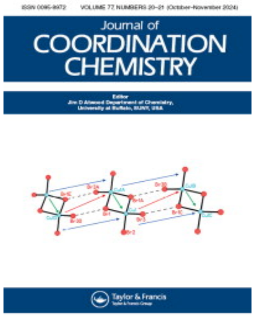

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2-Acetylpyridine thiosemicarbazones cause rapid substitution of amine and pyridyl ligands coordinated to cobalt(III)

Lee Roecker[a], Rachel Ceaglske[a], Madeline Clevenger[a], Lucas Runyan[a], Dovell Wilson[a], Jordyn Wilker[a] and Sean Parkin[b]

[a]Department of Chemistry, Northern Michigan University, Marquette, Michigan, USA; [b]Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA

ABSTRACT

The reaction of 2-acetylpyridine 4-phenyl-3-thiosemicarbazone, 2-acetylpyridine 4-methyl-3-thiosemicarbazone and 2-acetylpyridine 4-allyl-3-thiosemicarbazone with $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$, $(dien)Co(OSO_2CF_3)_3$ and $[(picen)Co(OSO_2CF_3)_2]CF_3SO_3$ results in the rapid substitution of coordinated amine and pyridyl ligands to form cobalt(III) complexes coordinated by two deprotonated 2-acetylpyridine thiosemicarbazone ligands, each bound tridentate through the sulfur atom and two nitrogen atoms (N_2S). While the mechanism of this reaction remains unclear, it is suspected that an electron transfer reaction occurs between the thiosemicarbazone and the metal complex resulting in reduction to cobalt(II). Rapid ligand loss from cobalt(II) followed by chelation of the tridentate ligands and subsequent re-oxidation to cobalt(III) results in formation of the final product. The resulting complexes were characterized by NMR. In addition, the solid-state structure (X-ray) of the methyl derivative confirms the coordination mode of the ligand.

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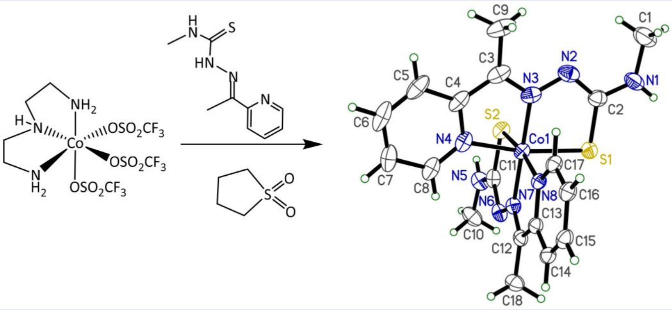
KEYWORDS

Cobalt(III); thiosemicarbazones; substitution reactions; trifluoromethanesulfonato ligands; crystal structure

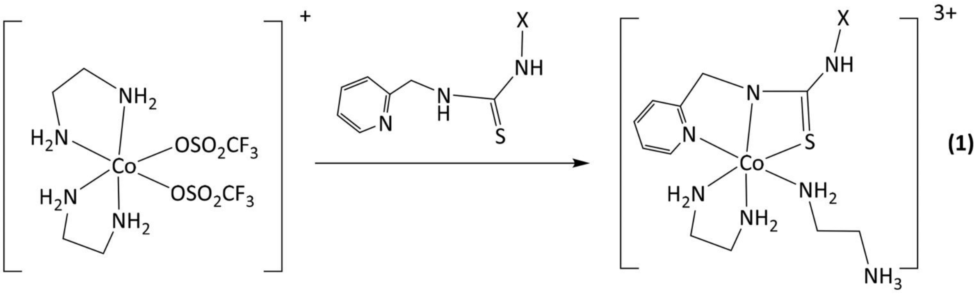
GRAPHICAL ABSTRACT



CONTACT Lee Roecker lroecker@nmu.edu Department of Chemistry, Northern Michigan University, Marquette, Michigan, USA; Sean Parkin s.parkin@uky.edu Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA.

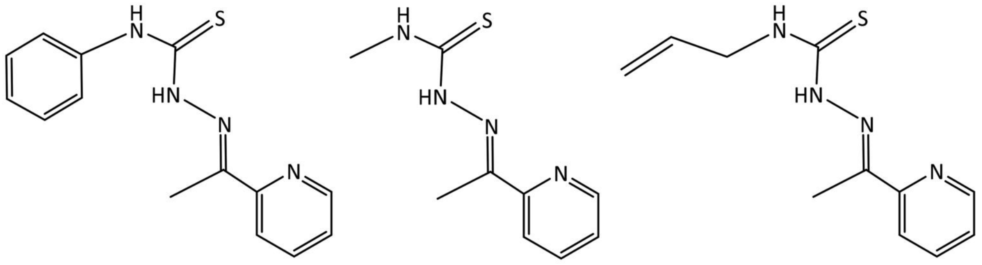
1. Introduction

The original intent of this research was to explore a synthetic strategy for the production of cobalt(III) complexes coordinated by a hypodentate ligand. Two synthetic strategies for formation of cobalt(III) complexes coordinated by hypodentate amine ligands have been reported. Such complexes have been prepared by addition of a potentially hypodentate amine to reactive or labile starting materials [1–4]. $[(NH_3)_5CoNH_2CH_2CH_2NH_3)]^{4+}$, for example, is formed in 40% yield from the reaction of excess $[(NH_3)_5CoOSMe_2]^{3+}$ with ethylenediamine [1]. The second strategy (Equation 1) arises from the unexpected result of reaction of *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$ with 2-pyridylmethylthiourea derivatives that produced cobalt(III) complexes coordinated by a hypodentate ethylenediamine ligand in approximately 50% yield [5]. Structural evidence suggested [5] that the thiourea ligand induced a structural *trans* effect that was of sufficient magnitude to labilize what is usually a stable Co-N bond. To explore this strategy as a general synthetic approach to the production of cobalt(III) complexes coordinated by hypodentate ligands, we turned our attention to the analogous reaction of 2-acetylpyridine thiosemicarbazones (Figure 1) with *cis*-$[(en)_2Co(OSO_2CF_3)_2]^+$. Richardson and coworkers previously showed that these ligands coordinate to iron(II) and to iron(III) tridentate (N_2S) [6] while Oliveira and coworkers prepared cobalt(III) complexes similarly coordinated and evaluated their potential as anti-*Mycobacterium tuberculosis* agents [7]. Reaction of these ligands with $[(en)_2Co(OSO_2CF_3)_2]^+$ could potentially produce complexes with a hypodentate ethylenediamine or a hypodentate thiosemicarbazone ligand. The hypodentate complexes produced could be used in the synthesis of thiosemicarbazone complexes containing more than one metal center [3]; these might be of interest given the bioactivity of related complexes [8,9].



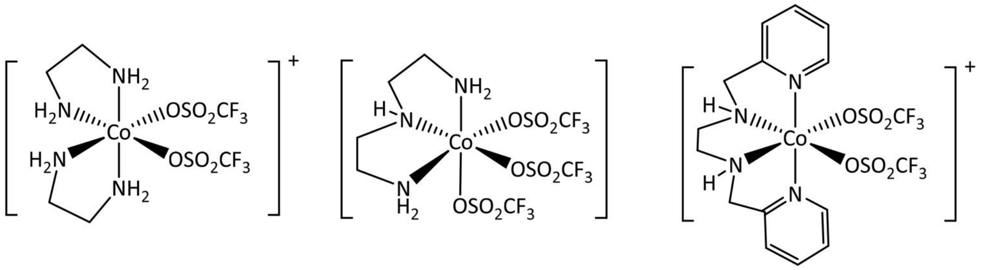
(1)

This paper presents observations on the reaction of three thiosemicarbazones (Figure 1) with three cobalt(III) amine complexes (Figure 2). No evidence for hypodentate coordination of amine or thiosemicarbazone ligands was observed as the coordinated amine ligand(s) are completely and rapidly displaced resulting in formation of cobalt(III) complexes coordinated by two N_2S bonding ligands. These complexes were characterized by NMR spectroscopy. In addition, the solid-state crystal structure of the methyl derivative confirms the coordination mode of the ligand.



HAp4pT **HAp4mT** **HAp4aT**

Figure 1. Line drawings and naming conventions (after reference 6) of the thiosemicarbazone ligands used in this study.



$[(en)_2Co(OSO_2CF_3)_2]^+$ **$(dien)Co(OSO_2CF_3)_3$** **$[(picen)Co(OSO_2CF_3)_2]^+$**

Figure 2. Cobalt precursors examined in this study.

2. Experimental

2.1. General data

All chemicals were reagent grade and used as received. ^1H and ^{13}C NMR were recorded with a JEOL ECZ400S/L1 spectrometer in either d_6-DMSO, d_6-acetone or d_1-chloroform with TMS as an internal reference. The thiosemicarbazones were prepared by a literature procedure [6] and recrystallized two times. The cobalt precursors $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$ and $[(dien)Co(OSO_2CF_3)_3]$ were also prepared by a literature procedure [10]. $[(picen)Co(OSO_2CF_3)_2]CF_3SO_3$ was prepared from $[(picen)CoCl_2]Cl$ [11] in a manner analogous to the other cobalt precursors. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN, USA).

2.2. Characterization of ligands

2.2.1. HAp4pT

δ_H (400 MHz, d_6-DMSO) 2.50 (s, 3H), 7.26 (t, 1H), 7.39 (m, 3H), 7.55 (dd, 2H), 7.82 (t, 1H) 8.55 (d, 1H), 8.59 (d, 1H), 10.21 (s, 1H), 10.71 (s, 1H). δ_C (400 MHz, d_6-DMSO) 12.5, 121.3, 124.1, 125.6, 126.2, 128.1, 136.4, 139.2, 148.5, 149.2, 154.5, 177.3. δ_H (400 MHz, $CDCl_3$) 2.46 (s, 3H), 7.28 (t, 1H), 7.33 (t, 1H), 7.42 (t, 2H), 7.69 (d, 2H), 7.75 (t, 1H), 8.01 (d, 1H), 8.64 (d, 1H), 8.87 (s, 1H), 9.38 (s, 1H). δ_C (400 MHz, $CDCl_3$) 11.6, 120.3, 124.2, 124.3, 126.3, 128.8, 136.4, 137.7, 148.1, 149.0, 154.3, 176.3.

2.2.2. HAp4mT

δ_H (400 MHz, d_6-DMSO) 2.42 (s, 3H), 3.10 (d, 3H), 7.40 (t, 1H), 7.84 (t, 1H), 8.46 (d, 1H, 8.59 (d, 1H), 8.66 (d, br, 1H), 10.40 (s, 1H). δ_C (400 MHz, d_6-DMSO) 12.1, 31.2, 120.8, 123.9, 136.3, 147.9, 148.4, 154.7, 178.7.

2.2.3. HAp4aT

δ_H (400 MHz, d_6-DMSO) 2.43 (s, 3H), 4.31 (t, br, 2H), 4.15–5.22 (m, 2H), 5.97 (m, 1H), 7.40 (t, 1H), 7.83 (t, 1H), 8.44 (d, 1H), 8.61 (d, 1H), 8.85 (t, br, 1H), 10.44 (s (1H). δ_C (400 MHz, d_6-DMSO) 12.2, 46.0, 115.5, 120.8, 123.9, 134.9, 136.3, 148.2, 148.5, 154.7, 178.2.

2.3. Reaction of ligands with the cobalt trifluoromethanesulfonato precursors

In a typical procedure, 1.31 g (4.9 mmol) of HAp4pT were dissolved in 10.2 g of sulfolane followed by the addition of 0.858 g (1.6 mmol) of $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$. The solution quickly turned brown. After stirring overnight, the solution was poured into 100 mL of diethyl ether and stirred vigorously for 20 min resulting in formation of a brown oil and pale-yellow solution. The ether was decanted and the extraction repeated resulting in formation of a brown solid. This was isolated by filtration and air dried overnight (0.947 g, 79%). The crude product was recrystallized by addition of 10 mL of H_2O followed by 20 mL of acetone and stirred in a water bath at 55 °C–60 °C until the complex dissolved. Evaporation of the acetone at room temperature from an uncovered beaker resulted in crystalline product that was filtered and air dried (0.654 g, 55% overall, 69% from crude). Analogous products and similar yields were recovered from the reactions of ligands with $[(dien)Co(OSO_2CF_3)_3]$ or $[picenCo(OSO_2CF_3)_2](CF_3SO_3)$.

2.3.1. $[Co(Ap4pT]CF_3SO_3$

δ_H (400 MHz, d_6-DMSO) 3.00 (s, 3H), 7.09 (t, 1H), 7.39 (t, 2 H), 7.52 (t, 1H), 7.70 (d, 2H), 8.02 (d, 1H), 8.18 (m, br, 2H), 10.36 (s, 1H). δ_C (400 MHz, d_6-DMSO) 15.8, 120.4, 123.4, 125.6, 127.5, 128.9, 139.9, 140.2, 149.3, 156.7, 159.0, 175.4. δ_H (400 MHz, d_6-ACETONE) 3.08 (s, 3H), 7.12 (t, 1H), 7.40 (t, 2H), 7.54 (q, 1H), 7.77 (d, 2H), 8.17 (d, 2H), 8.21 (d, 1H), 10.36 (s, 1H). δ_C (400 MHz, d_6-ACETONE) 16.6, 121.9, 125.0, 126.8, 128.6, 130.2, 141.4, 141.5, 150.9, 158.7, 160.4, 178.2. Analysis Calc. for $CoS_3F_3O_3N_8C_{29}H_{26}$: C 46.65, H 3.51, N 15.01%. Found: C 46.44, H 3.87, N 14.98%. See Figure S1 for ^{1}H,^{13}C, APT and HETCOR NMR spectra.

2.3.2. $[Co(Ap4mT]CF_3SO_3{\cdot}H_2O$

δ_H (400 MHz, d_6-DMSO) 2.84 (m, 4H), 2.98 (s,2H), 3.40 (s, 2H, water), 7.47 (br s, 1H), 7.87 (s, 1H), 8.07 (m, 2H), 8.81 (br s, 1H). 15.0, 30.6, 32.2, 124.5, 126.4, 139.9, 148.8, 15.2, 155.6, 157.3, 178.3, 182.7. Analysis Calc. for $CoS_3F_3O_3N_8C_{19}H_{22}{\cdot}H_2O$: C 35.63, H 3.78, N 17.49%. Found: C 35.89, H 3.62, N 17.41%. See Figure S2 for ^{1}H, ^{13}C, APT and HETCOR NMR spectra.

2.3.3. [Co(Ap4aT]CF_3SO_3

δ_H (400 MHz, d_6-acetone) 2.92 (s, 3H), 4.15 (s, br, 2H), 5.10 (d, 1H), 5.22 (d, 1H), 5.94 (s, br, 2H), 7.48 (t, 1H), 8.05 (m, 3H) δ_C (400 MHz, d_6-acetone) 15.0, 49.1, 116.8, 122.4 (q, $CF_3SO_3^-$)125.6, 127.4, 135.0, 140.9, 150.0, 157.2, 158.7, 180.1. Analysis Calc. for $CoS_3F_3O_3N_8C_{23}H_{26}$: C 40.95, H 3.88, N 16.61%. Found: C 41.12, H 3.99, N 16.84%. See Figure S3 for ^{1}H, ^{13}C, APT and HETCOR NMR spectra.

2.4. X-ray crystallography

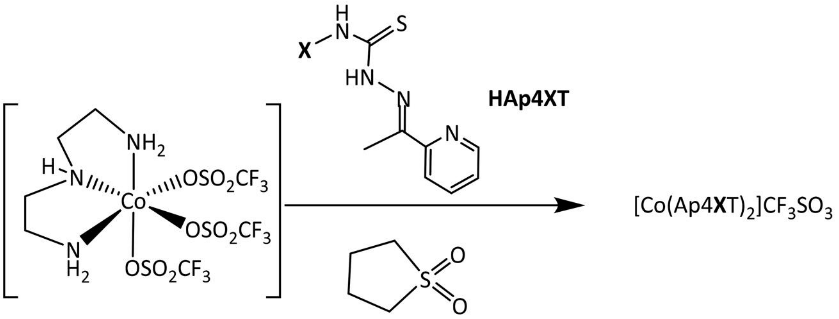
X-ray diffraction data were collected at 90.0(2) K on a Nonius kappaCCD diffractometer and processed using Denzo-SMN [12]. Data scaling and absorption corrections were by established methods [12,13]. The structure was solved by direct methods [14] and refined against F^2 by weighted full-matrix least-squares [15]. Hydrogen atoms were found in difference maps and refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and relevant details of the structure determination are summarized in Table 1 and selected geometrical parameters are given in Tables 2 and 3.

Crystallographic information files have been deposited with the Cambridge Crystallographic Data Centre and assigned the deposit code 2330333. These can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Synthesis

Reaction of cobalt(III) precursors containing labile trifluoromethanesulfonato ($CF_3SO_3^-$) ligands with thiosemicarbazones does not result in formation of cobalt(III) complexes coordinated by a hypodentate ligand. Instead, when the cobalt(III) precursors are added to sulfolane solutions containing thiosemicarbazone, the solution immediately turns brown forming complexes of the type $[Co(Ap4XT)_2]^+$ as illustrated in Equation (2) and Figure 3.



(2)

Having a $CF_3SO_3^-$ ligand coordinated to the cobalt(III) center appears to be a prerequisite for the reaction to occur as no reaction is observed when $[Co(en)_3](CF_3SO_3)_3$ or the aqua complex, *cis*-$[(en)_2Co(NH_2CH_2CH_2CH_2CH_3)H_2O]^{3+}$, are reacted under identical conditions and only a minor amount of an uncharacterized brown product is

Table 1. Crystal data and structure refinement for [Co(Ap4mT]$CF_3SO_3 \cdot H_2O$.

Empirical formula	C19 H23.50 Co F3 N8 O3.75 S3
Formula weight	636.07
Crystal size [mm^3]	0.26 × 0.25 × 0.09 mm
Temperature [K]	150(2)
Wavelength [Å]	0.71073
Crystal system, space group	Monoclinic, $P\ 2_1/n$
Unit cell dimensions	
a [Å]	13.2981(2)
b [Å]	12.5806(2)
c [Å]	15.6886(3)
α [deg.]	90
β [deg.]	100.4215(8)
γ [deg.]	90
Volume [Å^3]	2581.38(8)
Z	4
Calculated density [g cm^{-3}]	1.637
Absorption coefficient [mm^{-1}]	0.972
$F(000)$	1302
θ range for data collection	2.089° to 27.532°
Limiting indices	$-17 \leq h \leq 17$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$
Reflections collected/unique	45587/5943 ($R_{int} = 0.0399$)
Completeness to $\theta = 25.242$ [%]	100.0
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.908 and 0.782
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5943/1/347
Goodness-of-fit on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	R_1 0.0564, wR_2 0.1641
R indices (all data)	R_1 0.0959, wR_2 0.1887
Largest diff. peak and hole [e Å^{-3}]	0.952 and −0.764

Table 2. Selected bond lengths [Å] for [Co(Ap4mT]$^+$.

Co(1)-S(2)	2.2219(11)	Co(1)-S(1)	2.2402(12)
Co(1)-N(3)	1.876(3)	Co(1)-N(7)	1.884(3)
Co(1)-N(4)	1.956(3)	Co(1)-N(8)	1.947(3)
S(1)-C(2)	1.751(5)	S(2)-C(11)	1.731(5)
N(1)-C(2)	1.317(6)	N(5)-C(11)	1.343(5)
N(2)-C(2)	1.318(6)	N(6)-C(11)	1.328(5)
N(2)-N(3)	1.362(5)	N(6)-N(7)	1.388(4)
N(3)-C(3)	1.309(6)	N(7)-C(12)	1.303(5)

Table 3. Selected bond angles [°] for [Co(Ap4mT]$^+$.

N3-Co1-S1	86.15(12)	N7-Co1-S2	86.61(10)
N7-Co1-S1	93.56(10)	N3-Co1-S2	92.82(10)
N8-Co1-S1	89.11(9)	N4-Co1-S2	90.49(10)
N4-Co1-S1	168.82(12)	N8-Co1-S2	169.88(9)
S2-Co1-S1	92.62(4)	N3-Co1-N7	179.35(14)
N3-Co1-N8	97.24(13)	N7-Co1-N4	97.34(15)
N3-Co1-N4	82.97(16)	N7-Co1-N8	83.34(13)
C2-S1-Co1	93.28(17)	C11-S2-Co1	94.05(14)
N1-C2-N2	116.7(4)	N6-C11-N5	117.7(4)
N1-C2-S1	118.6(4)	N6-C11-S2	125.3(3)
N2-C2-S1	124.7(4)	N5-C11-S2	117.0(3)

formed with *trans*-$[(en)_2CoCl_2]CF_3SO_3$ after 3 days of stirring. While the synthetic utility of labile $CF_3SO_3^-$ ligands coordinated to otherwise inert transition metals has been documented [10] (the strongly electronegative F and O atoms significantly weaken the

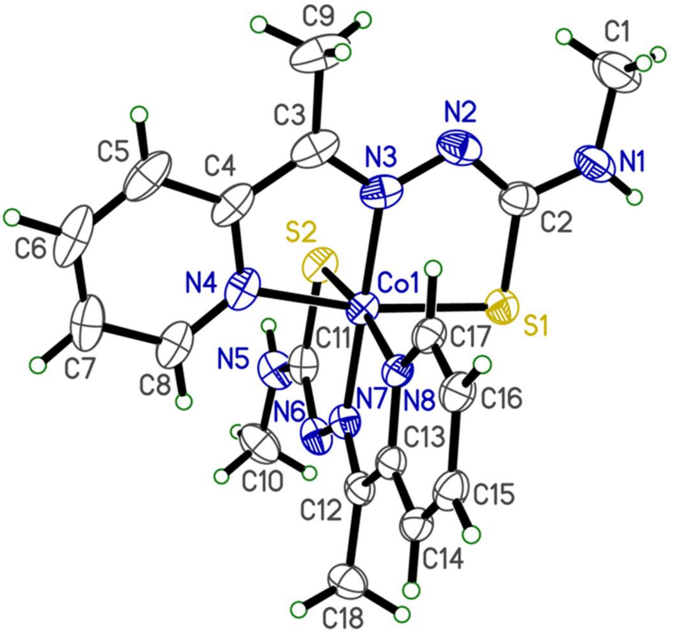


Figure 3. Ellipsoid plot and atom numbering scheme for $[Co(Ap4mT)_2]^+$. Ellipsoids represent a 50% probability level while hydrogen atoms are drawn as arbitrary circles.

Co-O bond), the reactions observed here occur much faster than substitution would allow. A more likely process would be one in which an outer sphere electron transfer reaction occurs between ligand and metal complex resulting in reduction of cobalt(III) to cobalt(II). Rapid loss of the amine/pyridyl ligand(s) would result from the labile cobalt(II) center followed by coordination of the thiosemicarbazone ligands and re-oxidation to cobalt(III). Oliveira and coworkers have observed reversible electrochemistry for these complexes, indicative of the binding ability of the tridentate ligands to cobalt(II) [7]. Also consistent with this line of reasoning is that coordination of the electron-withdrawing $CF_3SO_3^-$ ligand would be expected to make the complexes easier to reduce compared to the coordination of other, less electron-withdrawing ligands. Thus, if the process was an outer-sphere mechanism, the reactions with $[(en)_2Co(OSO_2CF_3)_2]^+$ would be expected to go faster.

The ability of related ligands to participate in oxidation-reduction reactions has precedence in the reaction of $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$ with 2-pyridylmethylthiourea derivatives (Equation 1). In addition to the characterized cobalt(III) products, a black solid (10%–15% of the total cobalt) that appears to contain cobalt(II) was also produced [5]. The mechanism of the reaction in these cases, however, is probably different as they occur much more slowly. In addition, reaction of analogous ligands that do not contain a pyridyl group do not result in formation of black product suggesting that ligand substitution is important. In addition, reaction of the analogous pyridyl complexes where O is substituted for S also do not produce any black solids [16] suggesting that a combination of both a sulfur atom and a pyridyl group are important to the observed process. No additional details, however, are available.

After the initial stage of this project, when it was thought that substitution of the labile $CF_3SO_3^-$ ligand from $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$ was the first step of the reaction, we turned to $[(dien)Co(OSO_2CF_3)_3]$ and then to $[(picen)Co(OSO_2CF_3)_2]CF_3SO_3$ anticipating that the greater denticity of the dien or picen ligands might resist labilization and an intermediate form (one complexed by a single thiosemicarbazone ligand) could be isolated. No intermediate forms were isolated, however, as the reaction with each cobalt complex occurred quickly upon mixing.

When a three-fold excess of ligand is used, yields of recrystallized product, based on cobalt precursor, averaged 64% when using $[(en)_2Co(OSO_2CF_3)_2]CF_3SO_3$ or $[(dien)Co(OSO_2CF_3)_3]$ (crude yields are about 20% higher). When a 1:1 ratio of ligand to cobalt complex is used, the average crude yield of product is 41%. Based on cobalt, the maximum yield possible is 50% if only complexes containing two tridentate ligands are produced.

While the resulting complexes are produced in an acceptable yield and are of high purity, their preparation was not the goal of our investigation. The method of Oliveira and coworkers [7] is a more direct procedure to follow if one desires to prepare complexes like $[Co(Ap4XT)_2]^+$. In their synthesis, complexes are produced directly from the reaction of $[Co(H_2O)_6]Cl_2$ with two equivalents of ligand in refluxing ethanol. We used this method to independently prepare samples for NMR comparison.

3.2. NMR spectroscopy

The ^1H NMR of $[Co(Ap4pT)_2]^+$ (Figure S1) clearly characterizes the complex and loss of the resonances due to the coordinated amine ligand(s) of the starting material demonstrate that the amines are displaced from the cobalt(III) precursor. The broad $N\mathit{H}_2CH_2$- resonances, typically in the range of 4 – 6 ppm, and the broad $NH_2C\mathit{H}_2$- resonances, centered about 2.4 ppm [5] found in the starting materials, are absent in the final products. Upon coordination, disappearance of the C(S)N*H*N signal that was present at 10.71 ppm in the free ligand is consistent with deprotonation of the ligand, a necessity for the complex to have an overall charge of +1. The ^1H NMR of the methyl derivative is slightly more complicated due to the inequivalence of the methyl group—this has been discussed previously [7].

The ^{13}C NMR of $[Co(Ap4pT)_2]^+$ (Figure S1) confirms the symmetrical coordination of two thiosemicarbazone ligands. Also, the absence of the $NH_2C\mathit{H}_2$- resonances, typically observed in the range of 41–46 ppm in the case of the starting materials and related complexes [5], confirms the loss of ligands from the precursor complex. Not clearly evident in Figure S1B, but readily apparent in the ^{13}C of the other complexes (Figures S2 and S3) is a quartet centered at 120.7 ppm due to the counterion, $CF_3SO_3^-$. NMR spectra (^1H, ^{13}C, APT, and HETCOR) are provided as supplementary material for all three complexes (Figures S1 – S3). These are consistent with the proposed structures and the ^1H spectra are identical to those previously reported [7].

3.3. Crystal structure of $[Co(Ap4mT)_2]CF_3SO_3 \cdot H_2O$

The displacement ellipsoid plot and atom numbering scheme for $[Co(Ap4mT)_2]^+$ are shown in Figure 3. The ligands are ostensibly flat: the RMS deviation from the mean plane of ligand C1—C9 is 0.0375 Å, with the largest deviations being 0.713 Å for both C1 and S1, while the RMS deviation for ligand C10—C18 is 0.192 Å, with the largest out-of-plane displacement being 0.0356 Å for N6. Moreover, the ligands are essentially perpendicular, with a dihedral angle of 89.87(4)° between the mean planes of the ligands.

Bond lengths and angles are similar to those reported in the structures of two other $[Co(Ap4XT)_2]^+$ ions where X = H or phenyl [7]. As expected, the substituent on N1 has little effect on the coordination of the ligand as all bond lengths and angles are similar in these three structures. The average Co-S distance in these cations is 2.22(1) Å. This Co-S distance is shorter than that observed in three thiourea complexes [5,17] in which the S atom is part of a four-membered ring (Equation 1) where the average distance is 2.30(1) Å. Easing of steric restraints in the five-membered ring formed by the thiosemicarbazones allows the S atom to more closely approach the metal. The average S-C distance in the three thiosemicarbazone complexes is 1.742(6) Å which is essentially identical to the average S-C distance of 1.743(8) Å observed in the thiourea complexes mentioned above. There is a significant amount of single-bond character in the C-S bond due to electron delocalization throughout the ligand and metal.

4. Conclusion

It is apparent that 2-acetyl thiosemicarbazone ligands are exceptional labilizers of ligands coordinated to cobalt(III) as they quickly and completely displace bi-, tri- and tetradentate amine ligands. These reactions occur more rapidly than ligand substitution would allow suggesting than an outer sphere electron transfer initiates the process by first reducing the cobalt(III) to the labile cobalt(II) oxidation state. This renders their usefulness to induce hypodentate coordination, the original intent of this project, of limited synthetic value. We are continuing to explore the use of trans effect ligands as an approach to producing cobalt(III) complexes coordinated by hypodentate amine ligands.

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Disclosure statement

The authors declare no conflicts of interest.

ORCID

Lee Roecker http://orcid.org/0000-0001-9287-5960
Sean Parkin http://orcid.org/0000-0001-5777-3918

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