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Cobalt(III) complexes with 2-acetyl- and 2-formylpyridine ^4N-methylthiosemicarbazones

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Abstract

Cobalt(III) complexes of 2-acetyl- and 2-formylpyridine ^4N-methylthiosemicarbazone, $[Co(L4M)_2]BF_4$ and $[Co(4M)_2]BF_4$, respectively, have been synthesized, their crystal structures solved and their spectral properties measured. The crystal structures show that each complex has its two ligands coordinated in a *mer* configuration, but that the stereochemistry of the thiosemicarbazone moiety's ^4N position of coordinated L4M and 4M is different. The complexes' bond lengths and bond angles are compared with other thiosemicarbazone complexes. The ^1H and ^{13}C NMR spectra show uncomplexed HL4M and H4M to be in the *E* and *Z* configurations, respectively, and that the two ligands within each complex are nearly identical

Key words. Crystal structures, Cobalt complexes, Semicarbazone complexes

Introduction

Heterocyclic thiosemicarbazones, as well as their metal complexes, are important because of potentially beneficial biological activity [1]. Although there have been numerous studies involving the isolation of complexes and their spectral and magnetic characterization [2, 3], comparatively few crystal structures of these complexes, particularly those with two thiosemicarbazone ligands per coordination sphere, have been determined.

Results of studies of bis(thiosemicarbazone)chromium(III) and -iron(III) complexes that are relevant are as follows. The thione $\{={}^1N\text{–}{}^2NH\text{–}C(=S){}^4NH_2\}$ and thiol $\{=N\text{–}N=C(\text{–}S\text{–})NH_2\}$ forms of pyruvic acid thiosemicarbazone are coordinated to chromium(III) as tridentate ligands in a meridional conformation with the expected bond length differences for the metal–ligand and thiosemicarbazone moiety [4]. Bis(salicylaldehyde thiosemicarbazonato)chromium(III) perchlorate has two equivalent tridentate ONS ligands arranged in a meridional conformation [5]. The meridional configuration has also been found for an iron(III) complex of equivalent 2-acetylpyridine 3-azabicyclo[3.2.2]nonylselenomicarbazonato ligands (i.e. loss of ^2NH proton) [6]. However, the structure of bis(isoquinoline-1-carboxaldehyde thiosemicarbazonato)nickel(II) monohydrate was reported with small differences in the bond lengths of the two coordinated ligands [7]. Similarly, small differences were noted in the bond lengths for the two ligands in bis(acetylpyrazine ^4N-dimethylthiosemicarbazone)nickel(II) [8].

Crystal studies have also been reported for four-coordinate nickel(II) and copper(II) thiosemicarbazone complexes, which were demonstrated to have the most potent biological activity [9] Planar arrangements have been reported for nickel(II) complexes of 2-acetylpyridine azabicyclo[3.2.2]nonylthiosemicarbazone [10], salicylaldehyde ^4N-phenylthiosemicarbazone [11] and two acetylpyrazine ^4N-substituted thiosemicarbazones [12]. Representative copper(II) complexes of heterocyclic thiosemicarbazones are the following: $[Cu(HPictsc)H_2O]Cl\cdot H_2O$, where $H_2Pictsc$ is 3-hydroxy-5-hydroxymethyl-4-formyl-2-picoline thiosemicarbazone [13], a dinuclear complex of 2-formylpyridine thiosemicarbazone [14, 15], a mononuclear complex formed by the above dinuclear copper(II) complex and saccharin [16], as well as additional complexes of 2-formylpyridine thiosemicarbazone [17] The structure of a 2-acetylpyridine 3-hexamethyleneiminylthiosemicarbazone

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nickel(II) complex has also been reported [18]. Here we report the structures and spectral properties of bis(2-acetylpyridine ^4N-methylthiosemicarbazonato)-cobalt(III) tetrafluoroborate, $[Co(L4M)_2]BF_4$, and bis(2-formylpyridine ^4N-methylthiosemicarbazonato)cobalt(III) tetrafluoroborate trihydrate, $[Co(4M)_2]BF_4 \cdot 3H_2O$. Some of the spectral information on $[Co(L4M)_2]BF_4$ was included in an NMR study of 2-acetylpyridine ^4N-alkylthiosemicarbazones reported previously [19] and prompted this present study.

Experimental

Syntheses and materials

The synthesis of the two thiosemicarbazones, HL4M and H4M, was accomplished by refluxing ^4N-methylthiosemicarbazide with an equimolar amount of either 2-acetylpyridine or 2-pyridinecarboxaldehyde for 2 h. The solids separated on cooling and, after evaporating some of the solvent at 35 °C, the solids were filtered and washed with cold isopropanol. All organic reagents were purchased from Aldrich Chemical Company, Milwaukee, WI. The bis complexes were prepared by a 2 h reflux of an anhydrous ethanol 1:2 mixture of cobalt(II) tetrafluoroborate hydrate (Alfa) and either HL4M or H4M. The red–brown products (~ 90% yield), which formed on refluxing, were filtered hot, washed with cold isopropanol and dried on a warm plate (35 °C). The crystals were grown by slow evaporation of dilute dimethyl sulfoxide solutions at 35 °C.

Physical measurements

The spectral and physical measurement of the powder samples and their solutions were made as previously reported [2, 19].

Determination of the crystal structure of $[Co(L4M)_2] \cdot BF_4$

A reddish brown prismatic crystal of $[Co(L4M)_2]BF_4$ of approximate dimensions $0.15 \times 0.20 \times 0.45$ mm was mounted on a glass fiber and used for data collection on a CAD4 Enraf-Nonius four-circle automatic diffractometer. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range 9–15°. Data were collected at 293 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.70930$ Å) and the $\omega/2\theta$ scan technique. The data were corrected for Lorentz and polarization effects, and for absorption by an empirical method [20]. The structure was solved by direct methods [21] which revealed the position of all non-hydrogen atoms, and refined on F by a full-matrix least-squares procedure using anisotropic temperature factors [22]. BF_4^- appears to occur in two positions related by a pseudo-mirror plane. Hydrogen atoms were constrained to idealized positions (C–H = 0.95 Å) and added to the structure factors calculations as fixed contributions ($B_{iso} = 4.0$ Å^2), and their positional parameters were not refined. A secondary extinction correction was applied [23] and the final coefficient, refined in the last least-squares cycle, was 1.048×10^{-7}. After all shift/e.s.d. ratios were less than 0.001, the refinement converged to the agreement factors shown in Table 1. Form factors were taken from the literature [24]. Computations were performed on a DEC MicroVAX 3500 computer with plots from SCHAKAL [25]. A summary of crystal data, experimental details and refinement results are listed in Table 1.

Determination of the crystal structure of $[Co(4M)_2]BF_4 \cdot 3H_2O$

The structure of $[Co(4M)_2]BF_4 \cdot 3H_2O$ was determined as above, using a reddish brown prismatic crystal of approximate dimensions $0.25 \times 0.25 \times 0.40$ mm, except as follows The unit cell was determined and refined from angular data of 25 selected reflections in the range $8 < \theta < 15°$. Intensities were measured at 243 K. Lorentz–polarization corrections were applied, as well as an empirical absorption correction [20]. Atoms in the BF_4^- ion and the oxygen of the three water molecules showed very high thermal motion. In the disordered BF_4^-, F(42) is associated with F(41), and from their refined multiplicities, the occupancy factors for the two orientations are found to be 0.5. A summary of crystal data, experimental details and refinement results are listed in Table 1.

Results and discussion

Structure of $[Co(L4M)_2]BF_4$ and $[Co(4M)_2]BF_4$ $3H_2O$

The positional parameters for the two cobalt(III) cations are listed in Tables 2 and 5, the important bond lengths in Tables 3 and 6, and the important bond angles in Tables 4 and 7 for $[Co(L4M)_2]BF_4$ and $[Co(4M)_2]BF_4$ $3H_2O$, respectively. Tables 3, 4, 6 and 7 are arranged to allow for a convenient comparison of the two ligands of the complex. See also 'Supplementary material'. Schakal diagrams of the structures of these compounds are shown in Figs. 1 and 2 [25].

The cobalt(III) ion in both complexes is octahedrally coordinated by the two approximately planar tridentate ligands arranged in a *mer*-configuration. Both molecules are chiral, and coordination for both ligands is via the pyridine nitrogen, the azomethine nitrogen and the thiolato sulfur atoms. One noticeable difference between the two complexes is the orientation of the ^4N-methyl

TABLE 1. Crystal data, data collection and structure refinement parameters for the two cobalt(III) complexes

Compound	$[Co(L4M)_2]BF_4$	$[Co(4M)_2]BF_4 \cdot 3H_2O$
Chemical formula	$C_{18}H_{22}BCoF_4N_8S_2$	$C_{16}H_{24}BCoF_4N_8O_3S_2$
Formula weight	560.30	586.29
Crystal class	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	9.017(2)	10.493(1)
b (Å)	13.281(1)	16.183(2)
c (Å)	19.757(5)	15.025(2)
β (°)	99.36(1)	98.44(1)
V (Å^3)	2334.4(8)	2523.8(9)
Z	4	4
λ(Mo Kα) (Å)	0.70930	0.70930
ρ_{calc} (g cm^{-3})	1.594	1.544
μ (cm^{-1})	9.592	8.99
$F(000)$	1144	1200
Absorption correction min.–max.	0.751–1.261	0.603–1.357
Max (sin θ)/λ	0.639	0.638
Total no. reflections measured	5638	5404
θ Range (°)	3–27	3–27
No. unique reflections (R_{int})	4982 (0.033)	4902 (0.046)
No. observed reflections (criterion)	2816 ($I > 3\sigma(I)$)	2502 ($I > 3\sigma(I)$)
R	0.048	0.084
R_w	0.054	0.094
Largest peak (e/Å^3)	0.424	1.184

TABLE 2. Positional parameters ($\times 10^4$) for $[Co(L4M)_2]BF_4$ with standard deviations in parentheses

Atom	x/a	y/b	z/c
Co	1657.2(8)	7226.1(6)	4973.3(4)
S(11)	1004(2)	5854(1)	5501.8(7)
S(21)	−690(2)	7566(1)	4496.9(8)
N(11)	2309(5)	8562(4)	4719(2)
N(12)	1443(5)	7904(4)	5794(2)
N(13)	875(5)	7471(4)	6327(2)
N(14)	102(6)	5961(4)	6694(2)
N(21)	3765(5)	6840(4)	5182(2)
N(22)	1790(5)	6547(3)	4147(2)
N(23)	565(5)	6374(4)	3635(2)
N(24)	−1900(6)	6770(4)	3323(3)
C(11)	2297(7)	9251(5)	5226(3)
C(12)	2731(8)	10231(5)	5147(4)
C(13)	317(1)	10527(6)	4545(4)
C(14)	3175(9)	9837(6)	4036(4)
C(15)	2741(7)	8838(5)	4132(3)
C(16)	1761(7)	8859(4)	5829(3)
C(17)	657(6)	6496(5)	6225(3)
C(21)	4260(6)	6397(4)	4644(3)
C(22)	5760(7)	6105(5)	4696(3)
C(23)	6728(7)	6251(6)	5300(4)
C(24)	6221(6)	6689(5)	5848(3)
C(25)	4719(7)	6976(5)	5773(3)
C(26)	3108(6)	6242(4)	4052(3)
C(27)	−645(6)	6847(4)	3767(3)
C(141)	−94(9)	6359(6)	7362(3)
C(161)	156(1)	9505(6)	6428(4)
C(241)	−2055(9)	6208(6)	2688(4)
C(261)	3416(7)	5780(6)	3399(3)

TABLE 3 Selected bond lengths (Å) for $[Co(L4M)_2]BF_4$

Co–S(11)	2.228(2)[a]	Co–S(21)	2.219(2)
Co–N(11)	1.961(5)	Co–N(21)	1.947(4)
Co–N(12)	1.892(5)	Co–N(22)	1.886(4)
S(11)–C(17)	1.736(7)	S(21)–C(27)	1.736(5)
N(11)–C(11)	1.358(8)	N(21)–C(21)	1.355(7)
N(11)–C(15)	1.334(8)	N(21)–C(25)	1.344(7)
N(12)–N(13)	1.371(7)	N(22)–N(23)	1.390(6)
N(12)–C(16)	1.300(7)	N(22)–C(26)	1.298(7)
N(13)–C(17)	1.319(6)	N(23)–C(27)	1.321(7)
N(14)–C(17)	1.328(8)	N(24)–C(27)	1.318(7)
N(14)–C(141)	1.458(7)	N(24)–C(241)	1.45(1)
N(14)–H(140)	0.968(5)	N(24)–H(240)	0.963(5)
C(11)–C(12)	1.38(1)	C(21)–C(22)	1.394(9)
C(11)–C(16)	1.45(1)	C(21)–C(26)	1.447(7)
C(16)–C(161)	1.50(1)	C(26)–C(261)	1.495(9)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

(and ^{4}NH) group in the two complexes (Figs. 1 and 2). For $[Co(L4M)_2]^+$, the ^{4}N-methyl group(s) (C(141) and C(241)) is on the same side of the thiosemicarbazone moiety as the methyl group (C(161) and C(261)) of the azomethine function (i.e. *trans* to the sulfur and the *Z* isomer). For $[Co(4M)_2]^+$ the ^{4}N-methyl group (C(140) and C(240)) is *cis* to the sulfur and the *E* isomer. Other than a crystal packing effect, we see no reason why the arrangements of this portion of these two closely related ligands would be different. This is not a random effect since both ligands have the same arrangement in their respective complexes and thus, rotation about the C(17)–N(14) (and C(27)–N(24)) bond is probably restricted. A comparison of C(17)–N(14) to the two 'formal' C=N double bond distances (Fig. 3) is as follows: C(16)–N(12) = 1.300(7) and C(17)–N(13) = 1.319(6) with C(17)–N(14) = 1.328(8) Å for $[Co(L4M)_2]^+$ and C(16)–N(12) = 1.29(1) and C(17)–N(13) = 1.33(1) with C(17)–N(14) = 1.32(2) Å for

TABLE 4. Selected bond angles (°) for $[Co(L4M)_2]BF_4$

S(11)–Co–S(21)	93.36(6)		
S(11)–Co–N(11)	166.9(1)	S(21)–Co–N(21)	167.1(1)
S(11)–Co–N(12)	85.2(1)	S(21)–Co–N(22)	85.4(1)
S(11)–Co–N(21)	90.5(1)	S(21)–Co–N(11)	90.7(1)
S(11)–Co–N(22)	94.2(1)	S(21)–Co–N(12)	92.5(2)
N(11)–Co–N(12)	82.3(3)	N(21)–Co–N(22)	82.0(1)
N(11)–Co–N(22)	98.6(2)	N(12)–Co–N(21)	97.2(1)
N(12)–Co–N(22)	177.8(2)	N(11)–Co–N(21)	87.0(1)
C(11)–N(11)–C(15)	119.8(5)	C(21)–N(21)–C(25)	119.6(5)
N(13)–N(12)–C(16)	118.4(5)	N(23)–N(22)–C(26)	118.8(4)
N(12)–N(13)–C(17)	111.1(5)	N(22)–N(23)–C(27)	111.3(4)
C(17)–N(14)–C(141)	123.5(6)	C(27)–N(24)–C(241)	124.6(6)
C(17)–N(14)–H(140)	118.4(5)	C(27)–N(24)–H(240)	118.1(5)
C(141)–N(14)–H(140)	118.1(5)	C(241)–N(24)–H(240)	117.2(5)
N(11)–C(11)–C(12)	121.2(7)	N(21)–C(21)–C(22)	120.1(5)
N(11)–C(11)–C(16)	114.0(5)	N(21)–C(21)–C(26)	114.3(5)
N(12)–C(16)–C(161)	123.1(6)	N(22)–C(26)–C(261)	123.7(5)
S(11)–C(17)–N(13)	124.4(3)	S(21)–C(27)–N(23)	123.8(4)
S(11)–C(17)–N(14)	116.7(5)	S(21)–C(27)–N(24)	117.6(5)
N(13)–C(17)–N(14)	118.9(5)	N(23)–C(27)–N(24)	118.7(5)

TABLE 5. Positional parameters ($\times 10^4$) for $[Co(4M)_2]BF_4 \cdot 3H_2O$ with standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Co	2194(1)	1488(1)	1515.4(9)
S(11)	1547(2)	499(2)	534(2)
S(21)	1584(3)	2438(2)	475(2)
N(11)	3066(8)	2325(5)	2316(6)
N(12)	3845(8)	1329(5)	1185(6)
N(13)	4111(9)	738(6)	602(7)
N(14)	3226(8)	−274(7)	−327(7)
N(21)	2384(7)	644(6)	2479(6)
N(22)	577(8)	1639(5)	1867(6)
N(23)	−319(8)	2203(4)	1501(7)
N(24)	−76(1)	3112(7)	369(8)
C(11)	4370(10)	2381(8)	2216(8)
C(12)	5150(10)	2955(8)	2724(9)
C(13)	4670(10)	3450(9)	3309(8)
C(14)	3350(10)	3412(8)	3395(8)
C(15)	2640(10)	2824(8)	2883(8)
C(16)	4740(10)	1808(7)	1571(9)
C(17)	3070(10)	319(7)	252(7)
C(21)	1330(10)	617(8)	2895(8)
C(22)	1260(10)	69(8)	3588(9)
C(23)	2290(10)	−454(8)	3836(9)
C(24)	3350(10)	−409(8)	3421(8)
C(25)	3350(10)	158(7)	2738(8)
C(26)	320(10)	1194(7)	2547(8)
C(27)	50(10)	2568(7)	818(8)
C(140)	2220(10)	−795(9)	−780(10)
C(240)	−520(10)	3600(1)	−379(9)

TABLE 6. Selected bond lengths (Å) for $[Co(4M)_2]BF_4 \cdot 3H_2O$

Co–S(11)	2.213(4)[a]	Co–S(21)	2.217(3)
Co–N(11)	1.948(8)	Co–N(21)	1.956(9)
Co–N(12)	1.889(8)	Co–N(22)	1.868(8)
S(11)–C(17)	1.74(1)	S(21)–C(27)	1.78(1)
N(11)–C(11)	1.41(1)	N(21)–C(21)	1.35(1)
N(11)–C(15)	1.30(2)	N(21)–C(25)	1.31(1)
N(12)–N(13)	1.35(1)	N(22)–N(23)	1.37(1)
N(12)–C(16)	1.29(1)	N(22)–C(26)	1.31(1)
N(13)–C(17)	1.33(1)	N(23)–C(27)	1.29(2)
N(14)–C(17)	1.32(2)	N(24)–C(27)	1.34(2)
N(14)–C(140)	1.44(2)	N(24)–C(240)	1.44(2)
N(14)–H(140)	0.960(9)	N(24)–H(240)	0.963(1)
C(11)–C(12)	1.39(2)	C(21)–C(22)	1.38(2)
C(11)–C(16)	1.43(2)	C(21)–C(26)	1.45(2)
C(16)–H(16)	0.96(1)	C(26)–H(26)	0.96(1)

[a] Numbers in parentheses are e.s.d.s in the least significant digits

TABLE 7. Selected bond angles (°) for $[Co(4M)_2]BF_4 \cdot 3H_2O$

S(11)–Co–S(21)	90.2(1)		
S(11)–Co–N(11)	169.8(3)	S(21)–Co–N(21)	168.7(3)
S(11)–Co–N(12)	86.1(3)	S(21)–Co–N(22)	85.9(3)
S(11)–Co–N(21)	89.4(3)	S(21)–Co–N(11)	90.9(3)
S(11)–Co–N(22)	94.7(3)	S(21)–Co–N(12)	95.2(3)
N(11)–Co–N(12)	83.7(4)	N(21)–Co–N(22)	82.9(3)
N(11)–Co–N(22)	95.6(4)	N(12)–Co–N(21)	96.1(3)
N(12)–Co–N(22)	178.8(3)	N(11)–Co–N(21)	91.6(4)
C(11)–N(11)–C(15)	118.0(9)	C(21)–N(21)–C(25)	118(1)
N(13)–N(12)–C(16)	120.8(9)	N(23)–N(22)–C(26)	118.1(9)
N(12)–N(13)–C(17)	112(1)	N(22)–N(23)–C(27)	110.6(9)
C(17)–N(14)–C(140)	125(1)	C(27)–N(24)–C(240)	126(1)
C(17)–N(14)–H(140)	117.8(9)	C(27)–N(24)–H(240)	117(1)
C(140)–N(14)–H(140)	117(2)	C(240)–N(24)–H(240)	116(2)
N(11)–C(11)–C(12)	119(1)	N(21)–C(21)–C(22)	122(2)
N(11)–C(11)–C(16)	113(1)	N(21)–C(21)–C(26)	114(2)
N(12)–C(16)–H(16)	122(1)	N(22)–C(26)–H(26)	123(2)
S(11)–C(17)–N(13)	123.6(9)	S(21)–C(27)–N(23)	124.9(8)
S(11)–C(17)–N(14)	119.5(8)	S(21)–C(27)–N(24)	118.0(9)
N(13)–C(17)–N(14)	117(2)	N(23)–C(27)–N(24)	118(2)

$[Co(4M)_2]^+$. Thus, there is considerable double bond character to the C(17)–N(14) bond in both complexes and free rotation is unlikely.

These two complexes represent the first examples of bis(thiosemicarbazone) complexes in which tridentate ligands have different substituents attached to ^{4}N, and we are presently growing crystals of other example complexes to determine if this difference between the thiosemicarbazones derived from heterocyclic aldehydes and ketones is a common occurrence, as well as to find whether steric factors with bulkier ^{4}N-substituents will alter their stereochemistry.

For $[Co(L4M)_2]^+$, the metal–ligand bond distances for the two L4M ligands are similar (Table 3); the largest difference, 0.014 Å (almost within experimental error), is between the two cobalt–pyridine nitrogens, Co–N(11) and Co–N(21). This is in contrast to bis(acetylpyrazine ^4N-dimethylthiosemicarbazone)nickel(II) [8], which has a difference of 0.029 Å between the two Ni–S distances. There is a 0.021 Å difference, the largest for $[Co(4M)_2]^+$ (Table 6), between Co–N(12) and Co–N(22), the azomethine nitrogens. This is similar to $[Ni(Iq4DH)_2]$, which has bond distance differences

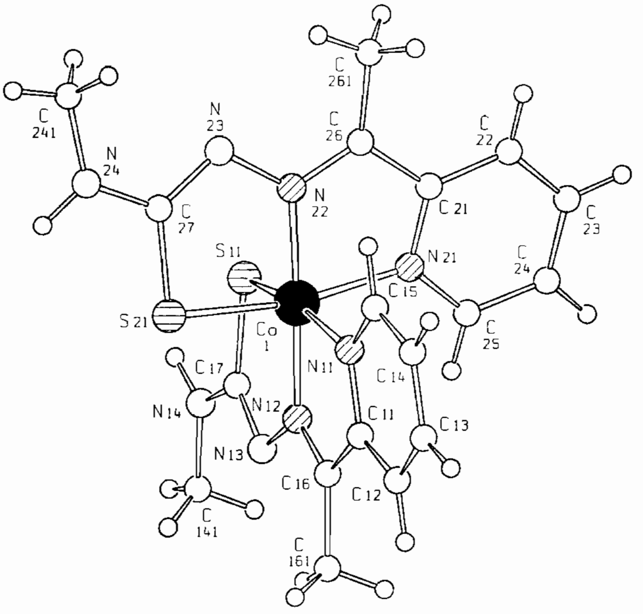

Fig 1 Schakal diagram of the $[Co(L4M)_2]^+$ cation.

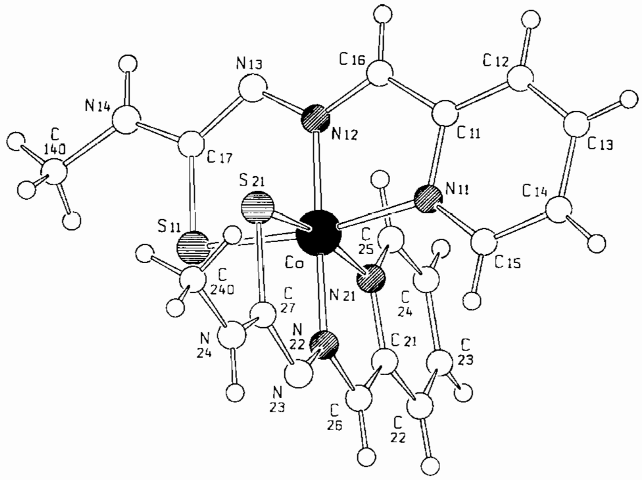

Fig 2. Schakal diagram of the $[Co(4M)_2]^+$ cation

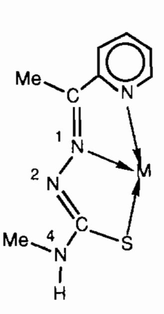

Fig 3. Conventional structural formula for the anion of a heterocyclic thiosemicarbazone.

for the Ni–N(12) and Ni–N(22), the azomethine nitrogens, of the same magnitude as its two Ni–S bonds, 0.013 Å [7]. The thiosemicarbazone moiety has similar bond distances for the two ligands of both $[Co(4M)_2]^+$ and $[Co(L4M)_2]^+$. The similarity of the bond distances is also generally true for 4M and L4M ligands in the two complexes; the expected largest difference is the azomethine C=N bonds which average 1.305 Å for 4M and 1.339 Å for L4M. The difference between the N(12)–N(13) bonds for 4M (average = 1.36 Å) and L4M (average = 1.38 Å) may also be significant in comparing thiosemicarbazones derived from aldehydes with those derived from ketones.

Table 8 is a compilation of some of the relevant bond lengths for the metal–ligand atoms and the thiosemicarbazone moiety for a number of tridentate thiosemicarbazone ligands coordinated to chromium(III), nickel(II) and copper(II), as well as the cobalt(III) complexes of this study. The thiosemicarbazone bond lengths that are expected to be most affected by coordination are the azomethine C=N (e.g. C(16)–N(12)) and thiolato C–S (e.g. C(17)–S(11)) bonds and, therefore, the largest differences in these bonds would also be expected in the complexes listed in Table 8. However, there is small variation in the azomethine C=N bond distances among the complexes, but there is considerably more variation in the C–S bond lengths. For example, the shortest C–S bonds are found for the chromium(III) complex of salicylaldehyde thiosemicarbazone [5], for th six-coordinate nickel(II) complexes [7, 8], and for $[Ni(Sal4Ph)NH_3]$ [11]. The longest C–S bonds are found for the remaining four-coordinate nickel(II) complexes and [Cu(Lhexim)Br] [27]; the present cobalt(III) complexes have intermediate C–S bond lengths. The other portion of the thiosemicarbazone moiety that shows a range of bond lengths is the bond between the thiol carbon and ^{4}N (e.g. C(17)–N(14)) and tends to change in the same manner as the C–S bond lengths. The remaining bonds listed in Table 8 show smaller differences in the thiosemicarbazone moiety's bond lengths.

As expected, and consistent with the discussion of the bond lengths of the thiosemicarbazone moiety, the six-coordinate complexes, with the exception of the present cobalt(III) complexes, have significantly longer M–S and M–N bonds (Table 8) than the four-coordinate complexes. It is surprising that the metal–thiosemicarbazone ligand bonds for $[Cr(HSal4DH)_2]ClO_4$ [5] are longer than the metal–sulfur and metal–nitrogen bonds for both hexacoordinated nickel(II) complexes [7, 8]. In contrast, the three metal–ligand bonds for the present cobalt(III) complexes are considerably shorter than found for $[Ni(Iq4DH)_2]$ [7] and $[Ni(Pz4DM)_2]$ [8]. Only the four-coordinate nickel(II) complexes [10–12] have shorter metal–ligand bonds than the present cobalt(III) complexes.

The important bond angles for $[Co(L4M)_2]BF_4$ and $[Co(4M)_2]BF_4 \cdot 3H_2O$ are listed in Tables 4 and 7, respectively. The intraligand metal–donor atom bond angles (i.e. S(11)–Co–N(11), S(11)–Co–N(12) and

TABLE 8. Comparison of thiosemicarbazone moiety and coordination site bond lengths (Å) for metal complexes[a]

Compound	C=N	N–N	N–C(S)	C–S	(S)C–N	M–S	M–N	M–N(rg)	Reference
[Co(L4M)$_2$]BF$_4$	1.298	1.390	1.321	1.736	1.318	2.219	1.886	1.947	this work
	1.300	1.371	1.319	1.736	1.328	2.228	1.892	1.961	
[Co(4M)$_2$]BF$_4$	1.30	1.35	1.33	1.74	1.32	2.213	1.889	1.948	this work
	1.31	1.37	1.29	1.78	1.34	2.217	1.868	1.956	
[Cr(HSal4DH)$_2$]$^+$ [b]	1.307	1.393	1.336	1.702	1.311	2.407	2.034		5
	1.288	1.388	1.344	1.707	1.307	2.425	2.041		
[Ni(Pz4DM)$_2$][c]	1.297	1.371	1.347	1.714	1.350	2.380	2.014	2.110	8
	1.300	1.366	1.335	1.729	1.353	2.409	2.017	2.096	
[Ni(Iq4DH)$_2$][d]	1.279	1.357	1.331	1.719	1.345	2.412	2.026	2.114	7
	1.295	1.356	1.326	1.735	1.350	2.425	2.013	2.110	
[Ni(Lbcn)NCS)][e]	1.300	1.373	1.317	1.764	1.346	2.138	1.846	1.912	10
[Ni(Pz4M)Cl][f]	1.312	1.376	1.317	1.756	1.327	2.169	1.852	1.923	12
[Ni(Pz4DM)Cl][c]	1.304	1.370	1.320	1.756	1.342	2.141	1.855	1.918	12
[Ni(Sal4Ph)NH$_3$][g]	1.316	1.393	1.333	1.717	1.357	2.166	1.844		11
[Cu(Lhexim)Br][h]	1.275	1.373	1.301	1.759	1.377	2.236	1.963	2.016	18

[a] E.s.d.s for these structures are comparable to those shown in Table 3 except for [Co(4M)$_2$]BF$_4$ (Table 5). [b] HSal4DH = monoanion (loss of hydroxy proton) of salicylaldehyde thiosemicarbazone. [c] Pz4DM = anion (loss of ^{2}N proton) of acetylpyrazine ^{4}*N*-dimethylthiosemicarbazone. [d] Iq4DH = anion (loss of ^{2}N proton) of isoquinoline thiosemicarbazones. [e] Lbcn = anion (loss of ^{2}N proton) of 2-acetylpyridine 3-azabicyclo[3.2.2]nonylthiosemicarbazone. [f] Pz4M = anion (loss of ^{2}N proton) of acetylpyrazine ^{4}*N*-methylthiosemicarbazone. [g] Sal4Ph = dianion (loss of hydroxy and ^{2}N proton) of salicylaldehyde ^{4}*N*-phenylthiosemicarbazone. [h] Lhexim = anion (loss of ^{2}N proton) of 2-acetylpyridine 3-hexamethyleneiminylthiosemicarbazone.

N(11)–Co–N(12) compared to S(21)–Co–N(21), S(21)–Co–N(22) and N(21)–Co–N(22)) are very similar for the two ligands within both complexes; any variation is of the same magnitude as the experimental error. However, there is considerable difference in these bond angles when comparing coordinated L4M with 4M. The acetyl derivative, L4M, has smaller angles for each of the intraligand metal–donor atom bonds; the largest difference in bond angles between coordinated L4M and 4M is S(11)–Co–N(11), *c.* 167 and *c.* 169.3°, respectively. For the smaller cobalt(III) ion, this angle is considerably greater than 159°, which was reported for both bis(isoquinoline thiosemicarbazonato)-nickel(II), [Ni(Iq4DH)$_2$] [7] and bis(2-acetylpyrazine ^{4}*N*-dimethylthiosemicarbazonato)nickel(II), [Ni([Ni-(Pz4DM)$_2$] [8]. The bond angles for the thiosemicarbazone moiety are similar for coordinated L4M and 4M; although well removed from the formyl (acetyl) function, the greatest difference occurs for S(11)–C(17)–N(14) Thus, there may be considerable differences in both bond distances and bond angles involving the thiol function of a thiosemicarbazone depending on whether it is prepared from an aldehyde or ketone. This apparent long range effect is also dependent on the nature of the metal ion and the coordination number as is shown in Table 9.

Spectroscopic studies of [CoL4M)$_2$]BF$_4$ and [Co(4M)$_2$]BF$_4$·3H$_2$O

Much of the spectroscopic information has already been reported for HL4M and [Co(L4M)$_2$]BF$_4$ [19, 26], as well as for H4M [27, 28]. Therefore, we include only those data that are useful for comparing the two cobalt(III) complexes. A decrease in the energy of ν(C=N) from 1580–1590 cm^{-1} in the spectra of HL4M and H4M to 1560 cm^{-1} for the cobalt(III) complexes is consistent with coordination of the azomethine nitrogen, as is the presence of a band at *c.* 440 cm^{-1} which is assignable to ν(Co–N). A second band at 1590–1600 cm^{-1}, assignable to ν(C=N), is expected in these complexes' spectra since the anionic ligands formally have a double bond between ^{2}N and ^{3}C (i.e. $={}^1\mathrm{N}{-}{}^2\mathrm{NH}{-}\mathrm{C}(=\mathrm{S}){}^4\mathrm{NR}_2$). Coordination of the thiol sulfur atoms is indicated by a decrease in energy of the thioamide IV band at 830 cm^{-1} to 720–740 cm^{-1}, as well as a band at 340–350 cm^{-1} assignable to ν(CoS). We are unable to assign ν(CoN) for the pyridinyl nitrogen with our spectrometer. The broad band assignable to ν_3(BF$_4$) and the weaker, narrow band due to ν_4(BF$_4$) are found at *c.* 1065 and 510 cm^{-1} in the spectra of both complexes.

HL4M has an n→π^* transition at 31 060 cm^{-1} [26] while the analogous band is found at 29 325 cm^{-1} for H4M, which also displays a weak shoulder at 25 320 cm^{-1} due to a thiosemicarbazone moiety n→π^* transition [27]. The higher energy n→π^* band blue shifts to 31 250 and 31 440 cm^{-1} in the spectra of [Co(L4M)$_2$]BF$_4$ and [Co(4M)$_2$]BF$_4$, respectively. Additional bands due to charge transfer and d–d transitions are present in both complexes. From solid state electronic spectra we have assigned $\nu_1(^1A_{1g}\rightarrow{}^1T_{1g})$ at *c.* 23 000 cm^{-1}, $\nu_2(^1A_{1g}\rightarrow{}^1T_{2g})$ at *c.* 26 000 cm^{-1}, $\nu_3(^1A_{1g}\rightarrow{}^3T_{1g})$ at *c.* 6500 cm^{-1} and $\nu_4(^1A_{1g}\rightarrow{}^3T_{2g})$ at *c.* 17 000 cm^{-1}. Assignment of the two higher energy

TABLE 9. Comparison of thiosemicarbazone moiety and coordination site bond angles (°) for metal complexes[a]

Compound	S-M-N(rg)	S-M-N	N(rg)-M-N	SC^2N	SC^4N	Reference
$[Co(L4M)_2]BF_4$	167.1	85.4	82.0	124.4	116.7	this work
	166.9	85.2	82.3	123.8	117.6	
$[Co(4M)_2]BF_4$	168.7	85.9	82.9	123.6	119.5	this work
	169.8	86.1	83.7	124.9	118.0	
$[Cr(Sal4DH)_2]ClO_4$[b]		82.0		120.6	120.8	5
		81.5		121.9	121.6	
$[Ni(Pz4DM)_2]$[c]	159.0	81.7	77.8	126.5	119.4	8
	158.2	81.3	78.0	126.3	119.6	
$[Ni(Iq4DH)_2]$[d]	158.9	81.1	78.2	126.7	117.9	7
	159.0	81.3	77.7	127.3	118.0	
$[Ni(Lbcn)NCS)]$[e]	171.0	87.0	84.0	122.1	119.2	10
$[Ni(Pz4M)Cl]$[f]	170.0	86.7	83.3	122.6	119.0	12
$[Ni(Pz4DM)Cl]$[c]	170.6	87.3	83.4	122.6	119.6	12
$[Ni(Sal4Ph)NH_3]$[g]		87.7		121.9	122.9	11
$[Cu(Lhexim)Br]$[h]	165.3	85.1	80.5	125.8	118.3	18

[a]Identification of the ligands is given in Table 8 and the e.s.d.s for these structures are comparable to those shown in Table 3 except for $[Co(4M)_2]BF_4$ (Table 5).

bands is difficult due to the overlap of intraligand and charge transfer bands in this region of the spectrum, but ν_4 is most difficult to assign because this weak spin forbidden band is often at the onset of the higher energy, more intense charge transfer bands. Calculation of ligand field parameters [29] gives $B = 700$ cm^{-1} and $Dq = 2410$ cm^{-1} for $[Co(L4DM)_2]^+$ [19] while bands at 20 800, 24 390, 6870 and 17 240 cm^{-1} for ν_1 through ν_4 give $B = 760$ cm^{-1} and $Dq = 2027$ cm^{-1} for $[Co(4M)_2]^+$. The higher value for B and lower value for Dq indicates less covalency and a weaker ligand field for 2-formylpyridine ^4N-methylthiosemicarbazone. This difference for the two complexes is larger than would be expected based on the similarity of their metal–donor atom bond distances discussed earlier and may be more related to the accuracy of the assignment of the d–d bands in these cobalt(III) complexes.

The ^1H NMR spectra of HL4M [19] and H4M [28] have been reported previously. Unfortunately H4M is not sufficiently soluble in $CDCl_3$ in order to obtain an acceptable spectrum so that it was recorded in d^6-DMSO. HL4M shows no hydrogen bonding by ^2NH, although 2-acetylpyridine ^4N-alkylthiosemicarbazones with larger alkyl groups do [19], and is considered to be 100% E isomer in solution. In contrast, H4M in DMSO shows only a low field signal ($\delta = 15.74$) for ^2NH suggesting it to be 100% Z isomer. Some of the 2-formylpyridine ^4N-dialkylthiosemicarbazones show a mixture of Z and E' (bifurcated hydrogen bonding isomer with a conjugated thiosemicarbazone moiety [10]) isomers.

The ^1H NMR spectrum of $[Co(L4M)_2]BF_4$ features the ^4NH peak shifted slightly downfield compared to the uncomplexed thiosemicarbazone because of coordination of the thiol sulfur resulting in reduced electron density at ^4N [19] ($\delta = 8.77$ to 8.79, but other cobalt(III) complexes of 2-acetylpyridine ^4N-alkylthiosemicarbazones showed shifts of greater magnitude). Similarly, the acetyl methyl group shifts downfield from $\delta = 2.39$ to 2.86 due to coordination of the azomethine nitrogen. In contrast, the ^6CH shifts upfield ($\delta = 8.59$ to 8.08) in the complex's spectrum compared to the free thiosemicarbazone. The coordination of the pyridine nitrogen would be expected to draw electron density from ^6C, which would result in the opposite shift. However, back π-bonding by the cobalt(III) to the ring may be the more important effect. For $[Co(4M)_2]BF_4$, ^4NH shifts from $\delta = 8.67$ in H4M to 8.78, the formyl proton from 7.39 to 7.92 and ^6CH from 8.56 to 8.33 which are in agreement with the chemical shifts found for $[Co(L4M)_2]BF_4$. The ^4NMe groups, which occupy different positions in the two complexes, show peaks at $\delta = 3.35$ in both H4M and $[Co(4M)_2]^+$, but at 3.29 and 3.43 for HL4M and $[Co(L4M)_2]BF_4$, respectively. This suggests that there is little change for the structure of H4M on complexation, but rotation about the C–^4N bond may take place on complexation of HL4M.

Comparing the ^{13}C spectra of HL4M with $[Co(L4M)_2]BF_4$ shows that the azomethine carbon (e.g. C(12)) is significantly shifted downfield (e.g. $\delta = 148$ to 157) indicating coordination of this nitrogen donor atom, but the thiol carbon (e.g C(17)) is shifted only slightly. We are presently unable to record a suitable ^{13}C NMR spectrum of $[Co(4M)_2]BF_4$.

Therefore, the spectral data are in general agreement with the crystal data, but trends in spectral data for apparently analogous compounds are best considered after solution of the complex's crystal structure.

Supplementary material

A complete list of bond distances and angles, as well as equivalent isotropic temperature factors and lists of F_o/F_c values are available from the authors on request.

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