Thio Crown Ether Chemistry. [Cobalt(II)·Hexathio-18-crown-6], an Octahedral Low-spin Complex of Co^{II}

JudithAnn R. Hartman, Eric J. Hintsa, and Stephen R. Cooper*

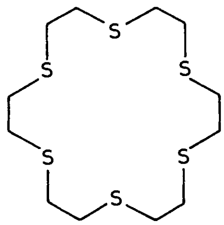
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

Hexathio-18-crown-6 wraps around Co^{II} to yield a rare example of a low-spin octahedral Co^{II} complex, as shown by structural, magnetic, and e.s.r. studies.

The preparation and definitive characterisation of octahedral low-spin Co^{II} complexes has long been a classic problem in co-ordination chemistry,[1] and even now few proven examples exist.[2,3] Strong field complexes of Co^{II} typically lose ligands to form low-spin five- or four-co-ordinate complexes rather than six-co-ordinate ones;[1] for this reason, proof that a complex contains low-spin octahedral Co^{II} demands both structural and magnetic data.

Recently we found that the Ni^{II} complex of hexathio-18-crown-6 (**1**)[4,5] has Ni–S bond lengths [range 2.376(1)—2.397(1) Å] much shorter than the typical value of 2.44 Å found for other Ni^{II}–sulphide complexes.†[6] The crown (**1**) apparently compresses the Ni co-ordination sphere by constraining the donor atoms to be close to the metal ion. Since the ionic radius of Ni^{II} (0.830 Å)[7] is in between those of high-spin and low-spin Co^{II} (0.885 and 0.79 Å, respectively), an intriguing question arose: would (**1**) compress Co^{II} enough to cause a spin state change? We report herein the synthesis and properties of $[Co^{II}\cdot(\mathbf{1})]^{2+}$, a rare example of an octahedral, low-spin Co^{II} complex.[5]

The crown (**1**) (20 mg, 0.055 mmol) (prepared as described previously)[8] was dissolved in 15 ml of acetone with heating and a hot solution of cobalt picrate (28.5 mg, 0.055 mmol) in 3 ml of acetone added to give a brown solution. After addition of 5 ml of MeCN and refluxing for 15 min the solution was allowed to cool slowly, whereupon dark brown parallelepipeds of diffraction quality were deposited.‡ The product was collected by filtration, washed with $CHCl_3$, and dried *in vacuo* overnight, yield 31 mg (64%). An *X*-ray diffraction data set was collected, and the structure solved by heavy atom methods and refined by cascade block-diagonal least-squares methods (with anisotropic thermal parameters for all non-hydrogen atoms) to $R = 4.19\%$ and $R_w = 4.27\%$.§



(1)

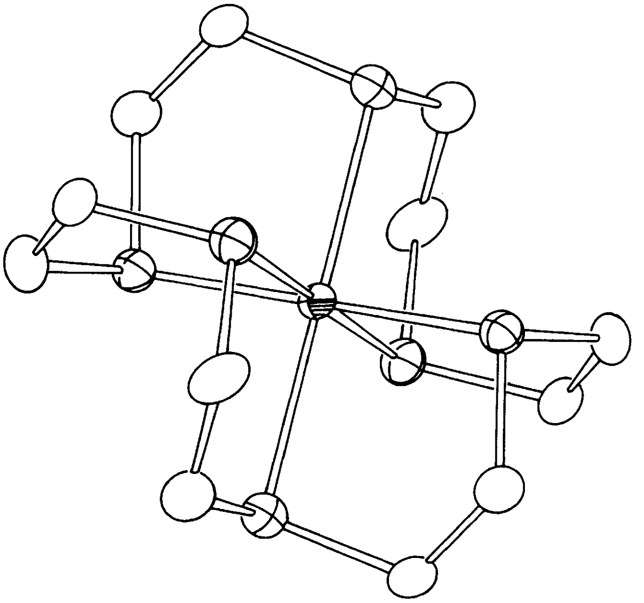


Figure 1. ORTEP drawing of the $[Co^{II}\cdot(\mathbf{1})]^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity).

The $[Co^{II}\cdot(\mathbf{1})]^{2+}$ cation (Figure 1) consists of the hexadentate ligand completely wrapped around the Co^{II} ion, to yield an octahedral complex with crystallographic inversion symmetry. As in the corresponding nickel complex, each three sulphur segment co-ordinates facially to give the *meso* geometric isomer [instead of the chiral (+)(−) racemic isomer, which has two meridionally co-ordinated loops]. Unlike the NiS_6 unit in the nickel complex, however, the CoS_6 co-ordination sphere in $[Co^{II}\cdot(\mathbf{1})]^{2+}$ suffers a remarkable tetragonal distortion from octahedral microsymmetry. The equatorial Co–S bond lengths are 2.251(1) and 2.292(1) Å, while the axial Co–S distance is 2.479(1) Å.¶ In fact, the complex bears a striking resemblance to a Jahn–Teller distorted Cu^{II} complex.

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† A complex that analysed as $[Co^{II}\cdot(\mathbf{1})](picrate)_2\cdot H_2O$ has been reported (ref. 5). However, this compound has a different room temperature magnetic moment (3.05 μ_B) from that of the present compound (1.8μ_B), which furthermore is unsolvated; hence they may or may not be the same material.

‡ In the absence of MeCN the product crystallised as platelike needles.

§ Satisfactory analytical data were obtained.

Crystal data: space group $P\bar{1}$, $a = 6.659(2)$, $b = 9.565(3)$, $c = 13.591(4)$ Å; $\alpha = 85.15(2)$, $\beta = 76.05(2)$, $\gamma = 76.08(2)°$; $D_c = 1.78\ g\ cm^{-3}$; $Z = 1$; 2869 unique reflections with $F > 3\sigma(F)$ were collected with a Syntex R3 diffractometer with Mo-K_α (0.71069 Å) radiation. $R = \Sigma(\mid F_o \mid - \mid D_C \mid)/\Sigma \mid F_O \mid$, $R_w = [\Sigma w(\mid F_O \mid - \mid F_C \mid)^2/\Sigma w F_O{}^2]^{1/2}$, and $w = 1/\sigma^2 F + 0.001\ F^2$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Curiously, in the very recently reported structure of the Co^{II} bis(trithio-9-crown-3) complex the opposite pattern appears: the equatorial Co–S bonds are long [Co–S 2.356(6) and 2.367(5) Å] while the axial bonds are short [Co–S 2.240(7) Å] ref. 9. The authors noted that the M–S bond lengths of the M^{II} bis(trithio-9-crown-3) complexes decrease in the order Cu>Ni>Co, whereas the ionic radii decrease Co>Cu>Ni. However, we note that the observed order is that predicted (ref. 7) if the Co^{II} complex is low-spin, consonant with the tetragonal distortion observed. Unfortunately no magnetic or e.s.r. data have been reported for this compound.

Magnetic susceptibility and e.s.r. measurements on $[\mathrm{Co^{II}}\cdot(\mathbf{1})]^{2+}$ establish that the resemblance to $\mathrm{Cu^{II}}$ is more than passing. The room temperature moment (corrected for diamagnetism) is $1.8\,\mu_B$; hence the $[\mathrm{Co^{II}}\cdot(\mathbf{1})]^{2+}$ cation is *low-spin.*[10] Low-spin $\mathrm{Co^{II}}$, like $\mathrm{Cu^{II}}$, is expected to be Jahn–Teller distorted since both ions have a ^2E_g ground state: the former by virtue of having a single e_g electron, the latter by having a single e_g hole. The e.s.r. spectrum of $[\mathrm{Co^{II}}\cdot(\mathbf{1})]^{2+}$ also indicates a low-spin configuration for the metal ion. At room temperature solid $[\mathrm{Co^{II}}\cdot(\mathbf{1})](\mathrm{picrate})_2$ || exhibits an axial e.s.r. spectrum with $g_{\parallel}$ *ca.* 2 and $g_{\perp}$ 2.09; double integration of the spectrum [relative to a fluid solution of $\mathrm{VO(acetylacetonato)_2}$ in $\mathrm{CHCl_3}$] established that the observed signal accounts for $95\pm10\%$ of the spins in the sample. Moreover, the observed g values indicate a $d_{z^2}{}^1$ ground state for the metal ion, in agreement with the axial elongation found in the crystal structure. Similar g values have been observed previously for the isoelectronic low spin $\mathrm{Ni^{3+}}$ ion,[12] and for tetragonally compressed $\mathrm{Cu^{II}}$ complexes.**[11]

Although analogy to phosphines would suggest that sulphides ought to generate quite strong ligand fields, they are generally considered to be weaker field ligands than ammonia.[13] However $[\mathrm{Co^{II}}\cdot(\mathbf{1})]^{2+}$ is low-spin, in contrast to the corresponding hexammine $[\mathrm{Co^{II}(NH_3)_6}]^{2+}$, which is high-spin;[14] hence either the ligand field strength of sulphides is much greater than hitherto imagined, or sulphides greatly decrease the spin pairing energy, or (**1**) forces the sulphur atoms close enough to the $\mathrm{Co^{II}}$ ion to generate a strong ligand field from a weak field ligand.

In conclusion, the present results both establish $[\mathrm{Co^{II}}\cdot(\mathbf{1})]^{2+}$ as a characterised example of an octahedral low-spin $\mathrm{Co^{II}}$ complex and emphasise[3] the utility of (**1**) as a ligand for transition metal ions. In addition, they also raise fundamental questions about the ligating properties of sulphides generally and thio crown ethers in particular.

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[||] The weak exchange interaction between $\mathrm{Co^{II}}$ ions (minimum separations 6.6 Å) washes out $^{59}\mathrm{Co}$ hyperfine structure, but does not affect the g values since there is only one type of magnetic site (*i.e.*, the lattice orders in a ferrodistorted fashion), ref. 11.

[**] From the electron-hole formalism similar spectra are to be expected for a tetragonally elongated $e_g{}^1$ complex and a tetragonally compressed $e_g{}^3$ complex.