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Insertion of COS into Group 2 metal–ethoxide bonds; crystal structures of $[Mg(OCSOEt)_2(EtOH)_4]$ and $[Sr_3(OCSOEt)_6(EtOH)_8]$*

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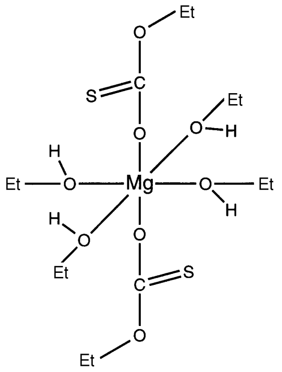
Some compounds of the alkaline-earth metals, which result from the insertion of COS into metal–ethoxide bonds, have been synthesized and characterised. The crystal structure of the first linear trinuclear metal strontium complex $[Sr_3(OCSOEt)_6(EtOH)_8]$ **2**, which resulted from the reaction of $[\{Sr(OEt)_2(EtOH)_4\}_n]$ with COS gas, has been determined. The octahedral monomer $[Mg(OCSOEt)_2(EtOH)_4]$ **1** resulted from the insertion of a molecule of COS into the ethoxide bonds of $[\{Mg(OEt)_2(EtOH)_4\}_n]$. The structures demonstrate three alternative co-ordination modes of the $OCS(OR)^-$ ligand.

In the last few years there has been a resurgence of interest in the chemistry of alkaline-earth-metal complexes, which can be attributed to their potential application as molecular precursors for metal oxide thin films *via* metal organic chemical vapour deposition (MOCVD) and sol–gel techniques. The insertion reactions of alkaline-earth-metal alkoxides and alkyls with small molecules such as SO_2, CO_2, COS and CS_2 have been relatively neglected compared to those associated with transition metals.[1,2] Darensbourg *et al.*[3] investigated the insertion reactions of tungsten aryloxide complexes and showed that they undergo facile COS and CO_2 insertion reactions. The insertion of COS into the M−O bond was irreversible whereas that of CO_2 was reversible. We have previously provided the first example of insertion of COS into the calcium–methoxide bond which resulted in the formation of the thiocarbonato-bridged dimer $[\{Ca(OCSOMe)_2(MeOH)_3\}_2]$.[4] In this paper we describe the extension of this work to other Group 2 metal alkoxides. Specifically, we describe the COS insertion into the M−O bonds of magnesium and strontium ethoxides. The crystal structures of the products $[Mg(OCSOEt)_2(EtOH)_4]$ **1** and $[Sr_3(OCSOEt)_6(EtOH)_8]$ **2** are described.



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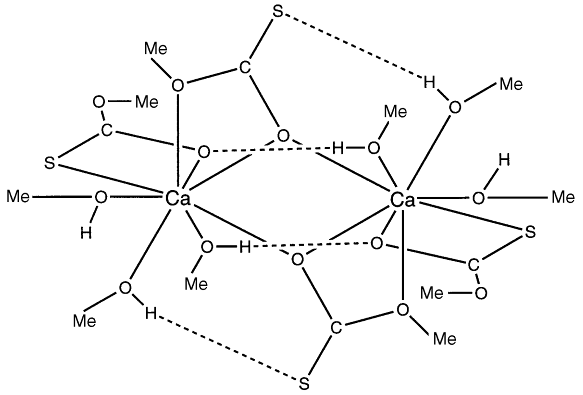

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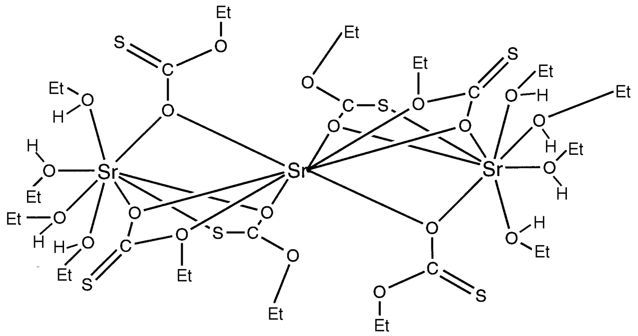

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Results and Discussion

The crystalline ethanol-solvated metal ethoxides $[\{Mg(OEt)_2(EtOH)_4\}_n]$ and $[\{Sr(OEt)_2(EtOH)_4\}_n]$ were suspended in ethanol and COS bubbled through the suspension at room temperature. An exothermic reaction occurred, reaching completion within 10 min and the products were isolated by reducing the volume. In both cases crystallisation from ethanol gave colourless crystals. On the basis of single-crystal X-ray studies, analytical data and spectroscopic measurements, the products have been formulated as the mono- and tri-meric thiocarbonato complexes $[Mg(OCSOEt)_2(EtOH)_4]$ **1** and $[Sr_3(OCSOEt)_6(EtOH)_8]$ **2**, respectively.

These characterisational results have confirmed that insertion of COS into the metal–alkoxide bonds has occurred [equations (1) and (2)]. Complexes **1** and **2** are moisture sensitive, but may be stored indefinitely under an inert atmosphere at room temperature without losing COS, although some reversible desolvation occurs. They are soluble in alcohols and co-ordinating and polar organic solvents, but have poor solubilities in hydrocarbons.

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* *Non-SI unit employed*: cal = 4.184 J.

$$[\{Mg(OEt)_2(EtOH)_4\}_n] + 2nCOS \longrightarrow n[Mg(OCSOEt)_2(EtOH)_4] \quad (1)$$

$$3[\{Sr(OEt)_2(EtOH)_4\}_n] + 6nCOS \longrightarrow n[Sr_3(OCSOEt)_6(EtOH)_8] + 4nEtOH \quad (2)$$

The IR spectra of complexes **1** and **2** (as Nujol mulls between CsI plates) were studied. The band at 1554 cm^{-1} of **1** has been assigned to the C=O stretching mode of the COS moiety and that at 1174 cm^{-1} to the C=S stretching mode. Complex **2** exhibits CO stretching vibrations at 1620 and 1568 cm^{-1}, implying two distinct co-ordination modes. The C=S and C–S stretching frequencies featured at 1176 and 930 cm^{-1} respectively. These bands have been assigned on the basis of previously published IR data for similar compounds.[1,5]

Proton NMR spectroscopic studies in $(CD_3)_2SO$ for complexes **1** and **2** clearly differentiate the ethanol and ethyl thiocarbonato groups. A doublet of quartets for the CH_2 of the co-ordinated ethanol molecules was observed at δ 3.41 for **1** and at 3.42 for **2**, while a quartet at δ 3.74 for **1** and 3.80 for **2** was assigned to the CH_2 of the ethyl thiocarbonato moieties. The two different CH_3 environments of the ethanol and the ethyl thiocarbonato moieties appeared in the same region as two superimposed triplets at approximately δ 1.04 for both complexes **1** and **2**. Similar assignments were possible in the $^{13}C-\{^1H\}$ NMR spectra of **1** and **2**. A characteristic signal for the thiocarbonato carbon, $OCS(OEt)^-$, was observed at low field, δ 184.5, in the $^{13}C-\{^1H\}$ NMR spectra for both complexes.

Mass spectroscopic studies using fast atom bombardment (FAB) (positive ion) techniques for complexes **1** and **2** yielded complicated fragmentation patterns which were not very helpful in their characterisation. Molecular ions were not observed, primarily because of the poor volatilities and mass-transport properties of these complexes.

The DSC trace for the magnesium complex **1** [Fig. 1(*a*)] shows two exotherms between 23 and 140 °C. This is mirrored in the TGA plot with a 72.5% weight loss, corresponding to loss of the ethanol and the COS molecules. The subsequent weight loss of *ca.* 18% represents the decomposition of $Mg(OEt)_2$ to MgO between 140 and 700 °C leaving a residue of 10.27%. The DSC trace of compound **2** [Fig. 1(*b*)] shows three endotherms. The first two reveal two overlapping reaction processes between 40 and 197 °C. These two endotherms are mirrored in the TGA spectrum with a weight loss of 52.1% representing the loss of ethanol and COS gas. The third endotherm on the DSC trace is observed at *ca.* 240 °C; this feature is coupled with a simultaneous loss of 11.3% on the TGA curve corresponding to the loss of the ethyl groups, to yield a strontium oxide residue by 900 °C (residue 30.0%). The observation of exotherms for **1** and endotherms for **2** with closely related complexes suggests that the thermodynamics of the decomposition process is sensitive to the nuclearity of the complex and the mode of co-ordination of the ethyl thiocarbonate ligand.

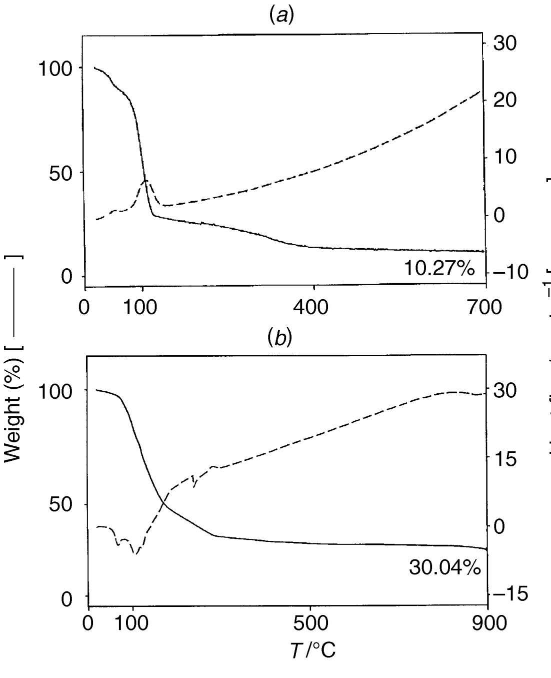


Fig. 1 The TGA/DSC curves of complexes (*a*) **1** and (*b*) **2**

Crystal structures

[Mg(OCSOEt)₂(EtOH)₄] 1. The insertion product **1** has the centrosymmetric monomeric structure shown in Fig. 2. Selected bond lengths and angles are listed in Table 1. The insertion of COS into the two metal–ethoxide bonds has resulted in *trans*-ethyl thiocarbonate ligands with four equatorial oxygen atoms from ethanol ligands completing an octahedral co-ordination geometry round the magnesium atom with O–Mg–O angles in the range 86.59–93.41(9)°. The bond distance from the metal to the oxygen donor of the ethyl thiocarbonate ligand [Mg–O(1a) 2.036(2) Å] is markedly shorter than the mean of those to the

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mg–O(1a)	2.036(2)	Mg–O(1c)	2.071(2)
Mg–O(1b)	2.095(2)	O(1a)–C(2a)	1.235(4)
C(2a)–O(3a)	1.337(5)	C(2a)–S(21a)	1.718(4)
O(1a)–Mg–O(1a′)	180.0	O(1a)–Mg–O(1c)	93.41(9)
O(1a)–Mg–O(1c′)	86.59(9)	O(1c)–Mg–O(1c′)	180.0
O(1a)–Mg–O(1b′)	91.66(9)	O(1c)–Mg–O(1b′)	91.27(10)
O(1a)–Mg–O(1b)	88.34(9)	O(1c)–Mg–O(1b)	88.73(10)
O(1b′)–Mg–O(1b)	180.0	C(2a)–O(1a)–Mg	142.8(2)
O(1a)–C(2a)–O(3a)	119.7(3)	O(1a)–C(2a)–S(21a)	126.8(3)
O(3a)–C(2a)–S(21a)	113.4(3)	C(2b)–O(1b)–Mg	124.9(2)

Symmetry transformation used to generate equivalent atoms: −*x*, −*y*, −*z*.

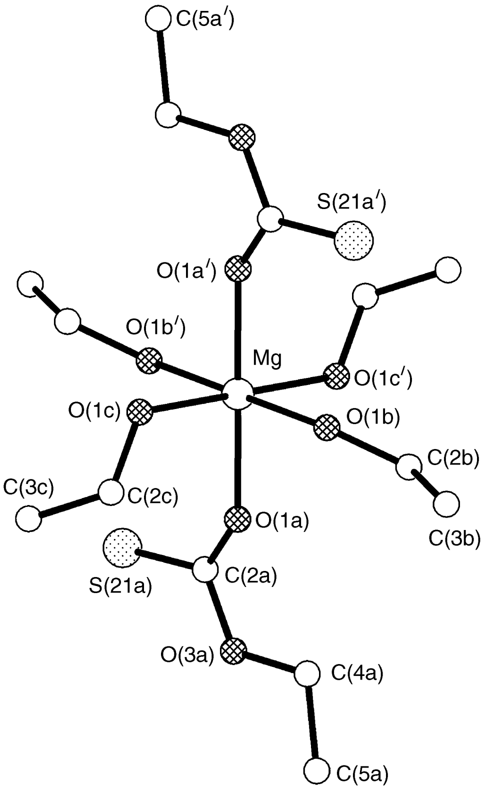


Fig. 2 Crystal structure of $[Mg(OCSOEt)_2(EtOH)_4]$ **1**

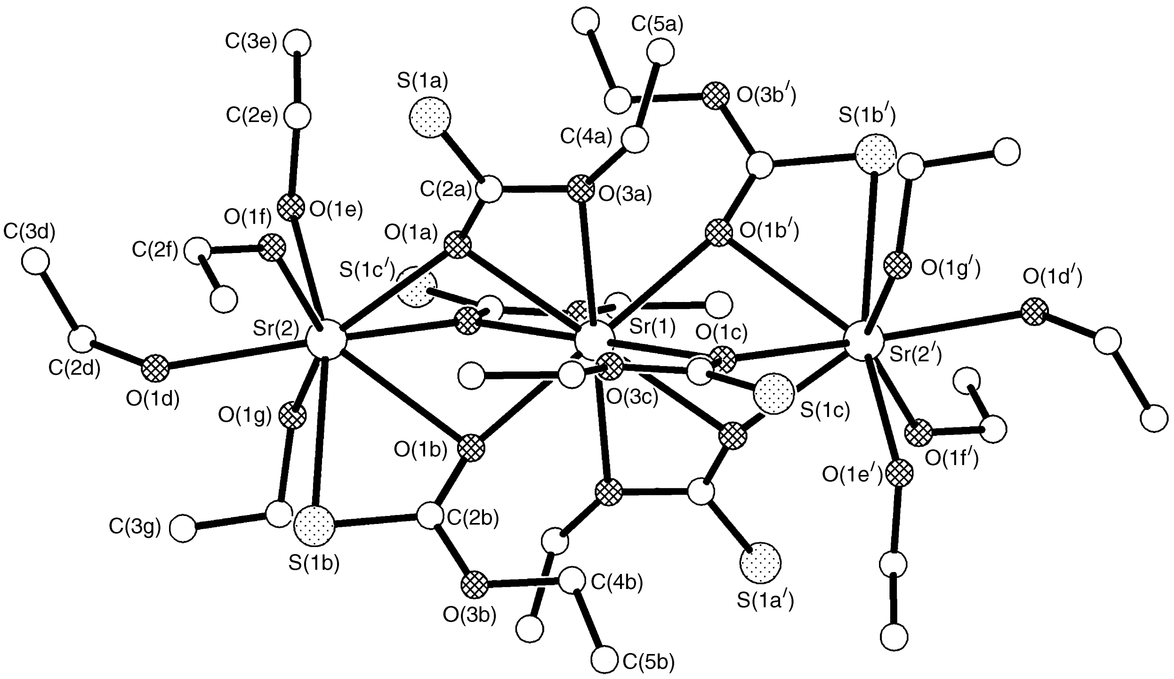


Fig. 3 Crystal structure of $[Sr_3(OCSOEt)_6(EtOH)_8]$ **2**

two independent ethanol groups, 2.083(2) Å, the latter being similar to the value of 2.069(3) Å reported for the Mg–O bond length in hexa(ethanol)magnesium(II) chloride.[6]

The monomeric structure observed for $[Mg(OCSOEt)_2(EtOH)_4]$ **1**, with two monodentate thiocarbonate ligands, provides a marked contrast to the trinuclear structure of **2** (see below) and to the dimeric eight-co-ordinate calcium complex $[\{Ca(OCSOMe)_2(MeOH)_3\}_2]$ **3**, obtained by insertion of COS into calcium–methoxy bonds (the only previous example of this type of insertion product to be structurally characterised).[4] In the calcium complex **3** the two thiocarbonate ligands adopt a bidentate bonding mode, with one also bridging to the second metal atom to give a centrosymmetric dimer; this is very similar to that in the linear polymer resulting from insertion of SO_2 into the Ca–OMe bond.[7] The preference of the ethyl thiocarbonate ligand to adopt a monodentate bonding mode in **1**, resulting in a discrete six-co-ordinate magnesium complex, may be attributed to the small size of the magnesium(II) ion.

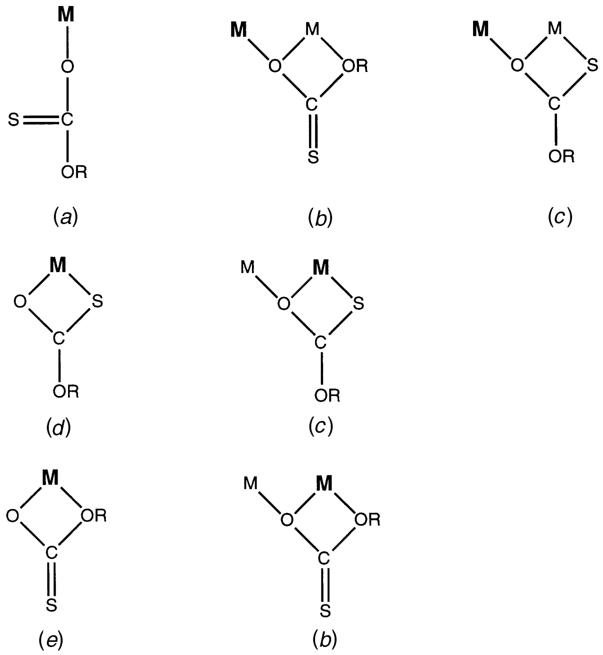
$[Sr_3(OCSOEt)_6(EtOH)_8]$ 2. The product of COS insertion into the Sr–OEt bond is a novel linear trinuclear molecule **2**, which is centred on a site of C_i symmetry in the crystal with a Sr(1)···Sr(2) distance of 3.959 Å. The molecular structure is shown in Fig. 3 while selected bond lengths and angles are given in Table 2. The structure is quite unlike those observed for either the magnesium or calcium analogues. Remarkably, the central strontium atom, located on the inversion centre, is bonded *only* to ethyl thiocarbonate ligands, all six being involved in an eight-co-ordinate geometry at strontium [Sr(1)–O range 2.521–2.764 Å]. The two outer strontium atoms are also eight-co-ordinated, each having four ethanol ligands [Sr(2)–O 2.533–2.566 Å]; the remaining four sites are occupied by donation from bridging thiocarbonate ligands *via* three oxygen atoms [Sr–O 2.577–2.785(5) Å] and one sulfur atom [Sr(2)–S(1b) 3.025(3) Å].

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

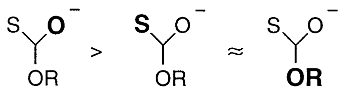
Sr(1)–O(1b)	2.521(5)	Sr(1)–O(1c)	2.570(6)
Sr(1)–O(1a)	2.604(5)	Sr(1)–O(3a)	2.764(6)
Sr(1)···O(3c)	3.157(5)	Sr(2)–O(1f)	2.533(6)
Sr(2)–O(1g)	2.549(7)	Sr(2)–O(1d)	2.557(5)
Sr(2)–O(1e)	2.566(6)	Sr(2)–O(1a)	2.577(6)
Sr(2)–O(1c′)	2.614(6)	Sr(2)–O(1b)	2.785(5)
Sr(2)–S(1b)	3.025(3)	S(1a)–C(2a)	1.710(10)
O(1a)–C(2a)	1.239(10)	C(2a)–O(3a)	1.361(9)
O(3a)–C(4a)	1.447(10)	S(1b)–C(2b)	1.708(8)
O(1b)–C(2b)	1.250(9)	C(2b)–O(3b)	1.335(10)
O(1c)–C(2c)	1.254(9)	C(2c)–O(3c)	1.352(9)
C(2c)–S(1c)	1.710(9)	O(3c)–C(4c)	1.451(9)
O(1a)–Sr(1)–O(1a′)	180.0	O(1b)–Sr(1)–Sr(1b′)	180.0
O(1c)–Sr(1)–O(1c′)	180.0	O(3a)–Sr(1)–O(3a′)	180.0
O(1b)–Sr(1)–O(1c)	106.3(2)	O(1b)–Sr(1)–O(1c′)	73.7(2)
O(1b)–Sr(1)–O(1a′)	108.2(2)	O(1c)–Sr(1)–O(1a′)	65.3(2)
O(1b)–Sr(1)–O(1a)	71.8(2)	O(1c)–Sr(1)–O(1a)	114.7(2)
O(1b)–Sr(1)–O(3a)	107.5(2)	O(1c)–Sr(1)–O(3a)	75.6(2)
O(1a)–Sr(1)–O(3a)	47.3(2)	O(1b)–Sr(1)–O(3a′)	72.5(2)
O(1c)–Sr(1)–O(3a′)	104.4(2)	O(1a)–Sr(1)–O(3a′)	132.7(2)
O(1b)–Sr(1)–O(3c)	72.9(2)	O(1f)–Sr(2)–O(1g)	149.2(2)
O(1f)–Sr(2)–O(1d)	76.3(2)	O(1g)–Sr(2)–O(1g)	75.4(2)
O(1f)–Sr(2)–O(1e)	90.7(2)	O(1g)–Sr(2)–O(1e)	75.6(2)
O(1d)–Sr(2)–O(1e)	86.5(2)	O(1f)–Sr(2)–O(1a)	69.3(2)
O(1g)–Sr(2)–O(1a)	136.1(2)	O(1d)–Sr(2)–O(1a)	145.2(2)
O(1e)–Sr(2)–O(1a)	88.6(2)	O(1f)–Sr(2)–O(1c′)	131.5(2)
O(1g)–Sr(2)–O(1c′)	71.2(2)	O(1d)–Sr(2)–O(1c′)	144.2(2)
O(1e)–Sr(2)–O(1c′)	73.1(2)	O(1a)–Sr(2)–O(1c′)	65.0(2)
O(1f)–Sr(2)–O(1b)	108.1(2)	O(1g)–Sr(2)–O(1b)	99.4(2)
O(1d)–Sr(2)–O(1b)	130.5(2)	O(1e)–Sr(2)–O(1b)	141.0(2)
O(1a)–Sr(2)–O(1b)	68.1(2)	O(1c′)–Sr(2)–O(1b)	68.8(2)
O(1f)–Sr(2)–S(1b)	98.1(2)	O(1g)–Sr(2)–S(1b)	87.4(2)
O(1d)–Sr(2)–S(1b)	77.33(14)	O(1e)–Sr(2)–S(1b)	159.1(2)
O(1a)–Sr(2)–S(1b)	112.27(14)	O(1c′)–Sr(2)–S(1b)	113.25(14)
O(1b)–Sr(2)–S(1b)	53.16(12)	Sr(2)–O(1a)–Sr(1)	99.7(2)
Sr(1)–O(1b)–Sr(2)	96.4(2)	Sr(1)–O(1c)–Sr(2′)	99.6(2)

Symmetry transformation used to generate equivalent atoms: $-x + 1, -y, -z + 1$.

In the overall structure four of the thiocarbonate ligands are chelating, and one oxygen atom of each of the six thiocarbonate ligands is involved in forming bridges between the central and outer strontium atoms. The two symmetry-related outer metal atoms are each chelated *via* an oxygen and a sulfur atom of one ligand [Sr(2)–O(1b) 2.785(5), Sr(2)–S(1b) 3.025(3) Å]; the oxygen atom of both of these symmetry-related chelate rings also bridges to the central strontium atom [Sr(1)–O(1b) 2.521(5) Å]. These two bridging atoms adopt *trans* sites in what may be envisaged as a very distorted hexagonal-bipyramidal co-ordination geometry at the central atom Sr(1); the 'equatorial'



Scheme 1 Various co-ordination modes adopted by the OCS(OR)$^-$ ligand in complexes **1**–**3**. The metal atoms indicated in bold type emphasise alternative co-ordination modes for that particular metal ion



Scheme 2

co-ordination sites are occupied by oxygen atoms from two pairs of symmetry-related ethyl thiocarbonate ligands, one pair of which is chelating [Sr(1)–O(1a) 2.604(5), Sr(1)–O(3a) 2.764(6) Å], and one is monodentate [Sr(1)–O(1c) 2.570(6), Sr(1) · · · O(3c) 3.157(5) Å]. One oxygen atom from each of these four ethyl thiocarbonate groups also bridges to one of the two symmetry-related outer strontium atoms [Sr(2)–O(1a) 2.577(6), Sr(2)–O(1c′) 2.614(6) Å]. A number of oligomeric complexes of strontium with oxygen ligands have been reported,[8] including triangular trimers but to the best of our knowledge **2** is the first example of a linear trinuclear complex.

The OCS(OEt)$^-$ ligand in complexes **1** and **2** exhibits in total five alternative co-ordination modes which can be divided into three different classes based on the arrangement around specific metal centres as shown in Scheme 1. In the magnesium complex **1** the OCS(OEt)$^-$ ligand is monodentate with only the terminal oxygen directly bonded to Mg [Scheme 1(*a*)]; in the strontium compound **2** it exhibits three different co-ordination modes. First, it acts as a bidentate ligand with both the terminal oxygen and sulfur atoms co-ordinated to the central strontium [Scheme 1(*d*)]. Secondly, there is an alternative bidentate mode, chelating *via* two oxygen donors [(*e*)]. Finally, it adopts a monodentate co-ordination as in the magnesium complex **1**, but in this case the terminal oxygen is also involved in bridging two strontium atoms [(*b*) and (*c*)]. The two bidentate modes adopted by the OCS(OEt)$^-$ ligand in the strontium complex **2** are analogous to those adopted by the OCS(OMe)$^-$ ligand in the calcium complex **3**.

The terminal oxygen of the OCS(OR)$^-$ group is the most nucleophilic. The different co-ordination modes observed in these complexes (Scheme 1) suggest that the nucleophilic character decreases in the order shown in Scheme 2. A metal ion such as Mg^{2+} which is a hard or class ‘a’ metal ion has a preference to co-ordinate exclusively through the terminal oxygen, *i.e.* in a monodentate fashion [Scheme 1(*a*)]; it usually adopts a six-co-ordinate geometry with small oxygen ligands. Moving down the group to the heavier alkaline-earth metals Ca^{2+} and Sr^{2+}, the increase in ionic radii and basicity results in the preference for higher co-ordination numbers and the introduction of the S and OR groups into the co-ordination sphere in order to make up the co-ordination number. The O · · · HO hydrogen bonding between the two halves of the molecule in **3**, which appears to assist oligomerisation, is absent in **2** where there is an increased number of bridging thiocarbonato groups. Comparison of the alkyl thiocarbonato-complexes **1**, **3** and **2** of Mg, Ca and Sr demonstrates clearly how the increasing size of the metal ion leads to more oligomerisation and increased utilisation of the S and OR donor groups. Magnesium is able to achieve co-ordinative saturation by utilising only the terminal oxygen of the ligand and the ethanol donor groups. Each of the calcium ions in the dimeric methyl thiocarbonato-complex is eight-co-ordinate with two ligands bridging the two metals. The tri-nuclear strontium complex also exhibits an eight-co-ordinate geometry at the metals with all ethyl thiocarbonate ligands adopting bridging modes.

This research has demonstrated that the insertion of COS into Group 2 metal–alkoxide bonds leads to a range of crystalline derivatives which are reasonably air stable and soluble in organic solvents. The crystallographic structural determinations of complexes **1**–**3** have revealed interesting alternatives. The OCS(OR)$^-$ ligand appears to be a flexible ligand which can use its alternative donor sites and bridging modes to co-ordinate to a wide range of metals and thereby form a series of crystalline derivatives with low molecular weights. The thermogravimetric results indicate that the insertion of the COS molecule may be reversed at higher temperatures. The reaction of COS with the Group 2 alkoxides has shown a sequence going down the Group. The weakly bound sulfur atoms of the terminal alkyl thiocarbonate ligands suggest that complexes **2** and **3** may react further with class ‘b’ metal ions to form mixed-metal complexes.

Experimental

General procedures

All manipulations were carried out under an atmosphere of dry nitrogen using standard glove-box (Miller-Howe FF160) and Schlenk techniques. All solvents were rigorously dried and deoxygenated by standard procedures. The samples for NMR and infrared studies were handled in a glove-box, but those for microanalysis and thermogravimetric analysis were not. This has lead to some differences concerning the extent to which ethanol molecules of crystallisation were detected by the spectroscopic and analytical techniques.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer using Nujol mulls between 25 × 4 mm CsI plates. The Nujol was dried with 4 Å molecular sieves prior to use (and stored in a glove-box); the samples were protected from the atmosphere by an O-ring-sealed Presslok holder (Aldrich Chemicals). The NMR spectra were recorded on a JEOL GS 270 MHz spectrometer, ^{1}H referenced internally to the residual ^{1}H impurity present in the deuteriated solvent. Chemical shifts are recorded in parts per million (δ) relative to SiMe$_4$ ($\delta = 0$) using $(CD_3)_2SO$ ($\delta = 2.52$). The ^{13}C NMR spectra are referenced to $(CD_3)_2SO$ ($\delta = 40.6$). Controlled thermal analyses of the complexes were investigated using a Polymer Laboratories 1500H simultaneous thermal analyser, controlled by an Omni-Pro 486DX-33 personal computer. The mass of the samples investigated was between 10 and 25 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 cm^3 min^{-1}) nitrogen gas, using heating rates of 5 °C min^{-1}.

Table 3 Crystal data and structure refinement details for compounds **1** and **2**

	1	**2**
Formula	$C_{14}H_{34}MgO_8S_2$	$C_{34}H_{78}O_{20}S_6Sr_3$
M_r	418.84	1262.18
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	7.408(1)	11.290(3)
b/Å	16.253(1)	11.761(2)
c/Å	9.864(1)	13.138(4)
α/°		73.78(2)
β/°	104.96(1)	87.78(30)
γ/°		62.30(2)
U/Å^3	1147.4(1)	1474.6(6)
Z	2	1
D_c/Mg m^{-3}	1.212	1.421
F(000)	452	652
Crystal size/mm	0.40 × 0.16 × 0.14	0.32 × 0.40 × 0.50
λ/Å	1.541 78	0.710 73
μ(Mo–Kα) or μ(Cu–Kα)/mm^{-1}	2.660	2.976
θ Range/°	5.4–55.0	1.6–25.0
hkl Ranges	−7 to 7, −17 to 17, −10 to 10	−1 to 12, −12 to 13, −15 to 15
Reflections collected	3132	5839
Unique reflections	1404	5004
Minimum and maximum transmission	0.430, 0.676	0.512, 0.584
Data, restraints, parameters	1404, 25, 128	5003, 139, 322
Goodness of fit on F^2, S	1.031	1.003
Final $R1$, $wR2$		
$I > 2\sigma(I)$	0.0645, 0.1719	0.0677, 0.1124
All data	0.0714, 0.1801	0.1637, 0.1491
Weighting, w^{-1}	$[\sigma^2(F_o)^2 + (0.193P)^2 + 0.73P]$	$[\sigma^2(F_o)^2 + (0.0414P)^2 + 2.16P]$
Largest peak and hole/e Å^{-3}	0.388, −0.537	0.604, −0.626

$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$, $wR2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma [w(F_o^2)^2]^{\frac{1}{2}}$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$ where n = number of reflections and p = total number of parameters.

Starting materials

Strontium granules and dibutylmagnesium were obtained from Aldrich Chemicals Co. and were used as received.

Preparations

Tetra(ethanol)bis(ethyl thiocarbonato)magnesium, [Mg(OCSOEt)$_2$(EtOH)$_4$] 1. Dibutylmagnesium in heptane (20 cm^3, 20 mmol) was added to ethanol (30 cm^3) at −40 °C resulting in an exothermic reaction. The reaction mixture was slowly warmed to room temperature, the solvent reduced in volume until all the heptane was removed and precipitation of the white solid [{Mg(OEt)$_2$(EtOH)$_4$}$_n$] was observed. Addition of ethanol (30 cm^3) resulted in the formation of a suspension of the magnesium ethoxide. Carbonyl sulfide gas was bubbled through the suspension at room temperature. This resulted in a vigorous exothermic reaction and dissolution of the ethoxide to yield a yellow solution, which was stirred for 1 h. A crystalline solid was isolated after cooling the solution to −20 °C (yield 6.21 g, 74.3%) (Found: C, 31.2; H, 5.8. Calc. for $C_6H_{10}MgO_4S_2$: C, 30.8; H, 4.3%). The analysis is based on the unsolvated molecular formula. IR (cm^{-1}) (Nujol): 3076m, 1554s, 1462s, 1376m, 1262s, 1174s, 1091s, 1050s, 884s, 803s, 724m, 690m, 525w, 462m, 396s and 336m. NMR [(CD$_3$)$_2$SO, 20 °C]: ^{1}H (270 MHz), δ 4.41 (t, CH$_3$CH$_2$O*H*, 4 H), 3.74 (q, OCSOC*H*$_2$CH$_3$, 4 H), 3.41 (m, CH$_3$C*H*$_2$OH, 8 H) and 1.04 (t, CH$_3$, OCSOR/ROH, 18 H); ^{13}C (67.94 MHz), δ 183.42 (s, O*C*SOR), 59.53 (s, OCSO*C*H$_2$CH$_3$), 56.66 (s, CH$_3$*C*H$_2$OH), 19.19 (s, *C*H$_3$CH$_2$OH) and 15.62 (s, OCSOCH$_2$*C*H$_3$). Mass spectrum (positive-ion FAB): *m/z* 235, [Mg(OCSOEt)$_2$]$^+$; 282, [Mg(OCSOEt)$_2$(EtOH)]$^+$.

Octakis(ethanol)hexakis(ethyl thiocarbonato)tristrontium, [Sr$_3$(OCSOEt)$_6$(EtOH)$_8$] 2. Strontium metal (1.2 g, 13.7 mmol) was suspended in ethanol (50 cm^3) and the mixture refluxed for 2 h resulting in dissolution of the metal and evolution of hydrogen gas, yielding a clear solution. Carbonyl sulfide gas was bubbled through the solution at room temperature resulting in an exothermic reaction to give a yellow solution, which was stirred for 1 h. A crystalline solid was isolated by cooling the solution to −20 °C (yield 3.87 g, 67%) (Found: C, 21.6; H, 3.2. Calc. for $C_{18}H_{38}O_{16}S_6Sr_3$: C, 22.4; H, 3.9%) [analysis based on Sr$_3$(OCSOEt)$_6$·4H$_2$O]. IR (cm^{-1}) (Nujol): 3195w, 1620m, 1568s, 1466s, 1377s, 1302w, 1261w, 1176s, 1152w, 1085s, 1051s, 930w, 890m, 801m, 721w, 693m, 681m, 557w and 529m. NMR [(CD$_3$)$_2$SO, 20 °C]: ^{1}H (270 MHz), δ 4.39 (t, CH$_3$CH$_2$O*H*, 8 H), 3.80 (q, OCSOC*H*$_2$CH$_3$, 12 H), 3.42 (m, CH$_3$C*H*$_2$OH, 16 H) and 1.04 (t, CH$_3$, OCSOR/ROH, 42 H); ^{13}C (67.94 MHz), δ 184.76 (s, O*C*SOR), 60.13 (s, OCSO*C*H$_2$CH$_3$), 56.67 (s, CH$_3$-*C*H$_2$OH), 19.19 (s, *C*H$_3$CH$_2$OH) and 15.15 (s, OCSOCH$_2$*C*H$_3$). Mass spectrum (positive-ion FAB): *m/z* 193, [Sr(OCSOEt)]$^+$; 299, [Sr(OCSOEt)$_2$]$^+$; 346, [Sr(OCSOEt)$_2$(EtOH)]$^+$ and 596, [Sr$_2$(OCSOEt)$_4$]$^+$.

X-Ray crystallography

Data were collected using a Siemens P4 diffractometer equipped with a Siemens LT2 low-temperature device with graphite-monochromated radiation using ω–2θ scans at 173 K. No significant decay in the intensity of three standard reflections measured after every 100 was observed. The data were corrected for Lorentz-polarisation factors and for absorption (ψ scans). The crystal data, data collection and refinement details are summarised in Table 3.

Both structures were solved by direct methods and in each case all non-hydrogen atoms were located from subsequent Fourier-difference syntheses. All non-hydrogen atoms were assigned anisotropic thermal parameters and refined using full-matrix least squares on F_o^2.[9] The hydrogen atoms for each of the compounds were included at calculated positions with C−H bond distances of 0.99 and 0.98 Å for the methylene and methyl groups respectively. The hydroxylic hydrogens in **1** were located in a Fourier-difference synthesis but those in **2** were not located. During refinement all the hydrogens were allowed to ride on their parent atom and assigned isotropic thermal parameters equal to $1.2U_{eq}$ of the parent atom for the methylene groups and $1.5U_{eq}$ for the methyl and hydroxyl groups. In complex **1** the methyl group of one ethanol C(3c)/C(4c) was disordered (60/40) over two sites. In **2** two of the ethanol groups were disordered; in one case the methylene carbon was disordered (50/50) over two sites C(2e)/C(2e′) and for the second ethanol two distinct conformations (50/50) were resolved C(2g), C(3g) and C(4g), C(5g).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/318.

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