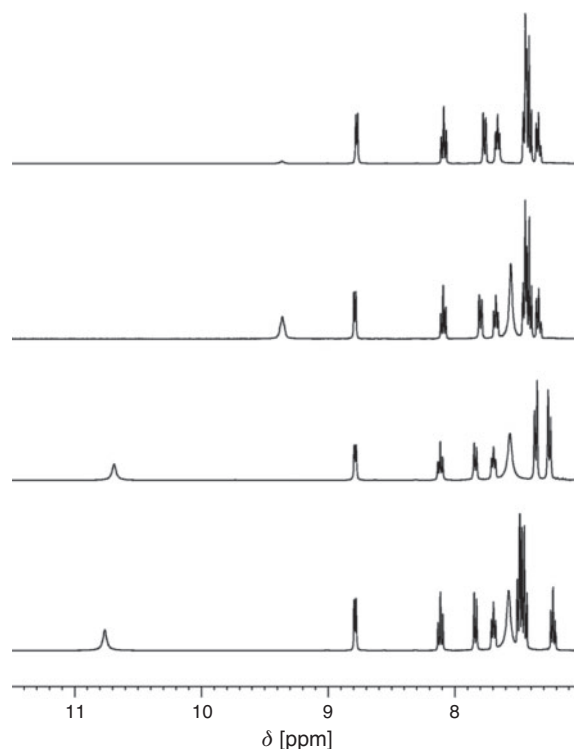


Fig. 8. ^1H NMR spectra from 7.0 to 11.5 ppm of the hypodentate complexes **Co-1a** $^{3+}$ (lower) followed by **Co-1b** $^{3+}$ and **Co-2** $^{3+}$ in d_6 -DMSO. The upper spectrum is that of **Co-2** $^{3+}$ in d_6 -DMSO after three drops of D_2O have been added.

and must be a result of additional delocalisation throughout the tridentate ligand. An expanded version (0 to 11 ppm) of **Fig. 8** is available (see **Fig. S1** in the Supplementary Material).

Fig. 9 illustrates the ^{13}C -APT NMR spectra for the same complexes used to generate **Fig. 7**. Most of the signals of the thiourea ligand shift only slightly upon coordination, but two shift by 10 ppm. The $-\text{CH}_2\text{py}$ resonance at 48.9 ppm of the non-coordinated ligand shifts upfield to 45.8 upon *endo* coordination, slightly downfield to 50.4 upon *exo* coordination, and even more downfield to 59.4 ppm in the tridentate complex. The $-\text{C}=\text{S}$ resonance at 180.8 ppm shifts upfield to 175.0, 172.9, and 170.0 ppm in *endo* **Co-1b** $^{2+}$, *exo* **Co-1b** $^{2+}$, and tridentate **Co-1b** $^{3+}$, respectively.

Fig. 9 also illustrates that in the absence of hypodentate coordination of an ethylenediamine ligand—when the pyridyl thiourea ligand is bonded in a bidentate manner—that the signals attributable to $-\text{CH}_2\text{NH}_2$ appear as four distinct peaks around 45 ppm, always downfield of the solvent peak (d_6 -DMSO) centred at 39.5 ppm. Upon $\text{Co}-\text{N}(\text{en})$ bond cleavage, these signals spread out over a larger range down to 38 ppm. This is shown more clearly (**Fig. 10**) for the phenyl, 4-methoxy, and benzyl complexes (bottom to top) where each has signals at 41.1 and 38.6 ppm attributable to the hypodentate ethylenediamine ligand. In $[(\text{en})_2\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2]^{5+}$ the carbon atoms of the bidentate ethylenediamines appear at 45.2 and 44.0 ppm while those of the hypodentate ethylenediamines appear at 40.6 and 38.9 ppm in D_2O . $^{[8]}$ Location of these peaks in the complexes studied here shift only slightly in D_2O compared with d_6 -DMSO. These shifted ^{13}C signals are a clear indication of the hypodentate coordination mode of ethylenediamine. HMQC NMR experiments (**Figs S2–S3** in the

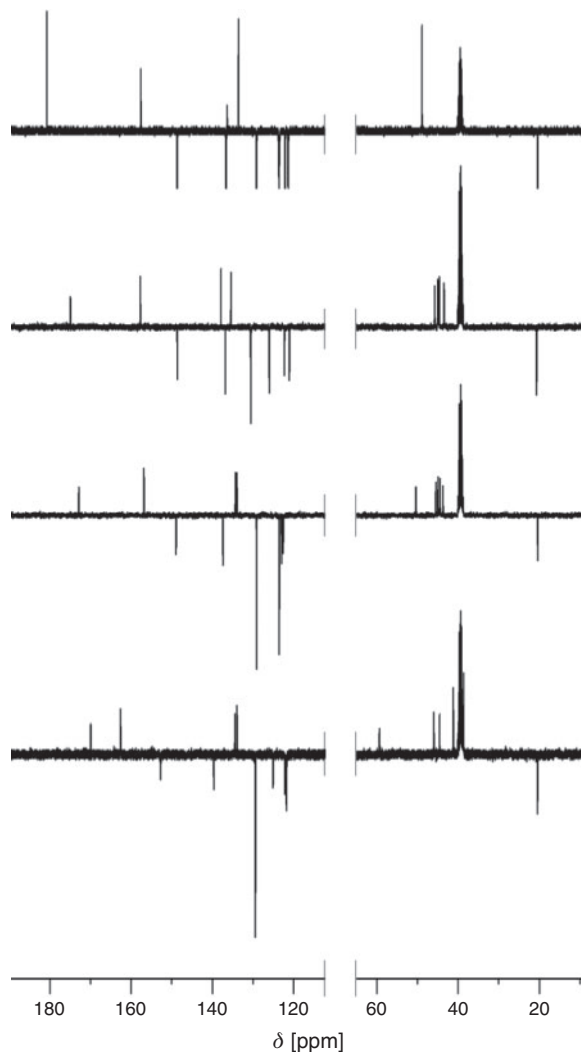


Fig. 9. ^{13}C NMR (APT) spectra of the ligand **1b** (upper) and its bidentate complexes *endo* **Co-1b** $^{2+}$, *exo* **Co-1b** $^{2+}$, and its tridentate complex **Co-1b** $^{3+}$ (lower) in d_6 -DMSO.

Supplementary Material) confirm that all signals in the ^1H NMR spectrum attributed to $-\text{CH}$ arise from hydrogen atoms that are connected to carbon atoms and that all signals attributed to $-\text{NH}$ arise from hydrogen atoms that are not connected to carbon atoms.

Comments on Other Reaction Products

Black Product

Copious amounts of a black product rapidly form during the reaction of pyridyl thiourea ligands with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ and need to be removed before purification of the other complexes by chromatography. IR and elemental analysis (the latter of which indicates about three sulfur atoms per cobalt) suggest that some form of the ligand is present, but ^1H NMR spectra in d_6 -acetone show no signals suggesting the black product contains Co^{II} . It is tempting to suggest that a redox reaction occurs between the ligand and $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ after initial binding through the pyridine since no black product is formed during the reaction with non-pyridyl containing ligands, but the issue remains unresolved. We have been unable to propose a structure for the black material that is consistent with the experimental observations.



$[(\text{en})_2\text{CoO}_2\text{CO}]^+$ was formed during all preparations. Despite being a relatively minor product, it warranted characterisation as the amount produced appeared to correlate with the amount of black product formed. The combination of ^1H and ^{13}C NMR spectra of this pink product confirms the presence of the ethylenediamine and carbonate ligands; the absence of any aromatic residues rules out coordination by the thiourea ligand. Electrospray mass spectrometry shows the presence of $[(\text{en})_2\text{CoO}_2\text{CO}]^+$ with a peak at 238. Stirring a sample of $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2](\text{CF}_3\text{SO}_3)$ in tetramethylene sulfone for three days without the addition of thiourea ligand produces only $[(\text{en})_2\text{Co}(\text{H}_2\text{O})_2]^{3+}$ after work-up. Thus, it does not appear that $[(\text{en})_2\text{CoO}_2\text{CO}]^+$ is a contaminant in the starting material. It is unclear whether the carbonate originates from ligand oxidation products or from CO_2 that is converted into carbonate under the basic conditions induced by the ligand.

Conclusion

While not our original intent, this work suggests an alternate strategy to the synthesis of hypodentate amine complexes—a potentially useful tool since the dangling amines can be modified or bound to other metals. While previous strategies have relied on the addition of an excess of the potentially hypodentate ligand to reactive or labile starting materials, the method described here generates the hypodentate ligand by cleavage of an existing metal–ligand bond. The structural evidence suggests that introducing a multidentate ligand that contains a functionality capable of inducing a significant STE onto Co^{III} will enhance the hypodentate coordination of multidentate ligands. We are currently exploring this idea by studying the reaction of various tridentate and tetradentate ligands with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2]^+$ and $[(\text{dien})\text{Co}(\text{OSO}_2\text{CF}_3)_3]$, respectively.

Experimental

General Data

All chemicals were of reagent grade and used as received with the exception of tetramethylene sulfone, which was vacuum-distilled before use. ^1H and ^{13}C NMR spectra were recorded with a JOEL JNM-FX-200 (Berea College) or a Bruker 400 (Bates College) NMR spectrometer in $\text{DMSO}-d_6$ with TMS as an internal reference. Mass spectra were recorded on a Thermo Finnigan LQC Deca Max (Berea College). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA.

Preparation of Ligands

A typical preparation is described here for the preparation of **1b**. *p*-Tolylisothiocyanate (5.0 g, 33.6 mmol) was slowly added to a stirred solution of 2-aminomethylpyridine (4.4 g 40.6 mmole) that had been dissolved in 100 mL absolute ethanol. A white precipitate formed quickly. After stirring for 20 min, the solution was filtered and the solid recrystallised from hot ethanol (7.9 g, 92 % yield).

Compound **1a**: δ_{H} (400 MHz, d_6 -DMSO) 4.80 (d, J 4.8, 2H), 7.13 (d, J 7.7, 1H), 7.28 (t, J 6.4, 1H), 7.35 (m, 3H), 7.50 (d, J 7.9, 2H), 7.78 (t, J 7.5, 1H), 8.30 (s, 1H), 8.53 (d, J 4.6, 1H), 9.90 (s, 1H). δ_{C} (400 MHz, d_6 -DMSO) (CH, CH_3) 121.4, 122.17, 123.18, 124.29, 128.65, 136.69, 148.71; (C, CH_2) 48.88, 139.16, 157.53, 180.69.

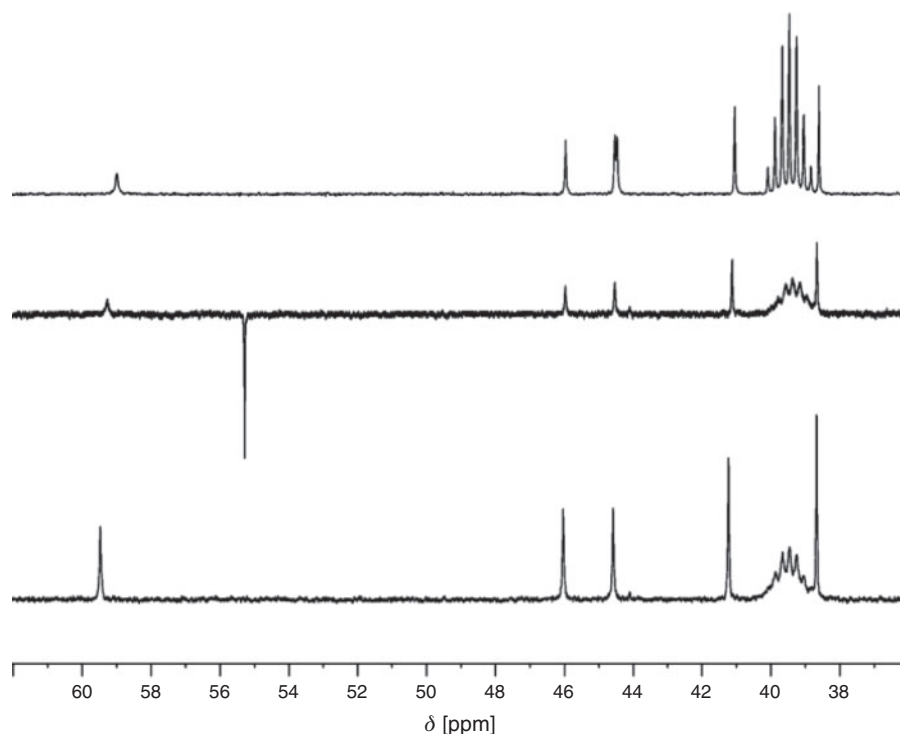


Fig. 10. ^{13}C NMR (APT) spectra of the hypodentate complexes with the ligand **1a** (lower), **1c** (middle), and **2** (upper) in d_6 -DMSO.

Compound **1b**: δ_{H} (400 MHz, d_6 -DMSO) 2.28 (s, 3H), 4.83 (d, J 4.5, 2H), 7.15 (d, J 8.5, 2H), 7.27 (t, J 6.1, 1H), 7.35 (d, 3H), 7.77 (t, J 7.6, 1H), 8.14 (s, 1H), 8.52 (d, J 4.8, 1H), 9.80 (s, 1H). δ_{C} (400 MHz, d_6 -DMSO) (CH, CH_3) 20.49, 121.34, 122.12, 122.60, 129.16, 136.65, 148.69; (C, CH_2) 48.92, 133.67, 136.42, 157.65, 180.75.

Compound **1c**: δ_{H} (400 MHz, d_6 -DMSO) 3.74 (s, 3H), 4.83 (d, J 5.0, 2H), 6.94 (d, J 8.7, 2H), 7.26 (d, J 6.4, 1H), 7.34 (m, 3H), 7.77 (t, J 7.5, 1H), 8.09 (s, 1H), 8.51 (d, J 5.3, 1H), 9.70 (s, 1H). δ_{C} (400 MHz, d_6 -DMSO) (CH, CH_3) 55.22, 113.98, 121.25, 122.08, 125.94, 136.63, 148.68; (C, CH_2) 48.97, 131.61, 156.62, 157.80, 181.09. Mp 183–186°C.

Compound **2**: δ_{H} (200 MHz, d_6 -DMSO) 4.76 (s, 2H), 4.84 (s, 2H), 7.34 (m, 7H), 7.76 (t, J 4.9, 1H), 8.12 (t, J 3.1, 1H), 8.27 (br s, 1H), 8.53 (d, J 4.9, 1H). δ_{C} (200 MHz, d_6 -DMSO) (CH) 121.9, 122.8, 127.5, 127.9, 128.8, 137.2, 149.3; (C, CH_2) 47.8, 49.5, 139.8, 158.6, C=S not observed. Mp 156–161°C.

Reaction of Ligands with $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2](\text{CF}_3\text{SO}_3)$

Isolation of Tridentate Complexes (Fig. 4d)

Compound **1b** (0.49 g, 1.91 mmol) was dissolved in 10 g of tetramethylene sulfone and $[(\text{en})_2\text{Co}(\text{OSO}_2\text{CF}_3)_2](\text{CF}_3\text{SO}_3)$ (1.00 g, 1.60 mmol) was added; the reaction mixture was sealed and stirred. The solution quickly darkened and a black precipitate formed. After 3 days the reaction solution was diluted with 300 mL of water and stirred for 20 min before filtering to remove the black precipitate and unreacted ligand (0.22 g total). The supernatant was sorbed onto Sephadex SPC-25 (3 cm internal diameter $\times$ 20 cm) and loaded as a broad brown/maroon band. After washing with water, elution with 200 mL of 0.2 M NaClO_4 quickly removed a pink band and separated a maroon band that was then removed with an additional 300 mL of 0.2 M NaClO_4 .

An orange band closely followed that was easily removed with 0.3 M NaClO_4 . Continued elution with 0.4 M NaClO_4 results in the resolution of the remaining brown/maroon band into two components with the most rapidly moving band being by far the most abundant. The minor upper band was physically removed by decanting the top portion of the column after which the remaining band was removed with 0.5 M $\text{Ba}(\text{ClO}_4)_2$. Refrigeration of the solution results in the deposition of the product as a brown/maroon powder (0.50 g, 43 % yield). All complexes were characterised by ^1H NMR and ^{13}C NMR (APT) spectroscopy as well as by the 2D-NMR experiment HMQC (Figs S2 and S3 in the Supplementary Material).

The following changes were made for the isolation of the product obtained from the reaction of **2**. After the reaction, the supernatant was loaded as a broad purple band. Elution was begun with 200 mL of 0.2 M NaClO_4 and quickly ramped up to 0.4 M NaClO_4 until only a broad purple band remained on the column. The bands eluted during this time were not characterised. Continued elution with 0.4 M NaClO_4 results in the resolution of the purple band into three components with the most rapidly moving band being by far the most abundant. The minor upper two bands were physically removed by decanting the top portion of the column, after which the remaining purple band was removed with 0.5 M $\text{Ba}(\text{ClO}_4)_2$. Refrigeration of the purple solution results in the deposition of an iridescent purple solid (0.65 g, 55 % yield).

Complex **Co-1a** $^{3+}$ (hypodentate): δ_{H} (400 MHz, d_6 -DMSO) 2.08 (s, 1H), 2.35 (br s, 3H), 2.85 (s, 4 H), 3.40 (s, 2H {water}), 3.85 (t, J , 11.5, 1H), 4.05 (t, J 11.5, 1H), 4.39 (s, 1H), 4.50 (s, 1H), 5.26 (q, J 10.3, 20.0, 2H) 5.44 (s, 1H), 5.61 (s, 1H), 7.22 (t, J 7.6, 1H), 7.48 (m, 4H), 7.58 (br s, 3H), 7.70 (t, J 7.5, 1H), 7.84 (d, J 7.5, 1H), 8.11 (t, J 7.5, 1H) 8.79 (d, J 5.6, 1H) 10.76 (s, 1H). δ_{C} (400 MHz, d_6 -DMSO) (CH, CH_3) 121.48, 122.14,

Table 3. Crystal data and structure refinement for the perchlorate salts of the cations **Co-1b**²⁺ (*endo* isomer) and **Co-1a**³⁺ (hypodentate)

Parameters	Co-1b ²⁺ (<i>endo</i> isomer)	Co-1a ³⁺ (hypodentate)
Empirical formula	[C ₁₈ H ₃₁ CoN ₇ S](ClO ₄) ₂ · H ₂ O	[C ₁₇ H ₃₀ CoN ₇ S](ClO ₄) ₃ · 0.5H ₂ O
Formula weight	653.40	729.82
<i>T</i> [K]	150(2)	90.0(2)
Wavelength [Å]	0.71073	1.54178
Crystal system, space group	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions:		
<i>a</i> [Å]	12.8586(4)	16.3321(17)
<i>b</i> [Å]	13.9798(5)	9.2677(8)
<i>c</i> [Å]	15.8054(5)	37.298(3)
α [deg.]	84.507(1)	90
β [deg.]	76.564(1)	97.291(6)
γ [deg.]	79.001(1)	90
<i>V</i> [Å ³]	2708.73(15)	5599.9(9)
<i>Z</i>	4	4
<i>D</i> _{calc} [g cm ⁻³]	1.602	1.731
Absorption coefficient [mm ⁻¹]	0.968	8.807
<i>F</i> (000)	1356	3000
Crystal size [mm]	0.42 × 0.26 × 0.12	0.20 × 0.10 × 0.02
θ range for data collection [deg.]	1.33 to 32.22	2.388 to 67.991
Limiting indices	−19 < <i>h</i> < 19 −20 < <i>k</i> < 20 −23 < <i>l</i> < 23	−19 ≤ <i>h</i> ≤ 19 −4 ≤ <i>k</i> ≤ 10 −44 ≤ <i>l</i> ≤ 44
Reflections collected/unique	49 467/19 118 (<i>R</i> _{int} 0.0311)	57 821/9614 (<i>R</i> _{int} 0.0487)
Completeness	99.9 % to θ 32.22°	94.5 % to θ 67.679°
Absorption correction	Multi-scan	Semi-empirical from equivalents
Max. and min. transmission	0.8927 and 0.6866	0.8643 and 0.4714
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	19 118/0/761	9614/284/810
Goodness-of-fit on <i>F</i> ²	1.083	1.117
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ 0.0562, <i>wR</i> ₂ 0.1282	<i>R</i> ₁ 0.0664, <i>wR</i> ₂ 0.1722
<i>R</i> indices (all data)	<i>R</i> ₁ 0.0713, <i>wR</i> ₂ 0.1346	<i>R</i> ₁ 0.0916, <i>wR</i> ₂ 0.1931
Largest diff. peak and hole [e Å ⁻³]	0.941 and −1.064	0.615 and −0.371

125.10, 129.02, 139.73, 152.78; (C, CH₂) 38.67, 41.23, 44.58, 46.03, 59.47, 136.65, 162.54, 169.92.

Complex **Co-1b**³⁺ (hypodentate): δ_{H} (400 MHz, *d*₆-DMSO) 2.06 (s, 1H), 2.34 (s, 3H), 2.40 (s, 2H), 2.60 (s, 1H), 2.86 (s, 4H), 3.38 (s, 2H {water}), 3.86 (t, *J* 10.7, 1H), 4.05 (t, *J* 10.5, 1H), 4.37 (s, 1H), 4.51 (s, 1H), 5.22 (q, *J* 7.7, 19.1, 2H), 5.45 (s, 1H), 5.61 (s, 1H), 7.25 (d, *J* 7.5, 2H), 7.36 (d, *J* 7.5, 2H), 7.56 (br s, 3H), 7.69 (t, *J* 6.4, 1H), 7.84 (d, *J* 7.8, 1H), 8.11 (t, *J* 7.2, 1H), 8.78 (d, *J* 5.6, 1H), 10.69 (s, 1H). δ_{C} (400 MHz, *d*₆-DMSO) (CH, CH₃) 20.47, 121.82, 122.14, 125.10, 129.43, 139.71, 152.80; (C, CH₂) 38.64, 41.21, 44.57, 46.01, 59.42, 133.96, 134.47, 162.63, 170.03. Anal. Calc. for CoSC₁₈H₃₁N₇Cl₃O₁₂ · H₂O: S 4.26, C 28.72, H 4.42, N 13.02. Found: S 4.39, C 28.66, H 4.39, N 13.02 %.

Complex **Co-1c**³⁺ (hypodentate): δ_{H} (400 MHz, *d*₆-DMSO) 2.06 (s, 1H), 2.27 (s, 1H), 2.37 (s, 1H), 2.50 (s, 1H), 2.85 (s, 4H), 3.40 (s, 6H {water}), 3.75 (s, 3H), 3.80 (t, *J* 10.7, 1H), 3.99 (t, *J* 10.5, 1H), 4.29 (s, 1H), 4.43 (s, 1H), 5.19 (q, *J* 7.7, 19.1, 2H), 5.38 (s, 1H), 5.56 (s, 1H), 7.00 (d, *J* 8.2, 2H), 7.36 (d, *J* 8.2, 2H), 7.56 (br s, 2H), 7.66 (t, *J* 6.2, 1H), 7.79 (d, *J* 8.2, 1H), 8.08 (t, *J* 7.6, 1H), 8.77 (d, *J* 5.1, 1H), 10.59 (s, 1H). δ_{C} (400 MHz, *d*₆-DMSO) (CH, CH₃) 55.27, 114.13, 122.10, 124.26, 125.07, 139.67, 152.98; (C, CH₂) 38.66, 41.13, 44.53, 45.97, 59.26, 128.98, 156.98, 162.68, 170.33.

Complex **Co-2**³⁺ (hypodentate): δ_{H} (400 MHz, *d*₆-DMSO) 2.03 (br s, 1H), 2.25 (br s, 1H), 2.37 (br s, 2H), 2.84 (br s, 4H), 3.40 (s, 4H {water}), 3.78 (t, *J* 11.8, 1H), 3.99 (t, *J* 11.8, 1H),

4.20 (s, 1H), 4.48 (s, 3H), 5.14 (q, *J* 2.5, 19.9, 2H), 5.48 (s, 1H), 5.61 (s, 1H), 7.34 (t, *J* 6.9, 1H), 7.43 (m, 4H), 7.56 (br s, 3H), 7.67 (t, *J* 6.3, 1H), 7.80 (d, *J* 8.5, 1H), 8.09 (t, *J* 8.2, 1H), 8.79 (d, *J* 5.6, 1H), 9.36 (t, *J* 5.6, 1H). δ_{C} (400 MHz, *d*₆-DMSO) (CH, CH₃) 122.09, 124.96, 127.48, 127.70, 128.50, 139.66, 152.89; (C, CH₂) 38.60, 41.05, 44.47, 44.53, 45.96, 58.98, 137.81, 163.25. Anal. Calc. for CoSC₁₈H₃₁N₇Cl₃O₁₂ · 2H₂O: S 4.16, Co 7.64, Cl 13.76. Found: S 4.21, Co 7.69, Cl 13.42 %.

Isolation of Bidentate Products (Fig. 4a, b)

The maroon and orange bands collected from the column (see above) for the reaction of ligand **1b** were diluted 10-fold with water and resorbed onto SPC-25, washed with water, and then removed with 0.5 M Ba(ClO₄)₂. Dark maroon crystals were formed from the maroon band (*endo* isomer) and an orange powder was formed from the orange band (*exo* isomer) upon refrigeration at 4°C.

Co-1b²⁺ (*endo*) maroon: δ_{H} (400 MHz, *d*₆-DMSO) 1.61 (s, 1H), 2.28 (s, 3H), 2.50 (m, 7H), 3.33 (s, 1H), 3.40 (s, 2H {water}), 3.91 (s, 1H), 4.42 (q, *J* 45.4, 16.5, 2H), 4.48 (s, 1H), 4.64 (s, 1H), 4.74 (s, 1H), 4.84 (s, 1H), 5.16 (s, 1H), 5.38 (s, 1H), 7.21 (m, 5H), 7.31 (t, *J* 6.6, 1H), 7.48 (d, *J* 8.1, 1H), 7.82 (t, *J* 8.1, 1H), 8.13 (t, *J* 6.6, 1H), 8.50 (d, *J* 4.0, 1H). δ_{C} (400 MHz, *d*₆-DMSO) (CH, CH₃) 20.68, 121.04, 121.30, 126.05, 130.57, 136.82, 148.67; (C, CH₂) 43.47, 44.68, 44.78, 44.99, 45.82, 135.45, 137.90, 157.75, 175.00.

Co-1b²⁺ (*exo*) orange: δ_{H} (400 MHz, *d*₆-DMSO) 2.20 (s, 1H), 2.29 (s, 3H), 2.5 (m, 7H), 3.40 (s, 8H {water}), 3.98 (s, 1H), 4.37 (q, 4H), 4.66 (s, 1H), 4.78 (s, 2H), 4.95 (s, 1H), 5.16 (s, 1H), 7.19 (m, 5H), 7.37 (t, *J* 6.6, 1H), 7.52 (d, *J* 8.1, 1H), 7.86 (t, *J* 8.1, 1H), 8.63 (d, *J* 3.8, 1H), 9.74 (s, 1H). δ_{C} (400 MHz, *d*₆-DMSO) (CH, CH₃) 20.46, 122.57, 122.99, 123.56, 137.46, 148.96; (C, CH₂) 43.75, 44.47, 44.96, 45.50, 50.39, 133.97, 134.37, 156.85, 172.92.

Isolation of Side Products

[(*en*)₂Co(CO₃)]ClO₄. The pink band that eluted first was allowed to evaporate until dark pink crystals formed. δ_{H} (200 MHz, D₂O) 2.92 (br m); (200 MHz, *d*₆-DMSO) 2.5 (br, 8H), 3.88 (s, 2H), 4.40 (s, 2H), 4.52 (s, 2H), 4.98 (s, 2H). δ_{C} (200 MHz, *d*₆-DMSO) 43.76, 44.20, 164.71. *m/z* 239 ([M⁺]). Calc. molecular weight 338.6.

Black Product. The black product accounts for 10–15 % of the total mass of the reactants in all preparations and can be brought to constant mass after two washings in refluxing ethanol—the following results are for the product obtained from the reaction of **1b**. Found: Co 6.44, S 11.89, C 40.09, H 3.23, N 13.88 %. ν_{max} (KBr)/cm^{−1} 3269, 3189, 1900, 1621, 1515, 1288 1166, 1032. *m/z*: [*z* = ?] 633.

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

X-Ray Crystallography

[C₁₈H₃₁CoN₇S](ClO₄)₂ · H₂O {**Co-1b²⁺** (*endo*)}
and [C₁₇H₃₀CoN₇S](ClO₄)₃ · 0.5H₂O {**Co-1a³⁺**
(hypodentate)}

X-Ray diffraction data were collected at either 150(2) K on a standard Siemens SMART 6000 CCD diffractometer using MoK α radiation (*endo* isomer) or at 90 K on a Bruker-Nonius X8 Proteum diffractometer using CuK α radiation (hypodentate). Crystals of the *endo* isomer were obtained as dark pink-red plates, while those of the hypodentate compound were thin red flakes. In each case, crystals were mounted in polyisobutene oil and mounted directly into a cold-stream of N₂ gas. Data frames were integrated using either *SAINT* or *SAINT-Plus*.^[19] The data were corrected for decay, Lorentz and polarisation effects. Absorption and beam irregularities were corrected by the multi-scan technique in *SADABS*^[20] and by *XABS2*^[21] (hypodentate). Both structures were solved using direct methods in *SHELXS*,^[22] and refined by full-matrix least-squares on F² using *SHELXL-97*.^[22] Both the *endo* isomer and the hypodentate compound were perchlorate salts, and each crystallised as hydrates with two independent molecules in the asymmetric unit. In addition, both compounds exhibited disorder, as is common with ethylenediamine ligands.^[23,24] 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. Water hydrogen atoms in the *endo* isomer structure were fixed, while those in the hypodentate structure were refined with restraints. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.^[25] Final models were checked using *Platon*^[26] and for the hypodentate compound by an *R-tensor*.^[27]

Crystal data and relevant details of the structure determination are summarised in Table 3 and selected geometrical parameters are given in Tables 1 (*endo*) and 2 (hypodentate). All

bond lengths (Tables S1 and S3) and angles (Tables S2 and S4) are provided as Supplementary Material. Crystallographic information files have been deposited with the Cambridge Crystallographic Data Centre and assigned the deposition codes 178348 and 981038. These can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Tables of all bond lengths and angles for the two structures (Tables S1–S4), an expanded version of Fig. 8 (Fig. S1), along with HMQC NMRs of **Co-1b³⁺** and **Co-2³⁺** (Figs S3 and S4) are available on the Journal's website.

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References

- [1] L. Roecker, M. Aiyegbo, A. Al-Haddad, E. Fletcher, R. Kc, J. Hurst, T. Lane, R. Larsen, N. Noinaj, S. L. Teh, S. K. Wade, S. Parkin, *Aust. J. Chem.* **2013**, *66*, 944. doi:10.1071/CH13150
- [2] L. Roecker, J. Akande, L. N. Elam, I. Gagua, B. W. Helton, M. C. Prewitt, A. M. Sargeson, J. H. Swango, A. C. Willis, T. Xin, J. Xu, *Inorg. Chem.* **1999**, *38*, 1269. doi:10.1021/IC980287P
- [3] D. R. Richardson, D. S. Kalinowski, V. Richardson, P. C. Sharpe, D. B. Lovejoy, M. Islam, P. V. Bernhardt, *J. Med. Chem.* **2009**, *52*, 1459. doi:10.1021/JM801585U
- [4] E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67. doi:10.1002/9780470166437.CH2
- [5] R. L. Fanshawe, A. Mobinikhaledi, C. R. Clark, A. G. Blackman, *Inorg. Chim. Acta* **2000**, *307*, 27. doi:10.1016/S0020-1693(00)00184-5
- [6] M. D. Alexander, C. A. Spillert, *Inorg. Chem.* **1970**, *9*, 2344. doi:10.1021/IC50092A028
- [7] D. A. House, P. J. Steel, *Inorg. Chim. Acta* **1999**, *288*, 53. doi:10.1016/S0020-1693(99)00033-X
- [8] D. B. Cordes, R. T. Tarak, S. M. McDonald, S. A. Cameron, C. R. Clark, A. G. Blackman, *Polyhedron* **2013**, *52*, 1227. doi:10.1016/J.POLY.2012.06.037
- [9] D. X. West, J. K. Swearingen, A. K. Hermetet, L. J. Ackerman, C. Presto, *J. Mol. Struct.* **2000**, *522*, 27 and references therein. doi:10.1016/S0022-2860(99)00314-2
- [10] Z. Weiqun, L. Baolong, Z. Liming, D. Jiangang, Z. Yong, L. Lude, Y. Xujie, *J. Mol. Struct.* **2004**, *690*, 145. doi:10.1016/J.MOLSTRUC.2003.11.029
- [11] Z. Weiqun, L. Kuisheng, Z. Yong, L. Lu, *J. Mol. Struct.* **2003**, *657*, 215. doi:10.1016/S0022-2860(03)00371-5
- [12] H. Arslan, U. Flörke, N. Külcü, *Türk. J. Chem.* **2004**, *28*, 673.
- [13] L. R. Gahan, T. M. Donlevey, T. W. Hambley, *Inorg. Chem.* **1990**, *29*, 1451 and references therein. doi:10.1021/IC00332A038
- [14] C. G. Barry, E. C. Turney, C. S. Day, G. Saluta, G. L. Kucera, U. Bierbach, *Inorg. Chem.* **2002**, *41*, 7159. doi:10.1021/IC025744N
- [15] R. C. Elder, L. R. Florian, R. E. Lake, A. M. Yacynych, *Inorg. Chem.* **1973**, *12*, 2690. doi:10.1021/IC50129A038
- [16] M. H. Dickman, R. J. Doedens, E. Deutsch, *Inorg. Chem.* **1980**, *19*, 945. doi:10.1021/IC50206A030
- [17] D. P. Fairlie, W. G. Jackson, G. M. McLaughlin, *Inorg. Chem.* **1989**, *28*, 1983. doi:10.1021/IC00309A043
- [18] F. D. Sancilio, L. F. Druding, D. M. Lukaszewski, *Inorg. Chem.* **1976**, *15*, 1626. doi:10.1021/IC50161A031
- [19] Bruker-AXS, *SAINT/SAINT-Plus* **2008** (Bruker-AXS: Madison, WI).

- [20] G. M. Sheldrick, *SADABS* **1996** (University of Goettingen: Goettingen).
- [21] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* **1995**, 28, 53. doi:[10.1107/S0021889894009428](https://doi.org/10.1107/S0021889894009428)
- [22] G. M. Sheldrick, *Acta Crystallogr.* **2008**, 64, 112. doi:[10.1107/S0108767307043930](https://doi.org/10.1107/S0108767307043930)
- [23] L. Pu, T. Hasegawa, S. Parkin, H. Taube, *J. Am. Chem. Soc.* **1992**, 114, 7609. doi:[10.1021/JA00045A070](https://doi.org/10.1021/JA00045A070)
- [24] T. Hasegawa, A. Li, S. Parkin, H. Hope, R. K. McMullan, T. F. Koetzle, H. Taube, *J. Am. Chem. Soc.* **1994**, 116, 4352. doi:[10.1021/JA00089A024](https://doi.org/10.1021/JA00089A024)
- [25] *International Tables for Crystallography, Vol. C: Mathematical, Physical and Chemical Tables* (Ed. A. J. C. Wilson) **1992** (Kluwer Academic Publishers: Dordrecht).
- [26] A. L. Spek, *J. Appl. Cryst.* **2003**, 36, 7. doi:[10.1107/S0021889802022112](https://doi.org/10.1107/S0021889802022112)
- [27] S. Parkin, *Acta Crystallogr.* **2000**, 56, 157. doi:[10.1107/S010876739901497X](https://doi.org/10.1107/S010876739901497X)