

An Unusual Co₂-containing Anion : Synthesis and Structure of

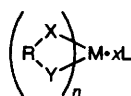
$[(\text{OxS})\text{Ca}\cdot 4\text{HMPA}]^+ \cdot [(\text{OxS})\text{Co}\cdot \mu\text{-(OxS)}_3\cdot \text{CoCl}]^-$ [$\text{OxS}^- = \text{C}_6\text{H}_4\text{O}\cdot (\text{C}=\text{S})=\text{N}^-$; HMPA = $\text{O}=\text{P}(\text{NMe}_2)_3$]

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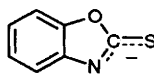
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Solid CoCl_2 dissolves in a toluene solution of $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$ to give $[(\text{OxS})\text{Ca}\cdot 4\text{HMPA}]^+ \cdot [(\text{OxS})\text{Co}\cdot \mu\text{-(OxS)}_3\cdot \text{CoCl}]^-$, **1**, the anion structure consists of two Co^{2+} centres linked by three symmetrically bridging OxS^- ligands such that one Co^{2+} (bonded through S to a terminal OxS^-) has a tetrahedral coordination sphere of four S atoms whilst the other (bonded to a terminal Cl^-) has a tetrahedral coordination sphere of three N and one Cl atoms.

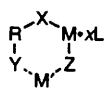
We described earlier a series of Group 1 and Group 2 metal chelate complexes of type $(\text{Y-R-X})_n\text{M}\cdot x\text{L}$, **A**, in which R is a heterocyclic framework, X and Y are electronegative centres, and L is a neutral ligand (*e.g.* HMPA).¹ Most attention has focused on the 2-mercaptobenzoxazolyl chelating ligand (OxS^- ; X, Y = N, S), **B**. These complexes can be prepared directly, by reacting Y-R-XH and L with the metal, metal hydride or an organometallic (*e.g.* Bu^nLi), or indirectly, by reacting Y-R-XH and L with the solid metal hydroxide to give first an aqua complex $(\text{Y-R-X})_n\text{M}\cdot x\text{L}\cdot y\text{H}_2\text{O}$ which can then be dehydrated by heating *in vacuo*. Solutions of the complexes have been found to dissolve solid salts of other metals ($\text{M}'\text{Z}$ etc). At its simplest, the basic principle of this process has been that the anion Z coordinates to the extant metal (M),



A; $n = 1$ or 2



B



C

displacing one of the chelating centres (say, Y) which then coordinates to the second metal (M'), **C**.

Two examples of such metal salt capture have been reported,² both using solutions of $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$:^{1c} (i) with PtCl_2 , the product is $[\text{Ca}_2\text{Cl}_3\cdot 6\text{HMPA}]^+ \cdot [(\text{OxS})_4\text{Pt}\cdot \text{Ca}\cdot \text{Cl}]^-$,^{2a} and (ii) with HgCl_2 , the product is $[(\text{OxS})\text{CaCl}\cdot 2\text{HMPA}]_2 \cdot (\text{OxS})_2\text{Ca}\cdot (\text{HgCl}_2)_2$.^{2b} In the first example, PtCl_2 has been stripped of its Cl^- ligands, whilst in the second HgCl_2 units are captured intact. However, a common feature is that both metals (M, M') are present together, along with OxS^- ligands: in the anion of (i) and in the whole molecule of (ii). Furthermore, in both examples, N of OxS^- remains coordinated to Ca^{2+} , but S is displaced and bonds to the captured metal (Pt or Hg), *i.e.* the essentials of **C** pertain. Here we describe a different type of behaviour, observed when a solution of $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$ dissolves CoCl_2 . The product is $[(\text{OxS})\text{Ca}\cdot 4\text{HMPA}]^+ \cdot [(\text{OxS})\text{Co}\cdot \mu\text{-(OxS)}_3\cdot \text{CoCl}]^-$, **1**; neither cation nor anion contains both metals.

Heating solid CoCl_2 with a toluene solution of $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$ caused dissolution of the solid, giving a dark-green solution. Cooling afforded green needle-shaped

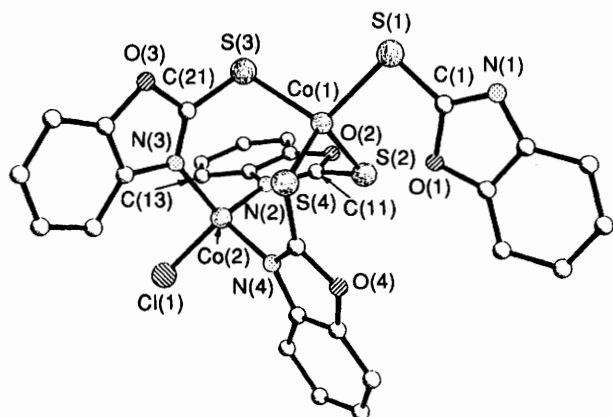


Fig. 1 The structure of $[(\text{OxS})\text{Co}-\mu-(\text{OxS})_3\text{-CoCl}]^-$, the anion of **1**. Hydrogen atoms on the OxS^- ligands have been omitted for clarity.

crystals of **1**[†] shown by X-ray diffraction[‡] to be $[(\text{OxS})\text{Ca}\cdot 4\text{HMPA}]^+ \cdot [(\text{OxS})\text{Co}-\mu-(\text{OxS})_3\text{-CoCl}]^-$. The cation has a fairly standard (but hitherto unobserved) structure, with an approximately octahedral Ca^{2+} cation being coordinated by a chelating OxS^- ligand [$\text{Ca}-\text{N}$, 2.546(8), $\text{Ca}-\text{S}$, 2.942(3) Å] and by four terminal HMPA ligands [mean $\text{Ca}-\text{O}$, 2.294(7) Å]. The structure of the anion is much more unusual (Fig. 1). Two Co atoms are bridged by three OxS^- ligands. These ligands bridge symmetrically in the sense that the three S centres bond to Co(1) [mean $\text{Co}(1)-\text{S}$, 2.352(3) Å] and the three N centres bond to Co(2) [mean $\text{Co}(2)-\text{N}$, 2.002(7) Å]. Each Co atom then completes tetrahedral coordination by attaching a terminal ligand; Co(1) with a fourth OxS^- bonding through S, a mode not observed previously for this ligand [$\text{Co}(1)-\text{S}(1)$ 2.304(3) Å] and Co(2) with a Cl⁻ ligand [$\text{Co}(2)-\text{Cl}(1)$ 2.242(3) Å]. The $\text{Co}(1)-\text{Co}(2)$ distance (3.64 Å) precludes any direct metal-metal bonding. Between them, the anion and the cation display OxS^- in three coordinating modes: chelating, terminal through S, and bridging. Somewhat surprisingly, however, distances within the $(\text{N}=\text{C}=\text{S})^-$ units of the ligands in these various modes show little variation: the $\text{N}=\text{C}$ distances are 1.300(13), 1.304(12) and (average) 1.317(12) Å, respectively and the $\text{C}=\text{S}$ distances are 1.696(9), 1.704(10) and (average) 1.705(10) Å, respectively.

[†] **1**: solid CoCl_2 (0.129 g, 1.0 mmol) was added to a solution of $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$ (1.40 g, 2.0 mmol) in toluene (10 ml) under a nitrogen atmosphere. Heating the blue mixture at 100 °C for 1 h caused dissolution of the solid to give a dark-green solution. Filtration followed by cooling to room temp. afforded green needles of **1**. First batch yield 0.121 g, 15% based on consumption of CoCl_2 ; the complex is very soluble in toluene but refrigeration produces only an oil; no other solid products could be isolated; m.p. 183–186 °C. Satisfactory elemental analysis was obtained.

[‡] *Crystal data* for **1**: $\{[\text{C}_6\text{H}_4\text{O}(\text{C}=\text{S})=\text{N}] \text{Ca} \cdot [\text{O}=\text{P}(\text{NMe}_2)_3]_4\}^+ \cdot \{[\text{C}_6\text{H}_4\text{O}(\text{C}=\text{S})=\text{N}] \text{Co} \cdot \mu\text{-}[\text{C}_6\text{H}_4\text{O}(\text{C}=\text{S})=\text{N}]_3\text{-CoCl}\}^-$, $\text{C}_{59}\text{H}_{92}\text{N}_{17}\text{O}_9\text{P}_4\text{S}_5\text{CaClCo}_2$, $M = 1661.07$, orthorhombic, space group $Pna2_1$, $a = 23.516(4)$, $b = 28.120(5)$, $c = 11.979(4)$ Å, $V = 7921(3)$ Å³, $Z = 4$, $D_c = 1.392$ Mg m⁻³, $[F(000)] = 3472$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.788$ mm⁻¹, $T = 153(2)$ K. Data were collected on a Stoe-Siemens diffractometer in the range $7^\circ \leq 2\theta \leq 45^\circ$ (10912 reflections collected, 10317 independent reflections). The structure was solved by direct methods⁵ and refinement, based on F^2 , was by full-matrix least squares techniques⁶ (for the Co-containing anion all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. Due to disorder in the Ca-containing cation the HMPA carbon and nitrogen atoms were refined isotropically and no hydrogen atoms were added to these carbons) to $R_1 = 0.0673$, $wR_2 = 0.1864$ for 9137 independent reflections [$F > 4\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The most striking feature of the anion structure is the way one metal centre [Co(1)] chooses to gather four 'soft' S atoms around it (including that of the terminal OxS^- ligand, which might have been expected to either chelate or to bond through N) whilst the other metal centre [Co(2)] has four 'hard' coordinating atoms (three N, Cl). Although there are over thirty known structures³ of $\text{Co}-\mu-(\text{X}-\text{C}-\text{Y})_n-\text{Co}$ species, with bridging atoms X,Y drawn from N,P,O and S, most have ligands with $\text{X} = \text{Y}$ (e.g. acetates $\text{O}=\text{C}(\text{Me})=\text{O}^-$ especially). Only three Co_2 -containing structures have bifunctional heteroatom bridges ($\text{X} \neq \text{Y}$), and only one of these has more than one such a bridge ($n > 1$). This is the polymeric structure of $[(4\text{-methylpyridine})_2\text{Co} \mu\text{-}(\text{NCS})_2]_\infty$ in which octahedral Co^{2+} centres are bridged by NCS^- ligands; however, these $\mu\text{-}(\text{NCS})_2$ pairs operate asymmetrically, a particular Co^{2+} being coordinated by the N centre of one of the bridging ligands and by the S centre of the other.⁴ Thus the anion structure of **1** is highly unusual on several counts: $\text{X} \neq \text{Y}$, $n = 3$, symmetrical bridging ligands. Furthermore, it is tempting to consider the metal centres in this structure—both formally Co^{2+} —as being in fact Co^+ (coordinated by four 'soft' S atoms) and Co^{3+} (coordinated by three N, one Cl). However, the electronic spectrum of a benzene solution of **1** (recorded over the range 430–2100 nm) exhibits only two absorptions in the UV-VIS region, as expected for tetrahedral Co^{2+} (d^7): at 1260 nm [7937 cm⁻¹; ν_2 , ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2(\text{F})$] and at 587 nm [17036 cm⁻¹; ν_3 , ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2(\text{F})$]. The latter band exhibits a marked shoulder which may reflect the presence of two Co^{2+} centres with slightly different ligand field environments.

It is not possible to speculate on how the reaction leading to **1** operates and so on why a conjunctive Ca-Co mixed-metal species is not formed (cf. the behaviour with PtCl_2 and HgCl_2). Obviously there is partial transfer of OxS^- ligands from Ca^{2+} to Co^{2+} and, presumably, of Cl⁻ ligands to Ca^{2+} . Since all of the CoCl_2 dissolved during the reaction and no $(\text{OxS})_2\text{Ca}\cdot 2\text{HMPA}$ could be recovered after it, the stoichiometry (1 : 1) of the reaction implies that species such as CaCl_2 and $(\text{OxS})\text{CoCl}$, one or both being complexed by excess HMPA, are formed also. However, despite solution concentration and prolonged refrigeration, no other products could be isolated. We are exploring other systems based on $(\text{OxS})_2\text{Sr}\cdot 3\text{HMPA}^{1c}$ and $(\text{OxSLi}\cdot \text{HMPA})_2$,^{1b} solutions of which will also dissolve solid CoCl_2 .

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References

- (a) D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1990, 643; (b) D. R. Armstrong, D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *Inorg. Chim. Acta*, 1991, **185**, 163; (c) P. Mikulcic, P. R. Raithby, R. Snaith and D. S. Wright, *Angew. Chem.*, 1991, **103**, 452; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 428; (d) F. A. Banbury, M. G. Davidson, A. J. Edwards, M.-I. Lopez Solera, P. R. Raithby, R. Snaith, D. Stalke and D. S. Wright, *Inorg. Chim. Acta*, 1993, **203**, 93.
- (a) M. G. Davidson, P. R. Raithby, R. Snaith, D. Stalke and D. S. Wright, *Angew. Chem.*, 1991, **103**, 1696; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1648; (b) M. G. Davidson, S. C. Llewellyn, M.-I. Lopez Solera, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 573.
- Search of the Cambridge Crystallographic Data Base.
- R. Micu-Semeniuc, E. Hila, G. Dobas-Roman and L. Ghergari, *Rev. Roum. Chim.*, 1983, **28**, 471.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- G. M. Sheldrick, SHELXL-92, Program for crystal structure refinement, University of Göttingen.