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COMMUNICATION

CARBONYL SULFIDE INSERTION REACTIONS INTO METAL–ALKOXIDE BONDS. SYNTHESIS AND MOLECULAR STRUCTURE OF DI[BIS(METHYLTHIOCARBONATO)TRIS (METHANOL)CALCIUM]

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Abstract—The reaction of COS gas with a suspension of $[M(OMe)_2]_n$ (M = Mg and Ca) in methanol yields the insertion compounds, $[M(\{OCS\}OMe)_2(MeOH)_x]_n$ (M = Mg, **1**, $x = 2$; M = Ca, **2**, $x = 3$) in high yield; the magnesium compound is polymeric, whilst X-ray crystallography reveals that the calcium complex **2** is a centrosymmetric dimer with eight coordinated calcium(II) ions and two distinct methylthiocarbonato (MTC) ligand coordination modes, the structural framework being stabilised by an extensive network of hydrogen bonding.

The reactions of COS with transition metals have received significant attention because it may model the reactions of CO_2,[1] and in particular the insertion reactions of COS into metal–hydrogen bonds have been widely studied.[2] In contrast, the COS insertion reaction into metal–oxygen bonds has been relatively neglected. The only structurally characterised COS metal–oxygen inserted compound is $[Et_4N][W(CO)_5SC(O)O\text{-}2,6\text{-}Ph_2\text{-}C_6H_3]$, where unidentate coordination *via* sulfur was observed.[3,4] Thus, to date no Group 2 metal complexes resulting from COS insertion have been synthesised and characterised. Furthermore, the ambidentate properties of the —COS— moiety may induce interesting structural features when coordinated to class "a" or hard metals such as magnesium and calcium. The mixed coordination involving hard and soft bases may also be of relevance in biological systems where magnesium and calcium ions are bound by oxygen and sulfur donor ligands.

In this communication we describe the reactions of $[Mg(OMe)_2]_n$ and $[Ca(OMe)_2]_n$ with COS; the former leads to insoluble polymers, whilst reaction

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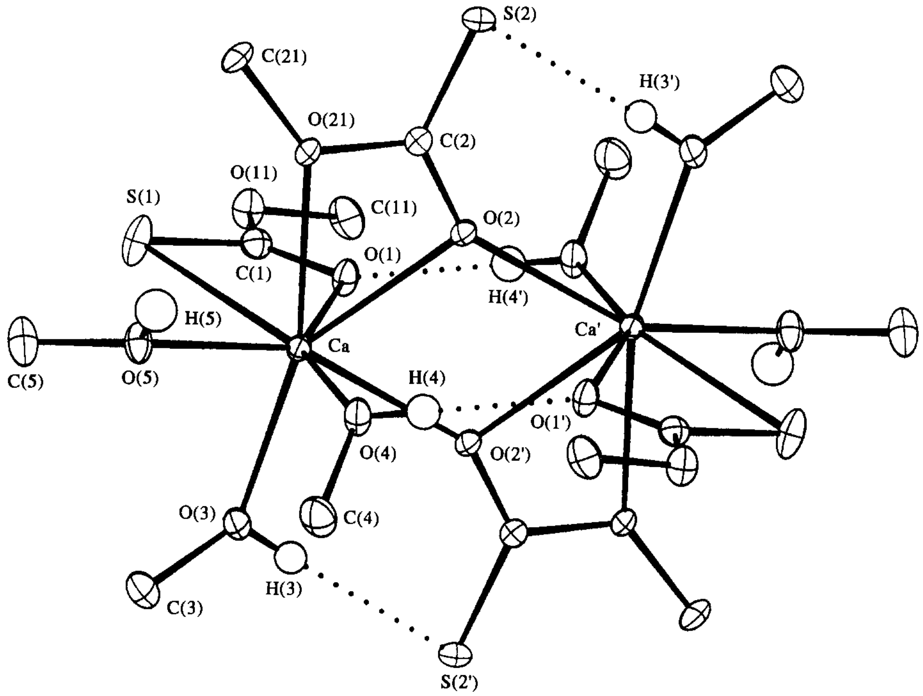

Fig. 1. Structure of the centrosymmetric dimer $[Ca(\{OCS\}OMe)_2(MeOH)_3]_2$ (**2**) showing the atom numbering scheme. Methyl hydrogens are omitted for clarity. Selected distances and angles: Ca—O(1), 2.461(2); Ca—O(2′), 2.420(2); Ca—O(3), 2.357(2); Ca—O(4), 2.395(2); Ca—O(5), 2.406(2); Ca—O(2), 2.521(2); Ca—O(21), 2.501(2); Ca—S(1), 2.961(2); Ca···Ca′, 4.082(2) Å; O(2)—Ca—O(2′), 68.61(7); Ca—O(2)—Ca′, 111.4(1)°. The primed atoms are generated by the symmetry $(-x, -y, -z)$.

with the latter results in discrete dimers which have good solubilities in organic solvents and have interesting structural features in the solid state.

When either $[Mg(OMe)_2]_n$ and $[Ca(OMe)_2]_n$ are suspended in methanol and COS is bubbled through the suspension at room temperature and atmospheric pressure an exothermic reaction occurs.* In the case of magnesium, a white precipitate formed which analysed correctly for $[Mg(\{OCS\}OMe)_2(MeOH)_2]_\infty$ (**1**); while for calcium, dissolution of the alkoxide was observed and the crystalline solid $[Ca(\{OCS\}OMe)_2(MeOH)_3]_2$ (**2**) formed on reducing the volume. The compounds are air sensitive and desolvate readily, but may be stored indefinitely under an inert atmosphere at room temperature without losing COS. Complex **1** is insoluble in alcohols but exhibits good solubilities in coordinating solvents, e.g. dmso. In contrast, complex **2** is soluble in alcohol, coordinating and polar organic solvents, but has poor solubilities in hydrocarbons. The insertion reactions of COS into the Group 2 metal–alkoxide bonds are irreversible, and the products are stable under reduced pressures and up to temperatures of 70°C.

An X-ray study of the complex **2** has confirmed the insertion of COS into both the metal–alkoxide bonds and the formation of a centrosymmetric dimer derived from $Ca(\{OCS\}OMe)_2(MeOH)_3$ with O,O- and O,S-chelating methylthiocarbonato ligands and bridges involving the two carbonyl oxygens from two O,O-methylthiocarbonato ligands

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*All reactions were carried out under dry nitrogen in dried and carefully deoxygenated solvents. **1**: to a suspension of the magnesium methoxide (10.00 mmol) in methanol (30 cm^3) was bubbled COS gas at room temperature and atmospheric pressure. This resulted in a vigorous exothermic reaction and precipitation of a white solid, insoluble in hot and cold alcohol, which was isolated by filtration. Yield 63%. **2**: to a suspension of the calcium methoxide (10.00 mmol) in methanol (30 cm^3) was bubbled COS gas at room temperature and atmospheric pressure. This resulted in a vigorous exothermic reaction and dissolution to yield a clear pale yellow solution. The resulting solution was stirred for a further 30 min, reduced *in vacuo* to *ca* 5 cm^3 and crystalline needles isolated at 0°C. Yield 54%.

(Fig. 1).† Each calcium is eight coordinated, bonded to the carbonyl oxygen and the sulfur atoms belonging to a chelating O,S-methylthiocarbonato ligand, two oxygen atoms belonging to a chelating and bridging O,O-methylthiocarbonato ligand, three oxygen atoms belonging to three terminally coordinated methanol molecules and one carbonyl oxygen chelating the second calcium and involved in the bridge formation. The metal coordination geometry may be described as square antiprismatic with the two tetragonal planes defined by S(1), O(1), O(21) and O(2), and O(2′), O(3), O(4) and O(5) respectively. The Ca—O—Ca′ bridges are asymmetric with Ca—O distances of 2.420(2) and 2.521(2) Å. Other Ca—O distances lie within 2.357(2)–2.501(2) Å. The Ca—S bond is quite long (2.961(2) Å) and underlines the unfavourable soft base–hard acid combination. An interesting feature of the structure is that the bridging chelating ligand uses both the hard ligating atoms but the terminal chelating ligand uses the hard and soft donor sites. In the former the methyl group is *cis* with respect to sulfur, whilst in the later it is *trans*.

It is also observed that all three methanol molecules are involved in hydrogen bonds which are fairly strong and impart extra stability to the molecular and crystal structures. Thus O(3) and O(4) and involved in O(3)—H(3)···S(2′) and O(4)—H(4)···O(1′) intradimer hydrogen bonds [O(3)···S(2′) = 3.112, H(3)···S(2) = 2.329, O(3)—H(3) = 0.792 Å, O(3)—H(3)—S(2′) = 170.3°; O(4)···O(1′) = 2.808, H(4)···O(1′) = 1.999, O(4)—H(4) = 0.811 Å, O(4)—H(4)—O(1′) = 174.9°], whilst O(5) forms an interdimer O(5)—H(5)···S(1) (at $1/2-x$, $-1/2+y$, $1/2-z$) hydrogen bond [O(5)···S(1) = 3.182, H(5)···S(1) = 2.319, O(5)—H(5) 0.886 Å, O(5)—H(5)—S(1) = 174.0°].

The IR spectra of complexes **1** and **2** indicate different methylthiocarbonato ligand coordination modes.‡ Complex **2** exhibits ν(CO) stretching mode at 1688 and 1607 cm^{-1}, implying two distinct coordination modes of the methylthiocarbonato ligands as confirmed by X-ray studies. In contrast, complex **1** displays a single ν(CO) absorption band at a lower frequency 1505 cm^{-1}, suggesting that the carbonyl oxygens are involved in bridge formation and have similar environments. The ν(C=S) stretching modes were observed at 1186 and 1193 cm^{-1} for **1** and **2** respectively. The crystal structure of **1** could not be determined due to the failures to grow suitable single crystals, but its greater insolubility is consistent with an extended polymeric structure. Multinuclear (^{1}H and ^{13}C-{^{1}H}) NMR spectroscopic studies in d_6-dmso clearly differentiated the methanol and methylthiocarbonato ligand environments in both compounds.

The COS insertion mechanism into Group 2 metal–alkoxide bonds is suggested to be similar to that of the related CO_2[3] and SO_2[6] insertion reactions.

The insertion of COS into Group 2 metal alkoxides and the reaction chemistry of the resulting alkylthiocarbonato complexes is an unexplored area and could be important for the incorporation of COS into organic compounds, in view of the related reactions of CO_2 and Group 2 alkoxides.[7] Also this research has demonstrated that COS provides a means of converting some insoluble alkoxides into soluble discrete molecular species which are well defined and may be structurally characterised. The weakly bound sulfur atom of the terminal methylthiocarbonato ligand suggests additional Lewis acid chemistry for this complex and the possibility of forming heterometallic hard–soft metal aggregates.

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† *Crystal data* for [Ca({OCS}OMe)$_2$(MeOH)$_3$]$_2$ (**2**): $C_{14}H_{36}Ca_2O_{14}S_4$, F.W. = 636.82. Monoclinic, $P2_1/n$, $a = 11.564(5)$, $b = 10.989(7)$, $c = 11.979(4)$ Å, $\beta = 94.31(5)°$, $V = 1517.9(13)$ Å^3, $F(000) = 672$, $Z = 2$, $D_c = 1.393$ g cm^{-3}, μ(Mo-$K\alpha$) = 6.82 cm^{-1}, T = 150(2)K. 6161 intensities were measured using a Fast TV area detector diffractometer (Mo-$K\alpha$, $\lambda = 0.71069$ Å), by following previously described procedures.[8] The data was corrected for Lorentz and polarisation effects and also for absorption.[9] The structure was solved by direct methods and refined on F_0^2 by full-matrix least squares using all 2303 unique data.[10] Final wR (on F_0^2) and R (on F) values were 0.0926 and 0.0452 respectively for 171 parameters and all 2303 data. The non-hydrogen atoms were all anisotropic. The methyl hydrogens were included in idealised positions with U_{iso} set at 1.5 times the U_{eq} of the parents. The OH hydrogens were located from difference map and refined isotropically. Full details of data collection and structure refinement, atomic coordinates, thermal parameters and tables of distances and angles have been deposited as supplementary material.

‡ Satisfactory analyses were obtained for **1** and **2**.

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