Sulfur Dioxide Insertion Reactions into Metal–Alkoxide Bonds: Synthesis and Crystal Structure of *catena*-Bis(methylsulfito)bis(methanol)calcium; a One-dimensional Polymer based on Eight-coordinate Calcium Ions

V-Cumaran Arunasalam,[a] Ian Baxter,[b] Michael B. Hursthouse,*[b] K. M. Abdul Malik,[b] D. Michael P. Mingos*[a] and John C. Plakatouras[a]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*

[b] *Department of Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff, Wales, UK CF1 3TB*

The reaction of SO_2(g) with a suspension of $[M(OMe)_2]_n$ (M = Mg and Ca) in methanol yields the crystalline compounds, $[M(O_2SOMe)_2(MeOH)_2]_\infty$ (M = Mg **1**, Ca **2**); the insertion reaction is of high yield and the X-ray crystal structure of complex **2** reveals that it is a chain polymer with eight-coordinated Ca^{II} ions and the methylsulfito anions acting as both chelating and bridging ligands.

Interest in the alkoxide chemistry of the alkaline earth metals has been rekindled by the possibility that they might find applications as precursors for metal oxide thin films *via* MOCVD and sol–gel techniques. However, unless multifunctional alcohols[1] and sterically crowded alkyl or aryl groups[2] are employed these compounds are generally polymeric insoluble solids, which are poorly characterised from a structural point of view. The reactions of these compounds with small molecules such as CO_2 and SO_2 have been relatively neglected although organomagnesium compounds are known to react with SO_2 to give sulfinic acids after hydrolysis,[3] while calcium oxide is used to scrub flue gases and for the desulfurisation of iron ores. In contrast, the corresponding reactions of the class 'b' or soft metal alkoxides of palladium, platinum and rhodium with SO_2 have been investigated in more detail.[4–6] Structural studies of these complexes reveal, as expected, *S*-coordinated SO_2 moieties.

In this communication we describe the reactions of $[Mg(OMe)_2]_n$ and $[Ca(OMe)_2]_n$ with SO_2, which lead to one-dimensional polymers, with good solubility in organic solvents and which have interesting structural features in the solid state.

When either $[Mg(OMe)_2]_n$ and $[Ca(OMe)_2]_n$ are suspended in methanol and SO_2 is bubbled through the suspension at room temp. and atmospheric pressure, an exothermic reaction occurs and the alkoxides dissolve.† The reaction is complete in 30 min. When the solution is cooled to −20 °C, the compounds $[M(O_2SOMe)_2(MeOH)_2]_\infty$ (M = Mg **1**, Ca **2**) crystallise as colourless needles in good yields.‡ The compounds are air stable,but desolvate readily and may be stored indefinitely under an inert atmosphere at room temp. without losing SO_2. The complexes are soluble in alcohols and polar organic solvents, but have poor solubilities in hydrocarbons.

The crystal structure of complex **2** is polymeric (part of which is shown in Fig. 1) and consists of infinite zig-zag chains of $[Ca(O_2SOMe)(MeOH)_2]_\infty$ parallel to the *a* axis and held together by van der Waals forces.§ To our surprise there is neither inter- nor intra-chain hydrogen bonds, which accounts for the high solubilities of these compounds.

The calcium atoms are eight-coordinated and have a distorted square-antiprismatic environment. Each methylsulfito-ligand is acting as a both chelating and bridging ligand whilst the methanol molecules are unidentate. The calcium coordination sphere comprises four oxygen atoms belonging to two chelating methylsulfito-ligands, two oxygen atoms of two bridging methylsulfito-ligands which are chelated to adjacent calcium atoms, and two oxygen atoms from coordinated methanols. The eight-coordination of calcium observed in **2** has been found in a number of other complexes with oxygen donor ligands.[7] The Ca–O bond lengths to the methylsulfito-ligands [2.374(3)–2.553(3) Å] are in the range observed for other ligands, *i.e.* β-diketonates,[8] alkoxides,[9] and carboxylates.[10]

It is interesting to note that the $Ca–O_{chelate}$ bonds are asymmetric and lie in the range 2.478(3)–2.553(3) Å, whilst the two nearly equal $Ca–O_{bridge}$ bonds [2.374(3)–2.387(3) Å] are much shorter than the $Ca–O_{chelate}$ bonds. This situation, in which the bridge bonds are smaller than the chelate bonds, may be explained by assuming that the negative charge of the methylsulfito group is localised at the bridging Ca–O bond while the double S=O bond is delocalised around the chelating site of the group. The small difference between the two $Ca–O_{chelate}$ bonds (mean difference: 0.06 Å) as well as the almost negligible difference between the two related S–O bonds (mean difference: 0.016 Å) are supportive of this opinion.

The dimensions of the O_2SOMe group are quite different from the values found in the literature for a variety of sulfito complexes, as shown in Table 1. In the soft metal complexes, the ligands are coordinated through sulfur whilst in the iridium complex the ligand is unidentate through O and the double S=O bond is localised.[11] The S–OMe bond is longer than the other S–O bonds, as noted in the other structures.

The uniqueness of structure of **2** rises from the fact that it is the first example to our knowledge of coordinated alkylsulfito-ligand to a Group 2 metal, as well as its unusual coordination mode.

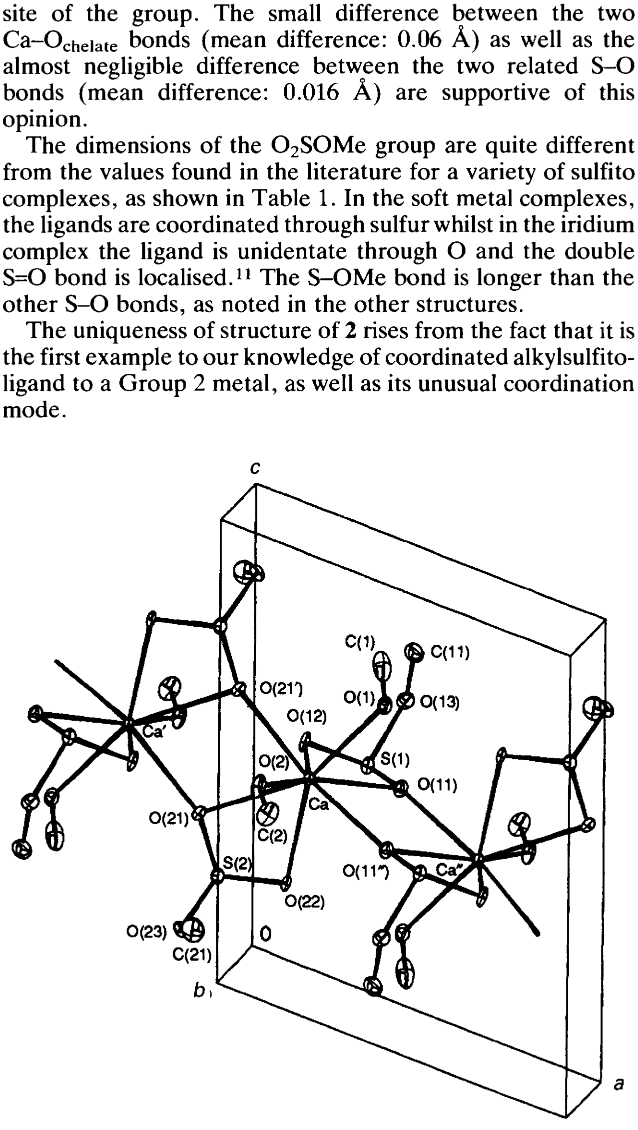

Fig. 1 Part of the polymeric structure of $[Ca(O_2SOMe)_2(MeOH)_2]_\infty$ **2** showing the atom numbering scheme. Relevant bond distances: Ca–O(21′) 2.374(3), Ca–O(11″) 2.387(3), Ca–O(22) 2.478(3), Ca–O(21) 2.535(3), Ca–O(1) 2.384(3), Ca–O(2) 2.410(4), Ca–O(12) 2.494(4), Ca–O(11) 2.553(3), Ca–Ca′ 4.004(3), Ca–Ca″ 4.021(3) Å. Symmetry transformations used to generate equivalent atoms: (′) $-x$, $2-y$, $1-z$; (″) $1-x$, $2-y$, $1-z$.

Table 1 Comparison of bond lengths (in Å) of sulfito complexes

Complex	S–O	S–OR
$[Ca(O_2SOMe)_2(MeOH)_2]_\infty$	1.499	1.624[a]
trans-$[Pt(SO_3Me)_2(PPh_3)_2]$	1.448	1.620[b]
$[Ni(tripod)(SO_3Et)][BF_4]$	1.443	1.559[c]
$[Ir(CO)(PPh_3)_2\{OS(O)OMe\}(SO_2)]$	1.456, 1.531	1.650[d]

[a] This work. [b] Ref. 5. [c] Ref. 6. [d] Ref. 11.

Compounds **1** and **2** exhibit IR bands attributable to the methylsulfito ligands, ν_{SO_2}/cm^{-1} **1** 1148, 987 and 680 cm^{-1}; and **2** 1141, 1065, 671 and 646. Multinuclear (^1H and ^{13}C-$\{^1H\}$) NMR studies in $(CD_3)_2SO$ of compounds **1** and **2** revealed broad resonances associated with the methanol and methylsulfito-ligands. In contrast, CPMAS ^{13}C–$\{^1H\}$ NMR of complexes **1** and **2** revealed more structural informaton, with compound **1** exhibiting six distinct methyl resonances, and complex **2**, two distinct signals due to coordinated methanol and methylsulfito-ligands.‡ The IR and NMR studies, suggest that the methylsulfito-coordination modes in **1** and **2** differ. Attempts are being made to grow single crystals of complex **1**.

Thermal gravimetric analysis (TGA) has confirmed the thermal stability of the coordinated methylsulfito-ligand. The TGA curve of **2** revealed the loss of the coordinated methanol molecules by *ca.* 70 °C, the decomposition of $[Ca(O_2SOMe)_2]_\infty$ into $CaSO_3$ between 100–200 °C and its subsequent decomposition to CaO above 900 °C, with the liberation of SO_2 gas. The corresponding differential scanning calorimetry plot shows endotherms in accord with the observed weight losses, but an exotherm was observed at *ca.* 375 °C (44.73 J g^{-1}), indicative of phase transformation of the decomposition product.

The mechanism for insertion of the SO_2 molecule into metal–alkoxide bonds may proceed either by a direct insertion or *via* an alcohol catalysed route [eqns. (1) and (2)]. In the latter case, the equilibrium leading to the alkylsulfito-ion is promoted in presence of a base such as an alkoxide [eqn. (1)]. Subsequently, the metal–alkoxide bond is cleaved and substituted by the chelating $-O_2SOR$ ligand.

$$SO_2 + ROH \overset{B^-}{\rightleftharpoons} {}^-O_2SOR + BH \qquad (1)$$

$$MOR + {}^-O_2SOR \xrightarrow{H^+} MO_2SOR + ROH \qquad (2)$$

Thus, the insertion reaction could be better described as a nucleophilic substitution reaction on the metal–alkoxide bond. A similar reaction mechanism has been postulated for the CO_2 insertion reaction into metal–oxygen and metal–nitrogen bonds.[12]

The binding of SO_2 and its reaction chemistry in calcium complexes could be important for improving the technology of sulfur dioxide removal. The utilisation of SO_2 metal compounds in synthetic organic reactions could also be important, since research described above has shown that SO_2 provides a means of converting insoluble alkoxides into soluble polymers which are well defined and structurally characterised.

We acknowledge Exxon Chemical Ltd. for a studentship to V. C. A., the SERC (M. B. H., K. M. A. M., J. C. P.), BP (D. M. P. M.) and the Royal Society (inert atmosphere glovebox).

Received, 12th September 1994; Com. 4/05544F

Footnotes

† All reactions were carried out under a dry nitrogen atmosphere in dried and carefully deoxygenated solvents. **1** and **2**: To a suspension of the metal methoxide (10.00 mmol) in methanol (30 ml) was bubbled SO_2 gas at room temp. and atmospheric pressure. This resulted in a vigorous exothermic reaction and dissolution of the methoxide to yield a clear solution. The resulting solution was stirred for a further 30 min and crystalline needles isolated at −20 °C. Yield, **1**, 67; **2**, 47%.

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

§ *Crystal data* for $[Ca(O_2SOMe)_2(MeOH)_2]_\infty$ **2**: $C_4H_{14}CaO_8S_2$, M_w = 294.35, triclinic, space group $P\bar{1}$, a = 7.870(5), b = 8.724(6), c = 9.934(5) Å, α = 108.44(3), β = 109.00(3), γ = 92.15(2)°, V = 599.8(6) Å^3, $F(000)$ = 308e, Z = 2, D_c = 1.630 g cm^{-3}, T = 150 K. 1571 Intensities were measured using a Fast TV area detector diffractometer (Mo-Kα, λ = 0.71069 Å), by following previously described procedures.[13] The data was corrected for Lorentz polarisation effects and also for absorbtion.[14] The structure was solved by direct methods and refined on F_o^2 by full-matrix least-squares analysis using all unique data.[15] The final wR (on F_o^2) and R (on F) values were 0.113 and 0.048, respectively for 149 parameters and all 1473 data.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 W. A. Herrmann, N. W. Huber and T. Priermeier, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 105; S. C. Goel, M. A. Matchett, M. Y. Chiang and W. E. Buhro, *J. Am. Chem. Soc.*, 1991, **113**, 1844.

2 P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Roya, *J. Chem. Soc., Chem. Commun.*, 1990, 1141; S. R. Drake, D. J. Otway, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, 1992, 1995.

3 W. Kitching and C. W. Fong, *Organomet. Chem. Rev.*, 1970, **A5**, 281; D. Masilamani and M. M. Rogic, *J. Am. Chem. Soc.*, 1978, **100**, 4634.

4 R. Ros, G. Carturan and M. Graziani, *Transition Met. Chem.*, 1975, **1**, 13; M. Graziani, R. Ros and G. Carturan, *J. Organomet. Chem.*, 1971, **27**, C19; R. A. Michelin, M. Napoli and R. Ros, *J. Organomet. Chem.*, 1979, **175**, 239; L. M. Green and D. W. Meek, *Organometallics*, 1989, **8**, 659.

5 G. R. Hughes, P. C. Minshall and D. M. P. Mingos, *Transition Met. Chem.*, 1979, **4**, 147.

6 C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 2377.

7 S. R. Drake, S. A. Miller and D. J. Williams, *Inorg. Chem.*, 1993, **32**, 3227; J. C. Barnes and J. D. Paton, *Acta Crystallogr. Sect. C*, 1984, **40**, 1809.

8 V. C. Arunasalam, I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik and D. J. Otway, *Inorg. Chem.*, 1994, submitted; V. C. Arunasalam, I. Baxter, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, manuscript in preparation.

9 N. Y. Turova, E. P. Turevskaya, V. G. Kessler, A. I. Yanovsky and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1993, 21.

10 O. Kumberger, J. Riede and H. Schmidbaur, *Chem. Ber.*, 1992, **124**, 2739.

11 S. L. Randall, C. A. Miller, T. S. Janik, M. R. Churchill and J. D. Atwood, *Organometallics*, 1994, **13**, 141.

12 D. A. Palmer and R. V. Eldik, *Chem. Rev.*, 1983, **83**, 651; M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, *J. Am. Chem. Soc.*, 1978, **100**, 1727; M. Kato and T. Ito, *Inorg. Chem.*, 1985, **24**, 504.

13 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

14 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1983, **39**, 158, adapted for FAST geometry by A. Karaulov, University of Wales College of Cardiff, 1990.

15 G. M. Sheldrick, SHELX-93, Program for Crystal Structure refinement, University of Göttingen, Germany, 1993.