Cobalt(III) Complexes of Neutral Selenium and Tellurium Donor Ligands: Synthesis and Nuclear Magnetic Resonance Studies

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The first examples of diseleno- and ditelluro-ether complexes of cobalt(III), [Co(MeSe-CH_2CH_2SeMe)$_2X_2$]BPh_4 (X = Cl, Br, or I) and [Co{o-C_6H_4(TeMe)$_2$}$_2X_2$]BPh_4 (X = Br or I), have been prepared by air oxidation of mixtures of anhydrous CoX_2, ligand, and $NaBPh_4$ in nitromethane. The complexes have been characterised by u.v.–visible and multinuclear n.m.r. (^{59}Co, ^{77}Se-{^1H}, and ^{125}Te-{^1H}) spectroscopy. The iodo complexes are *trans* isomers, but both *cis* and *trans* forms are present with the other halides.

Unless they are incorporated into a macrocyclic ring,[1–3] or 'supported' by stronger donors such as phosphines *e.g.* in *o*-$C_6H_4(PPh_2)(SeMe)$,[4,5] ligands with neutral Group 16 donor atoms (S, Se, or Te) are usually viewed as having little ability to co-ordinate to medium or high oxidation states of the 3*d* transition metals.[6,7] We were surprised to discover recently[8] that cobalt(III) complexes of dithioethers and open-chain tetrathioethers were readily obtained by air oxidation of mixtures of cobalt(II) halides, $NaBPh_4$, and the ligands in nitromethane. In an extension of this work we have examined similar reactions with diseleno- and ditelluro-ethers, and report the results below.

Experimental

Physical measurements were made as described previously.[4,8–10] The ligands were obtained by literature routes.[9,10] Anhydrous cobalt(II) halides were prepared by heating the hydrated halides (Alfa) *in vacuo* at 200 °C for 24 h. The complexes were prepared by the same general method exemplified below.

Typical Preparation.—Dibromobis(2,5-*diselenahexane*)*cobalt*(III) *tetraphenylborate*, [Co(MeSeCH_2CH_2SeMe)$_2Br_2$]BPh_4. Anhydrous cobalt(II) bromide (0.22 g, 1 mmol), $NaBPh_4$ (0.34 g, 1 mmol), and 2,5-diselenahexane (0.44 g, 2 mmol) were added in succession under nitrogen to nitromethane (20 cm^3), and the mixture stirred for 30 min. The nitrogen inlet was replaced with a drying tube packed with calcium chloride pellets which allowed access of dry air, and the mixture stirred overnight. The dark solution formed was filtered, and concentrated *in vacuo* to small volume. The solid which separated was rinsed with nitromethane (5 cm^3) and diethyl ether (10 cm^3) and dried *in vacuo*. Yield *ca.* 70% (Found: C, 39.4; H, 4.0. Calc. for $C_{32}H_{40}BBr_2CoSe_4$: C, 39.9; H, 4.1%). $E_{max.}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) = 14.51 (550), 16.58 (sh), 18.28 (660), 19.80 (660), and 26.68 (8 730).

[Co(MeSeCH_2CH_2SeMe)$_2I_2$]BPh_4 (Found: C, 36.9; H, 3.6. Calc. for $C_{32}H_{40}BCoI_2Se_4$: C, 37.4; H, 3.7%). $E_{max.}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) = 13.35 (505) and 20.32 (2 690).

[Co(MeSeCH_2CH_2SeMe)$_2Cl_2$]BPh_4 (Found: C, 43.4; H, 4.6. Calc. for $C_{32}H_{40}BCl_2CoSe_4$: C, 43.4; H, 4.5%). $E_{max.}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) = 14.97 (405), 18.28 (570), and 19.89 (585).

[Co{*o*-C_6H_4(TeMe)$_2$}$_2Br_2$]BPh_4 (Found: C, 37.9; H, 3.0. Calc. for $C_{40}H_{40}BBr_2CoTe_4$: C, 37.8; H, 3.1%). $E_{max.}/10^3$ cm^{-1} (diffuse reflectance) = 13.8, 17.95, and 23.0.

[Co{*o*-C_6H_4(TeMe)$_2$}$_2I_2$]BPh_4 (Found: C, 35.2; H, 2.8. Calc. for $C_{40}H_{40}BCoI_2Te_4$: C, 35.2; H, 2.9%). $E_{max.}/10^3$ cm^{-1} (diffuse reflectance) = 13.7, 20.4, and 25.0.

Results and Discussion

When a mixture of anhydrous cobalt(II) halide CoX_2 (X = Cl, Br, or I), $NaBPh_4$, and 2,5-diselenahexane (MeSeCH_2CH_2SeMe) (1:1:2 mol ratio) was stirred in dry nitromethane with free access of *dry* air the solution darkened rapidly and on concentration brown [Co(MeSeCH_2CH_2SeMe)$_2X_2$]BPh_4 (X = Cl or Br) or purple [Co(MeSeCH_2CH_2SeMe)$_2I_2$]BPh_4 separated. The solid complexes are stable in dry air for many weeks, but decomposed in moist air in a matter of hours. They are poorly soluble in chlorocarbons, but the chloro and bromo complexes dissolve easily in nitromethane ($MeNO_2$) to give brown solutions (green-brown when dilute). The iodo complex is insoluble in nitromethane but dissolves in 4-methyl-1,3- dioxacyclopentan-2-one (propanediol carbonate) $\mathrm{Me\overline{CHOC(O)OC}H_2}$ (mdcpo), and in dimethylformamide (dmf) although in the latter it decomposes fairly rapidly with liberation of the selenium ligands. There was no apparent reaction when PhSeCH_2CH_2SePh was used in place of 2,5-diselenahexane, but 2,6-diselenaheptane, MeSe$(CH_2)_3$SeMe, appeared to generate a cobalt(III) complex in solution as evidenced by the appearance of ^{59}Co n.m.r. resonances in the region of +9 000 p.p.m., characteristic of such a species (see below). However on concentration of the solution only dark green, impure cobalt(II) materials were isolated. Successful isolation of cobalt(III) diselenoethers appears to require both five-membered chelate rings and methyl terminal substituents (which confer stronger donor power than the phenyl analogues), results reminiscent of the dithioether chemistry.[8]

The formation of complexes with the softer ditelluroethers was expected to be more difficult, and in keeping with this we obtained no evidence for the formation of cobalt(III) complexes even in solution with 2,6-ditelluraheptane, MeTe$(CH_2)_3$TeMe. Unfortunately, 2,5-ditellurahexane, MeTeCH_2CH_2TeMe, which would afford five-membered rings is unknown,[11] but using 1,2-bis(methyltelluro)benzene, *o*-C_6H_4(TeMe)$_2$, in similar reactions to those above afforded red-brown [Co{*o*-C_6H_4(TeMe)$_2$}$_2Br_2$]BPh_4 and purple [Co{*o*-C_6H_4(TeMe)$_2$}$_2I_2$]BPh_4. When anhydrous $CoCl_2$ was used a brown solution was produced but this decomposed rapidly on concentration

Table. Nuclear magnetic resonance data

Complex	$\delta(^{59}Co)^a$/p.p.m.	$\delta(^{77}Se)^b$/p.p.m.	Solvent
$[Co(MeSeCH_2CH_2SeMe)_2Cl_2]BPh_4$	8 694, 8 645	259	$MeNO_2$[c]
$[Co(MeSeCH_2CH_2SeMe)_2Br_2]BPh_4$	8 310, 8 228	257	$MeNO_2$[c]
	(8 285, 8 202)		$MeNO_2$–CD_2Cl_2
$[Co(MeSeCH_2CH_2SeMe)_2I_2]BPh_4$	7 689	256	mdcpo[d]
$[Co\{o\text{-}C_6H_4(TeMe)_2\}_2Br_2]BPh_4$	8 329, 8 248		mdcpo[d]
$[Co\{o\text{-}C_6H_4(TeMe)_2\}_2I_2]BPh_4$	8 773		mdcpo[d]

[a] At 298 K (values in parentheses at 240 K) relative to external 1 mol dm^{-3} $K_3[Co(CN)_6]$ in water ($\delta = 0$). [b] At 298 K relative to external neat $SeMe_2$ ($\delta = 0$). [c] Containing 5% deuterionitromethane. [d] Containing 5% deuterioacetone to provide the lock.

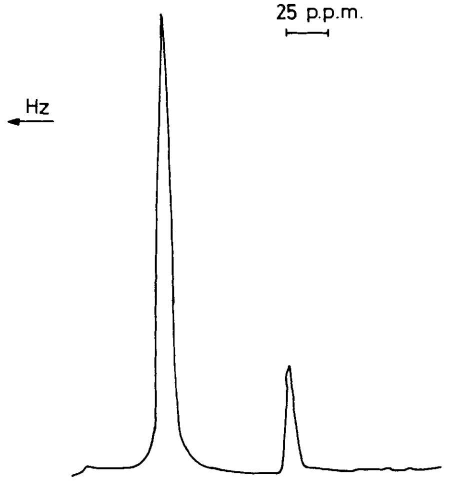

Figure. Cobalt-59 n.m.r. spectrum of $[Co(MeSeCH_2CH_2SeMe)_2Br_2]BPh_4$ in nitromethane at 298 K

and no complex was isolated. The iodo complex is poorly soluble in mdcpo, insoluble in MeCN and $MeNO_2$, and decomposes in dmf or dimethyl sulphoxide with loss of the ditelluroether, but the bromide dissolves easily in mdcpo.

Identification of the geometric isomers present used the combination of ^{59}Co n.m.r. and u.v.–visible spectroscopies which were found satisfactory for the thioether analogues.[8] The complex $[Co(MeSeCH_2CH_2SeMe)_2I_2]BPh_4$ exhibited a single ^{59}Co resonance (Table) and a *d*–*d* transition at 13.35 × 10^3 cm^{-1} showing this to be the *trans* isomer (the transition is $^1A_{1g} \longrightarrow {}^1E_g$ in D_{4h} symmetry).[12] Both the chloro and bromo complexes exhibit two ^{59}Co n.m.r. resonances with disparate intensities (the Figure shows a typical spectrum) and *d*–*d* spectral features consistent with the presence of both *trans* (major form) and *cis* (minor) isomers.[8] Attempts to study the ^{77}Se n.m.r. spectra of the complexes were hindered both by the poor solution stability of the complexes, and by the relatively poor sensitivity ($D_p = 5.26 \times 10^{-4}$)[13] which required long accumulations. For all three halogeno complexes, in addition to free-ligand signals at 122 p.p.m., a single broad resonance in each complex in the range 255—260 p.p.m. was observed (Table) and assigned to the *trans* isomers. For the chloro and bromo complexes very weak features at higher frequency were sometimes seen, probably due to the *cis* isomers, but these were not sufficiently well defined to be identified with certainty. The single resonance for the *trans* isomer indicates that the rate of pyramidal inversion is fast, and resonances for the individual invertomers were not seen {compare *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]^+$ where inversion is slow on the ^{77}Se n.m.r. time-scale at room temperature, and six distinct resonances were observed; for a *trans* isomer symmetry predicts a maximum of five invertomers with eight distinct Se resonances, although all may not be present in significant amounts}.[14] Attempts to investigate the inversion by variable-temperature n.m.r. studies were unsuccessful. On raising the temperature of the bromo complex in $MeNO_2$ solution to 330 K rapid decomposition occurred. At 240 K ($MeNO_2$–CD_2Cl_2)* the ^{59}Co n.m.r. resonances had broadened slightly and shifted to lower frequency (Table), but no ^{77}Se resonance was observed. Whilst this may indicate that the inversion rate was slowing, and the resonance too broadened to observe, it is probably due to the poor solubility at this temperature. Proton n.m.r. spectra were less helpful since the resonances were closely spaced, and complicated by the resonances of the free ligand due to some decomposition.

Addition of excess of $MeSeCH_2CH_2SeMe$ to a solution of $[Co(MeSeCH_2CH_2SeMe)_2Br_2]^+$ in $MeNO_2$ in an attempt to produce $[Co(MeSeCH_2CH_2SeMe)_3]^{3+}$ was unsuccessful; the ^{59}Co n.m.r. spectra of the solution remaining unchanged {compare the corresponding reactions of $[Co(L\text{–}L)_2Br_2]^+$ with L–L = o-$C_6H_4(PPh_2)_2$ or o-$C_6H_4(PPh_2)(SeMe)$[4,15] when the ^{59}Co n.m.r. spectra showed formation of the tris complex}. Reaction of $[Co(MeSeCH_2CH_2SeMe)_2Br_2]^+$, $AgBF_4$, and $MeSeCH_2CH_2SeMe$ (1:2:1 mol ratio) in $MeNO_2$ seemed to cause complete decomposition of the complex rather than substitution of the bromides, and it is probable that the diselenahexane cannot bind to the hard cobalt(III) centre in the absence of halide co-ligands which reduce the charge on the metal and soften it.

Using similar criteria to those above, $[Co\{o\text{-}C_6H_4(TeMe)_2\}_2I_2]BPh_4$ was identified as the *trans* isomer, whilst the bromo complex contains both *cis* and *trans* forms. Attempts to record ^{125}Te n.m.r. spectra for these two complexes were unsuccessful, due to the long accumulations required. After such accumulations only the free-ligand resonance at 377 p.p.m. (mdcpo) was clearly evident; some features in the region 560—600 p.p.m. may have been due to the co-ordinated ligand but these were very weak and ill defined.

One interesting observation from the ^{59}Co n.m.r. data is that the resonances of the dithio-,[7] diseleno-, and ditelluro-ether complexes occur at similar frequencies, an effect also observed for corresponding $[Co(S_2CNR_2)_3]$ and $[Co(Se_2CNR_2)_3]$.[16] This contrasts with the case with Group 15 donor ligands where replacement of phosphorus by arsenic, and then antimony, produces significant high-frequency shifts.[4,15] The reason for the different behaviour with Group 16 donor ligands is unclear (although the number of examples are small it appears genuine); certainly in the platinum(II) complexes replacement of sulphur by selenium and tellurium donors results in progressive low-frequency shifts in the ^{195}Pt resonances.[17]

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* A mixture of 95% $MeNO_2$ and 5% CD_2Cl_2 (v/v). The CD_2Cl_2 provides the lock and reduces the m.p. of the $MeNO_2$ (−29 °C), but also reduces the solubility of the complex.

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