Co-ordination Chemistry of Higher Oxidation States. Part 29.[1] Cobalt(III) Complexes of Bi- and Tetra-thioethers: Synthesis, Properties, and Cobalt-59 Nuclear Magnetic Resonance Data

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Open-chain tetrathioether complexes of cobalt(III) $[CoLX_2]BPh_4[L = MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$, $n = m = 2$; $n = 3, m = 2$; X = Cl, Br, or I] and unstable $[Co(MeSCH_2CH_2SMe)_2X_2]BPh_4$ (X = Cl or Br) are formed by air oxidation of CoX_2 and the ligand in nitromethane. The $CoS_6{}^{3+}$ complex $[CoL^1(MeSCH_2CH_2SMe)][BF_4]_3[L^1 = S(CH_2)_2S(CH_2)_3S(CH_2)_2S(CH_2)_3]$ is also described. Cobalt-59 n.m.r. data for these and $[CoL^1X_2]^+$ are reported and discussed.

Although a number of cobalt(II) thioether complexes are known,[2] the formation of cobalt(III)–thioether linkages usually requires support from other stronger donor groups, *e.g.* in the hybrid ligands $H_2N(CH_2)_nS(CH_2)_mS(CH_2)_nNH_2$ (m, n = 2 or 3),[3] o-$C_6H_4(PPh_2)(SMe)$,[4] and the thiol thioethers $S(CH_2CH_2SH)_2$ and RSCH=CHSH.[5] The only exceptions to this generalisation found in the literature are the complexes of the three macrocycles $S(CH_2)_2S(CH_2)_2S(CH_2)_2$,[6] $S(CH_2)_2S(CH_2)_3S(CH_2)_2S(CH_2)_3$ (L[1]), and o-$C_6H_4CH_2S(CH_2)_2S(CH_2)_3S(CH_2)_2SCH_2$ of types $[Co\{S(CH_2)_2S(CH_2)_2S(CH_2)_2\}][ClO_4]_3$[6] and $[CoL^1X_2]Y$ (X = Cl, Br, or I; Y = ClO_4, BF_4, or BPh_4).[7] Here we report the synthesis and properties of some cobalt(III) complexes of open-chain tetrathioethers and of dithioethers, and their ^{59}Co n.m.r. spectra.

Results

The most convenient preparations of $[CoL^1X_2]Y$ involve air oxidation of a mixture of CoX_2 and L^1 in nitromethane, either in the presence of a large anion (Y = ClO_4 or BF_4) or with subsequent addition of one (Y = BPh_4).[7] A similar reaction of CoX_2 with 1,2-bis(2′-methylthioethylthio)ethane, $MeS(CH_2)_2S(CH_2)_2S(CH_2)_2SMe$ (L^2),[8] in $MeNO_2$, followed by addition of $NaBPh_4$, afforded $[CoL^2X_2]BPh_4$ (Table 1). In contrast to $[CoL^1X_2]^+$ which are stable even in aqueous solution,[7] $[CoL^2X_2]BPh_4$ are decomposed immediately by water or alcohols† and hydrolyse slowly in moist air. They are slightly soluble in chlorocarbons, but dissolve readily in dry $MeNO_2$ or MeCN. Replacement of L^2, which produces five-membered chelate rings, by 1,2-bis(3′-methylthiopropylthio)ethane, $MeS(CH_2)_3S(CH_2)_2S(CH_2)_3SMe$ (L^3),[8] or 1,3-bis(2′-methylthiophenylthio)propane, 2-$MeSC_6H_4S(CH_2)_3SC_6H_4$-$SMe$-2 ($L^4$),[9] which afford mixtures of five- and six-membered rings, leads to markedly less stable $[CoLX_2]^+$ complexes, which decompose rapidly in moist air. 2,5-Dithiahexane (L^5), CoX_2, and $NaBPh_4$ in $MeNO_2$ gave $[CoL^5{}_2X_2]BPh_4$ (X = Cl or Br), but CoI_2 produced only the known[10] cobalt(II) complex $[CoL^5{}_2I_2]$. The complexes of L^5 are very unstable, decomposed rapidly on exposure to air, and the chloro complex decomposed immediately to blue $[\{CoL^5Cl_2\}_n]$[11] even in $MeNO_2$ in the absence of excess of L^5. No reaction was apparent between $PhS(CH_2)_2SPh$ and CoX_2 in $MeNO_2$. The reaction of CoX_2, LiX, and the tridentate 2,6,10-trithiaundecane, $(MeSCH_2CH_2CH_2)_2S$, in $MeNO_2$, in an attempt to prepare $[CoLX_3]$ type complexes, was unsuccessful. On stirring the mixtures in air, dark coloured solutions were obtained, but on concentration these afforded intractable oils. Dimethyl sulphide and $CoBr_2$ in $MeNO_2$ initially gave a dark solution on exposure to air, but this decomposed in a few hours, and no solid was isolated. The successful formation of cobalt(III) thioethers by air oxidation contrasts with our previous failure[12] to obtain them by halogen oxidation of the cobalt(II) analogues.

Table 1. Selected physical data

Complex	Colour	$E_{max.}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})	$\tilde{\nu}$(Co–X)/ cm^{-1}
$[CoL^1Cl_2]BF_4$	Red-violet	18 520 (590), 23 800[a]	342, 260
$[CoL^1Br_2]BF_4$	Red-brown	18 350 (620)[a]	240
$[CoL^1I_2]BPh_4$	Brown-black	15 750 (790), 20 410 (3 210)[a]	
$[CoL^2Cl_2]BPh_4$	Dark green	15 700 (140), 17 200 (180), 30 700 (sh)[b]	395, 342
$[CoL^2Br_2]BPh_4$[c]	Dark green	14 900 (sh), 16 900 (960), 19 900 (900), 21 500 (sh)[b]	290 (?), 245
$[CoL^2I_2]BPh_4$[d]	Dark brown-black	15 800 (1 250), 22 000 (3 280)[b]	
$[CoL^3Br_2]BPh_4$	Dark brown	15 200 (sh), 18 500, 24 000 (sh)[e]	300, 245
$[CoL^4Br_2]BPh_4$	Green-brown	15 800, 19 200 (sh), 24 600[e]	300, 242
$[CoL^5{}_2Cl_2]BPh_4$	Brown	15 600, 18 900 (sh), 22 000 (sh)[e]	375, 260
$[CoL^5{}_2Br_2]BPh_4$	Orange-brown	14 900, 18 850 (sh), 21 000[e]	310, 250
$[CoL^1(L^5)][BF_4]_3$	Dark red	19 530 (445)[a]	

[a] In $MeNO_2$ solution. [b] In MeCN solution. [c] Λ (10^{-3} mol dm^{-3} $MeNO_2$ solution) = 62 ohm^{-1} cm^2 mol^{-1}. [d] Λ = 62 ohm^{-1} cm^2 mol^{-1}. 1:1 Electrolytes in $MeNO_2$ have Λ *ca.* 60—90 ohm^{-1} cm^2 mol^{-1}. [e] Diffuse reflectance.

Travis and Busch[7] identified $[CoL^1X_2]^+$ as *cis* (X′ = Cl or Br) or *trans* (X = I) isomers, principally on the basis of their u.v.–visible spectra. Octahedral $Co^{III}L_6{}^{3+}$ species have two spin-allowed transitions $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$.[13] In *trans*-$[CoL_4X_2]^+$ (D_{4h}) the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition splits into two bands, $^1A_{1g} \longrightarrow {}^1E_g$ at lower energy and $^1A_{1g} \longrightarrow {}^1A_{2g}$ at higher energy. In *cis*-$[CoL_4X_2]^+$ (C_{2v}) the splitting of

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† CoI_2 and L^2 in alcohol produce $[CoL^2I_2]$.[8]

Table 2. Cobalt-59 n.m.r. data

Complex	Solvent	$\delta(^{59}Co)$*/p.p.m.
$[CoL^1Cl_2]BF_4$	$MeNO_2$	7 384
$[CoL^1Br_2]BF_4$	$MeNO_2$	7 062
$[CoL^1I_2]BPh_4$	$MeNO_2$	7 342
$[CoL^2Cl_2]BPh_4$	MeCN	7 583, 7 431
	$MeNO_2$	7 584, 7 433
$[CoL^2Br_2]BPh_4$	MeCN	7 225, 7 056, 6 869
	$MeNO_2$	7 210, 7 030, 6 856
$[CoL^2I_2]BPh_4$	$MeNO_2$	7 472
$[CoL^3Br_2]BPh_4$	$MeNO_2$	8 130, 7 921
$[CoL^5{}_2Br_2]BPh_4$	$MeNO_2$	8 115, 7 992
$[CoL^1(L^5)][BF_4]_3$	$MeNO_2$	6 830
	MeCN	6 821

* To high frequency of external 1 mol dm^{-3} $K_3[Co(CN)_6]$ in water ($\delta = 0$).

Table 3. Analytical data

	Analysis*/%	
Complex	C	H
$[CoL^1Cl_2]BF_4$	24.6 (24.7)	4.1 (4.1)
$[CoL^1Br_2]BF_4$	20.7 (20.9)	3.3 (3.5)
$[CoL^1I_2]BPh_4$	45.4 (45.3)	4.2 (4.5)
$[CoL^2Cl_2]BPh_4$	55.5 (55.6)	5.4 (5.8)
$[CoL^2Br_2]BPh_4$	49.1 (49.2)	4.9 (4.9)
$[CoL^2I_2]BPh_4$	43.5 (43.9)	4.7 (4.3)
$[CoL^3Br_2]BPh_4$	49.8 (49.7)	5.2 (5.1)
$[CoL^4Br_2]BPh_4$	53.9 (54.8)	4.9 (4.4)
$[CoL^5{}_2Cl_2]BPh_4$	55.2 (55.4)	5.3 (5.5)
$[CoL^5{}_2Br_2]BPh_4$	49.2 (49.1)	5.0 (4.6)
$[CoL^1(L^5)][BF_4]_3$	23.4 (23.7)	4.5 (4.2)

* Calculated values in parentheses.

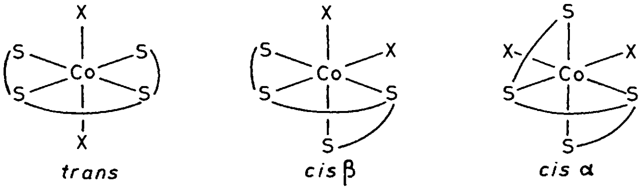

Figure 1. Geometric isomers of $[CoLX_2]^+$

the first band is much less, and is often not resolved. In practice a weak band at *ca.* 14 000—16 000 cm^{-1} is characteristic of *trans*-$[CoL_4X_2]^+$,[13] whilst the corresponding *cis*-$[CoL_4X_2]^+$ absorbs at ≥*ca.* 18 000 cm^{-1}. Our data on $[CoL^1X_2]^+$ (Table 1) are in excellent agreement with those of Travis and Busch,[7] and the presence of a single isomer of each complex is confirmed by the ^{59}Co n.m.r. data (Table 2). Based upon its single ^{59}Co n.m.r. resonance and a band in its u.v.–visible spectrum at 15 800 cm^{-1}, $[CoL^2I_2]BPh_4$ is also readily identified as a *trans* isomer.

For the other complexes of the tetrathioethers the situation is more complicated. The u.v.–visible spectra, and the presence of two or three ^{59}Co n.m.r. resonances (below) for each complex, suggest a mixture of isomers. For an open-chain quadridentate three geometric isomers of $[CoLX_2]^+$ are possible (Figure 1), *trans*, *cis* α, and *cis* β (ignoring for the moment invertomers produced by the chiral sulphur donors). The low-energy bands in the electronic spectra of $[CoL^2X_2]^+$ (X = Cl or Br) at *ca.* 15 000 cm^{-1}, overlapping with a further band or bands at *ca.* 17 000—18 000 cm^{-1}, demonstrate the presence of both *trans* and *cis* isomers. This is supported by the far-i.r. spectra where ν(Co–X) stretches of the *trans* isomers at *ca.* 390 (Cl) and 300 (Br) cm^{-1} were observed. The vibrations of the *cis* isomer(s) at lower frequency are less readily identified (Table 1). Distinction of *cis* α and *cis* β isomers by u.v.–visible spectra of *mixtures* of isomers is not possible, and the $[CoLX_2]^+$ complexes have insufficient solution stability to allow separation by fractional crystallisation or chromatography. [Contrast the studies of Bosnich *et al.*[14,15] of the much more stable cobalt(III) tetra-arsines.]

The diffuse reflectance u.v.–visible spectra of $[CoL^5{}_2X_2]BPh_4$ (Table 1) also indicate that both *cis* and *trans* isomers are present.

The reaction of $[CoL^1Cl_2]BF_4$ with L^5 and $AgBF_4$ (ratio 1:1:2) in nitromethane gave a deep red solution, and after removal of the precipitate of AgCl a dark red solid was isolated, $[CoL^1(L^5)][BF_4]_3$. The solid complex is very deliquescent, but its solutions in dry $MeNO_2$ or MeCN decompose only slowly. This complex is the second[6] reported example of a $[CoS_6]^{3+}$ with neutral donor ligands.

^{59}Co *N.M.R. Spectroscopy.*—The chemical shift range of cobalt(III) complexes exceeds 15 000 p.p.m.; this compensates to a considerable extent for the broad lines which result from fast quadrupole relaxation (^{59}Co, $I = \frac{7}{2}$, 100%). The chemical shifts are dominated by the donor set present, with only small variations being observed between geometric isomers.[16,17] Most data concern complexes with N, O, or C donor ligands.[17] and we have recently reported characteristic chemical shift ranges for complexes with P, As, or Sb donor ligands.[4,18] Data on sulphur ligand complexes are limited to $[Co(S_2CY)_3]$ (Y = NR_2, OR, SR, or R)[16,19] and $[Co\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2X_2]BF_4$ (X = Cl or Br),[4] and thus data on the thioethers are of interest both as an extension of the characteristic cobalt chemical shift data base and also in providing supporting evidence for their constitution.

The $[CoL^1X_2]^+$ complexes each gave a single ^{59}Co n.m.r. resonance (Table 2) with rather narrow lines ($W_{\frac{1}{2}}$ *ca.* 1 000 Hz); $[CoL^2I_2]BPh_4$ also gave only a single resonance, consistent with the presence of a single isomer (*trans*) as deduced from the u.v.–visible spectrum. For $[CoL^2Cl_2]^+$ [$\delta(MeNO_2)$ = 7 584 and 7 433 p.p.m.] and $[CoL^2Br_2]^+$ [$\delta(MeNO_2)$ = 7 210, 7 030, and 6 856 p.p.m.] (Figure 2) the observation of two or three resonances is attributable to the geometric isomers present. Changing the solvent from $MeNO_2$ to MeCN produced insignificant shifts in $\delta(^{59}Co)$ which rules out the possibility that one or more of the resonances may be due to solvolysis. The linewidth of ^{59}Co resonances reflects the field gradient at the nucleus, and hence the stereochemistry may sometimes be inferred from linewidth differences between the isomers.[16] In the present case the differences were small and hence the correlation of the resonances with particular isomers has not been attempted. The presence of a single resonance for $[CoL^1(L^5)]^{3+}$ at lower frequency than for $[CoS_4X_2]^+$ ions is good support for the $[CoS_6]^{3+}$ constitution.[16]

The chemical shift range for CoS_4X_2 moieties, δ *ca.* 7 000—8 200 p.p.m., compares with CoS_6 (δ = 6 830 p.p.m.) for $[CoL^1(L^5)]^{3+}$ and 6 500—7 200 p.p.m. for $[Co(S_2CNR_2)_3]$.[17,19] The presence of chiral co-ordinated terminal SMe groups in the di- and tetra-thioether complexes leads to further isomers (invertomers).[20] When pyramidal inversion is slow on the n.m.r. time-scale, such invertomers are n.m.r. distinguishable, *e.g.* for [Pt(dithioether)X_2] or [Pt(dithioether)Me_3X] the ^{195}Pt n.m.r. resonances of the invertomers differ by ≤*ca.* 30 p.p.m.[21,22] For the present cobalt complexes, all the observed resonances are accounted for by the geometric isomers deduced from u.v.–visible spectral evidence. We conclude that either inversion is fast or the differences in shift

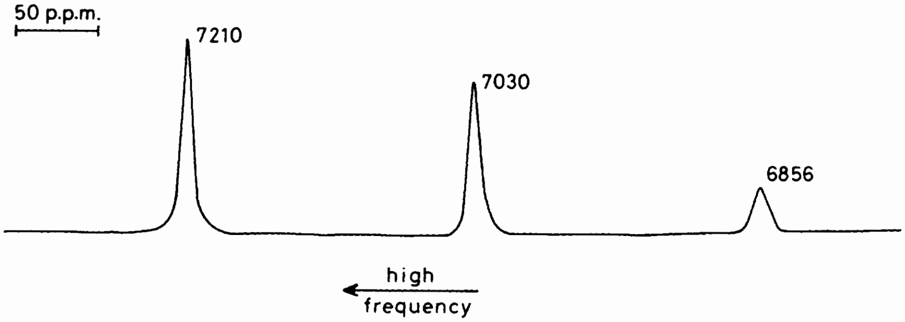

Figure 2. Cobalt-59 n.m.r. spectrum of $[CoL^2Br_2]^+$ in $MeNO_2$

are too small to resolve. Since the lines are relatively narrow, the latter seems unlikely. Inversion rates vary widely with the metal, ligand structure, *trans* ligands, *etc*.,[20] and little is known about cobalt(III) systems. The ^1H n.m.r. spectra are unhelpful since the MeS resonances of the different geometric isomers are almost coincident. The poor solution stability precludes variable temperature studies to probe this matter further.

Conclusions

Although (excluding macrocycles) thioethers are usually regarded as weakly co-ordinating ligands towards 3*d* metal ions in positive oxidation states, we note that, with the preparation of the above cobalt(III) complexes, thioether complexes are now known for more than half of the 3*d* metal(III) ions, *viz*. Ti,[23] V,[24] Cr,[25] Fe,[26] and Co.

Experimental

Anhydrous cobalt(II) halides were prepared by heating the hydrated salts (ALFA) *in vacuo*. The complexes $[CoL^1X_2]Y$[7] and the thioether ligands[8,9,12] were made by literature routes. Organic solvents were dried by conventional routes, and the isolated cobalt(III) thioethers were stored *in vacuo* or in a dry nitrogen atmosphere. Physical measurements were made as described previously.[1,4,18]

Typical Preparation.—$[CoL^5{}_2Cl_2]BPh_4$. Anhydrous cobalt(II) chloride (0.26 g, 2 mmol) was dissolved in nitromethane (20 cm^3) and L^5 (0.55 g, 4.5 mmol) added. The mixture was stirred overnight in air, and then $NaBPh_4$ (0.7 g, 2 mmol) sifted in. After stirring for 15 min, the solution was filtered and treated with diethyl ether until a brown solid separated. This was filtered off, rinsed with diethyl ether, and dried *in vacuo*. Yields typically 40—50% based on Co.

$[CoL^1(L^5)][BF_4]_3$. The complex $[CoL^1Cl_2]BF_4$ (1 mmol) was dissolved in dry $MeNO_2$ in a Schlenk apparatus under nitrogen; L^5 (0.13 g, 1 mmol) and $AgBF_4$ (0.39 g, 2 mmol) were added and the mixture stirred overnight. After filtration, the dark red solution was concentrated *in vacuo*, and the residue triturated with dry diethyl ether to produce a dark red deliquescent solid.

Acknowledgements

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