# The Synthesis and X-Ray Structure Characterisation of the Volatile Complexes [Sr(thd)2{Me(OCH2CH2)3OMe}] and [Sr2(thd)4{Me(OCH2CH2)2OMe}2(μ-H2O)] (Hthd = 1,1,1,6,6,6-Hexamethylheptane-2,4-dione)

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The reaction of [Sr3(thd)6(Hthd)] with one equivalent of triglyme [Me(OCH2CH2)3OMe] has yielded the monomeric species, [Sr(thd)2(triglyme)] 1; while with a 2 : 1 mixture of diglyme [Me(OCH2CH2)2OMe] and H2O the dimeric complex, [Sr2(thd)4(diglyme)2(μ-H2O)] 2 is obtained; the related [Sr(tfa)2]∞ reacts with one equivalent of hexamethyltriethylenetetramine to yield [Sr(tfa)2(hmteta)] 3; complexes 1 and 2 are the first structurally characterised discrete molecular strontium β-diketonates [hmteta = Me2NCH2CH2CH2N(Me)CH2CH2N(Me)CH2CH2NMe2].

Group 2 molecular precursors suitable for chemical vapour deposition (CVD) have previously concentrated on alkoxides,[1] aryloxides,[2] siloxides[3] and most especially β-diketonates.[4,5] The challenge in this area of main-group chemistry is to achieve coordinative saturation of the metal centres through the agency of sterically demanding organic ligands with either separate or attached Lewis bases, to reduce polymerisation processes. Indeed, given the high coordination numbers observed for these metals this offers a great degree of flexibility in terms of the complexes that may be formed.[1-6] Previously crown ethers,[7] e.g. [Ba(hfa)2(18-crown-6)] (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione), torands and cryptands have been used. We have addressed this problem by incorporating the requisite components of glyme-stabilised group 2 metal pseudo-halides, e.g. [Sr(SCN)2(triglyme)][8] and the oligomeric [Sr(OR)2]∞ complexes,[1,2,4] into discrete molecular species.

In these synthetic studies we have used the crystalline hydrocarbon-soluble metal ethoxides, [M(OEt)2(HOEt)4]n (M = Ca, Sr or Ba), as soluble sources of the metals.[9] Previously we have reported the facile reaction of these group 2 metal ethoxides and a range of β-diketonates at 25 °C,[10] to yield the group 2 metal β-diketonates, analogous to prior studies with transition metal alkoxides.[11] They have been used for CVD,[4] e.g. [Ba(thd)2]∞ (Hthd = 1,1,1,6,6,6-hexamethylheptane-2,4-dione),[5] but have drawbacks such as poor thermal stability and low volatility and are air and moisture sensitive.

We now report that treatment of the recently prepared oligomeric anhydrous complex [Sr(thd)2]∞ with triglyme in hexane at ambient temperature, leads to the isolation of the monomeric product, [Sr(thd)2(triglyme)] 1 in 79% yield according to eqn. (1).†

$$[\text{Sr(thd)}_2]_\infty + \text{triglyme} \xrightarrow[\text{room temp.}]{\text{hexane,}} [\text{Sr(thd)}_2(\text{triglyme})] \quad (1)$$
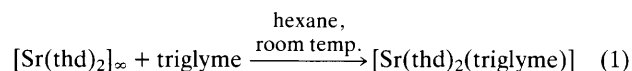
The structure of the complex was determined by X-ray crystallography on a single crystal grown from hexane, and a view of this is shown in Fig. 1.‡ The complex consists of an anhydrous mononuclear strontium β-diketonate, the first such strontium complex structurally characterised, and is further stabilised by a triglyme chelating ligand.

The strontium atom is coordinated by all eight oxygen atoms, with the triglyme ligand partially encapsulating the metal ion in the equatorial belt, and above and below this plane sit the β-diketonate ligands. The β-diketonate ligands asymmetrically chelate the metal centre with Sr–O(1), Sr–O(2) and Sr–O(3), Sr–O(4) distances of 2.502(1), 2.468(09) and 2.519(1), 2.489(09) Å, respectively. These distances are appreciably longer than the Sr–O distances in the recently characterised strontium aryloxide [Sr(OC6H2-But3)]·0.5thf (thf = tetrahydrofuran),[2] in which the Sr–O bond lengths were 2.32(1) Å (av.), but given the difference in overall coordination number (8 vs. 5) and a chelating β-diketonate vs. terminal aryloxide, the effective difference in Sr–O bond length between these two complexes is ca. 0.1 Å. A similar comparison may also be made with the only other structurally characterised strontium aryloxide, namely the tetrameric species [Sr4(OPh)8(PhOH)2(thf)6] which has a Sr–O bond distance of 2.450(7) Å.[2] The two thd SrO2 rings in 1 are almost planar with an angle of 87.1°.

The triglyme ligand chelates to the strontium metal centre, with Sr–O(5), Sr–O(6), Sr–O(7) and Sr–O(8) distances of 2.628(1), 2.715(1), 2.703(1) and 2.650(1) Å, respectively, with an average Sr–O(glyme) distance of 2.674(1) Å. One may note that the two glyme oxygens O(5) and O(8) bind closer to the strontium than O(6) and O(7), and this is primarily due to steric reasons and also that O(5) and O(8) are the on the ends of the glyme chain and are thus held less rigidly.
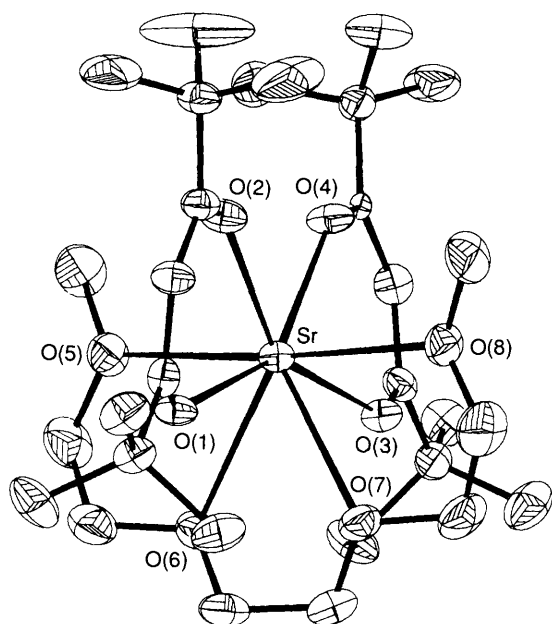
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**Fig. 1** Molecular structure of [Sr(thd)₂(triglyme)] **1** showing the atom numbering scheme. H-atoms have been omitted for clarity.

A space-filling model of **1** shows extensive shielding of the large dipositive cation $Sr^{2+}$ by the thd and triglyme ligands. The extensive solubility of **1** in most organic solvents (e.g. aliphatic, aromatic and coordination solvents) may be attributed to the encapsulation of the strontium cation by the surrounding ligands, so that an effective hydrocarbon sheath results.

The related complex [Sr₂(thd)₄(diglyme)₂(μ-H₂O)] **2** was prepared fortuitously via the addition of diglyme to a solution of [Sr(thd)₂]∞ in hexane at room temp. In an attempt to obtain X-ray crystals of [Sr(thd)₂(diglyme)], water was absorbed (either from solvent or air) and regular blocks of **2** were obtained in 68% yield. A deliberate synthesis was then attempted, by addition of a 2 : 1 mixture of diglyme and water to [Sr(thd)₂]∞ which also yielded **2** in excellent yield.

A view of the dinuclear unit of **2** is shown in Fig. 2. In the centrosymmetric complex, the coordination geometries of the strontium centres are both distorted. The complex **2** is directly related to the anhydrous complex **1** and consists of two strontium metal centres each coordinated by both thd and diglyme ligands, with the coordination environment of eight completed by the bridging water molecule.

The β-diketonate ligands bind asymmetrically to the metal centre with Sr–O(1), Sr–O(2) and Sr–O(3), Sr–O(4) distances of 2.520(1), 2.460(7) and 2.515(7), 2.459(6) Å, respectively. The angle between the two thd ligands is 93.45°. The diglyme ligand in **2** chelates to the strontium metal centre, with Sr–O(5), Sr–O(6) and Sr–O(7), distances of 2.686(7), 2.692(7) and 2.664(7) Å, respectively, with an average Sr–O(glyme) distance of 2.681(7) Å.

The water molecule O(8) sits symmetrically between the two [Sr(thd)₂(diglyme)] units with a Sr–O(8) distance of 2.967(7) Å and may be contrasted with the recent μ-H₂O observed in [Ba(hfa)₂(H₂O)]∞ which had a bond distance of 3.12(1) Å.¹² The water molecule in **2** presumably acts as a bridging ligand between two metal centres owing to the sterically congested situation at the strontium metal centre. In contrast, for [Ba(hfa)₂(H₂O)]∞ there is ample room for both bridging water molecules and Ba–F interactions in the one-dimensional chain. For these complexes the water molecule is engaging as a very effective bidentate ligand.

The small differences between the two chelate rings on the strontium metal centres are not observed in solution, as both the glyme and thd ligands are found to be time-averaged in
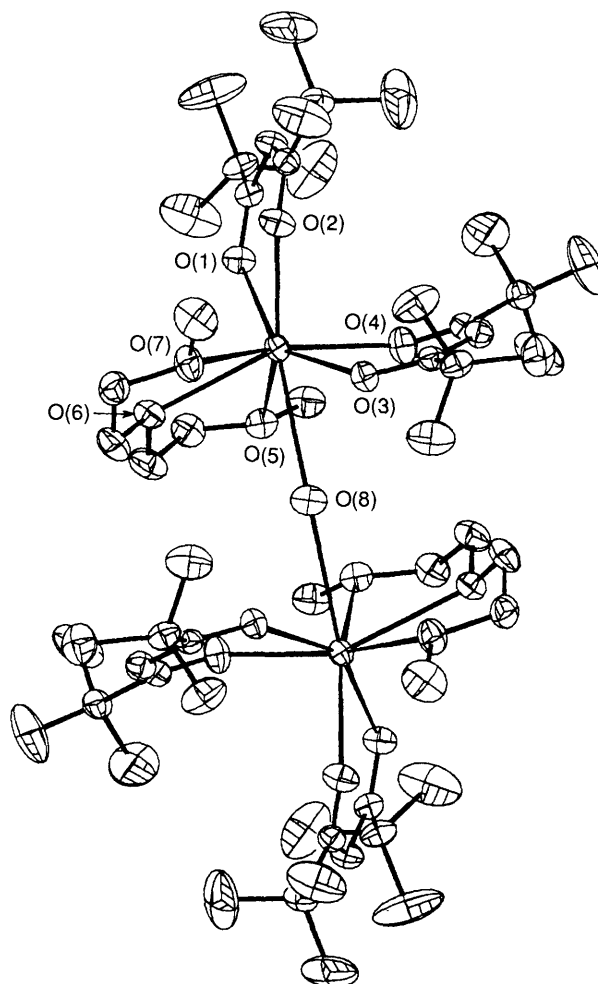


**Fig. 2** Molecular structure of [Sr₂(thd)₄(diglyme)₂(μ-H₂O)] **2** showing the atom numbering scheme. H-atoms have been omitted for clarity.

$C_6D_6$ on the NMR timescale. While IR shows clear evidence for the water molecule in **2** with a broad band observed at 3320 cm⁻¹.

To further illustrate the generality of this strategy to strontium β-diketonates, we have also studied the reactivity of [Sr(tfa)₂]∞,⁴,¹⁰ with a multidentate amine, hexamethyltri-ethylenetetramine (hmteta) in hexane at ambient temperature this yields [Sr(tfa)₂(hmteta)] **3**. Complex **3** has been characterised by IR and multinuclear NMR spectroscopy. Mass spectrometry has shown that **3** is also monomeric.

Complexes **1** and **2** are to the best of our knowledge the first examples of structurally authenticated strontium β-diketonates. Previous researchers, have used crown ethers to encapsulate alkaline earth metal hexafluoroacetylacetonate complexes,⁷ with glymes, [Ba(hfa)₂(tetraglyme)],⁶ or hydrated calcium [Ca(hfa)₂(H₂O)₂]₂ and barium [Ba(hfa)₂-(H₂O)]∞ complexes.¹² But to date, none of these complexes are water free, non-fluorinated and, most importantly, stable in the atmosphere, as is **1** or the fluorinated complex **3**.

On attempted sublimation all of these complexes decompose (> 150 °C and 10⁻³ Torr; 1 Torr = 133.3 Pa) to yield the parent β-diketonate [Sr(thd)₂]∞ for complexes **1** and **2** and [Sr(tfa)₂]∞ for **3**, and free Lewis base co-ligand. This thermal instability is presumably a result of the weak binding of these multidentate ligands to the strontium β-diketonates. Intermolecular interactions are undoubtedly present in the homoleptic complex [Sr(thd)₂]∞ (sublimes at 180 °C and 10⁻³ Torr) and the analogous hexafluoro- and trifluoro-acetyl-acetonates.

Mass spectroscopic data indicates that all of the complexes exist as monomeric species in the gas phase. In contrast with

this (and also recently observed for other group 2 hexafluoro-acetylacetonate complexes),[4] we have previously noted that $[Sr(thd)_2]_\infty$ is a trimeric species in its mass spectrum. The high stability of these complexes makes them ideal candidates for the deposition of thin films via CVD.

There are several features worthy of mention: (i) this synthetic strategy of using a preformed alkaline earth metal β-diketonate from a metal ethoxide is the first for strontium, and has been extended to Ca and Ba, and leads to water free complexes. (ii) The coordinative saturation of the hard acid metal centre by the multidentate Lewis base chelate and β-diketonate leads to air and moisture stable precursors of known stoichiometry, and is highly flexible since L–L may be varied with the use of either O or N functionalised chelates. (iii) The designed synthesis of volatile discrete molecular alkaline earth metal organics is now possible without having to use large sterically hindered ligands. Indeed, our strategy towards a tailored approach for CVD precursors, need not be limited to pure β-diketonates, any ligand of formula (A–R–BH),[13] where A is generally a pendant potential chelating site, R is the hydrocarbon chain linker (for β-diketonates this contains the acidic proton) and B is the predominate site of metallation, e.g. chelating alcohols containing ether or amine functionality, diolates, alkoxy substituted β-diketonates, mixed alkoxy β-diketonates or acetates [eqn. (2)].

$$[M(OEt)_2(EtOH)_4]_\infty + 2\ A{-}R{-}BH + L{-}L$$
$$\rightarrow [M(A{-}R{-}B)_2(L{-}L)] \quad (2)$$
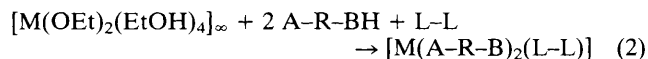
We consider an important requirement when designing alkaline earth molecular precursors is that sufficient coordinative saturation be incorporated into both ligand and Lewis base chelate, such that a low molecular mass monomer will result. A combined approach using this tailored synthetic rational to other transition and lanthanide metal molecular precursors is currently in progress.

## References

1 S. R. Drake, M. H. Chisholm, K. G. Caulton and K. Folting, J. Chem. Soc., Chem. Commun., 1990, 1349 and 1498 and references cited therein; H. Lutz, Z. Anorg. Allg. Chem., 1967, **353**, 207; 1968, **356**, 132; H. Staeglich and E. Weiss, Chem. Ber., 1978, **111**, 901; A. V. Novoselova, N. Ya Turova, E. P. Turevskaya, M. I. Yanovskaya, V. A. Kozunov and N. I. Koslova, Izv. Adv. Nauk SSSR, Neorg. Mater., 1979, **15**, 1055.

2 S. R. Drake, M. H. Chisholm, K. G. Caulton and K. Folting, Inorg. Chem., 1990, **29**, 2909 and references cited therein; S. R. Drake, D. J. Otway, M. B. Hursthouse and K. M. A. Malik, Polyhedron, 1992, **11**, 1959.

3 S. R. Drake, M. H. Chisholm, K. G. Caulton and W. E. Streib, Angew. Chem. Int. Ed. Engl., 1990, **29**, 1483; S. R. Drake, M. H. Chisholm, K. G. Caulton and K. Folting, Inorg. Chem., 1992, **31**, 3205.

4 A. P. Purdy, A. D. Berry, R. T. Holm, M. Fatemi and D. K. Gaskill, Inorg. Chem., 1989, **28**, 2799.

5 F. A. Kuznetsov, I. K. Igumenov and V. S. Danilovich, Physica C, 1991, **185**, 1957; G. Rossetto, P. F. Benetollo, M. Porchia and P. Zanella, Polyhedron, 1992, **11**, 979.

6 C. I. M. A. Spec and A. Makor, in Science and Technology of Thin Film Superconductors, ed. R. McConnell and S. A. Wolf, Plenum, New York, 1989, p. 281–284; P. van der Sluis, A. L. Spek, K. Timmer and D. A. Meinema, Acta Crystallogr., Sect. C, 1990, **46**, 1741.

7 J. A. T. Norman and G. P. Pez, J. Chem. Soc., Chem. Commun., 1991, 971; J. A. T. Norman and G. P. Pez, Volatile crown ligand beta-diketonate alkaline earth metal complexes, Eur. Pat. Appl. EP. 460627, 1990.

8 Y. Y. Wei, B. Tinant, J.-P. Declerq, M. van Meerssche and J. Dale, Acta Crystallogr., Sect. C, 1987, **43**, 1080.

9 V. C. Arunasalam, S. R. Drake, D. J. Otway, M. B. Hursthouse and K. M. A. Malik, Inorg. Chem., 1992, submitted for publication.

10 V. C. Arunasalam, S. R. Drake, M. B. Hursthouse, D. J. Otway and K. M. A. Malik, unpublished results.

11 See for example: D. C. Bradley, Chem. Rev., 1989, **89**, 1317 and leading references therein; K. G. Caulton and L. G. Hubert-Pfsalgraf, Chem. Rev., 1990, **90**, 969.

12 D. C. Bradley, M. Hasan, M. B. Hursthouse, M. Motevalli, O. F. Z. Khan, R. G. Pritchard and J. O. Williams, J. Chem. Soc., Chem. Commun., 1992, 575.

13 Note similar terminology previously used but in a very different context: F. A. Banbury, M. G. Davidson, A. Martin, P. R. Raithby, R. Snaith, K. L. Verhorevoort and D. S. Wright, J. Chem. Soc., Chem. Commun., 1992, 1152.