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A new oxide precursor: the synthesis of a bimetallic alkoxy derivative of strontium(II) and tantalum(V)

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The compound [SrTa$_2$(OEt)$_6$(μ-OEt)$_4$(μ-O-bis-dmap)$_2$] 1 has been prepared from the reaction of the mixed metal alkoxide [SrTa$_2$(OEt)$_8$(μ-OEt)$_4$] with the nitrogen containing ligand bis-dmapH [bis-dmapH = 1,3-bis(dimethylamino)propan-2-ol]; the bimetallic alkoxide is a potentially useful precursor for technologically important mixed metal oxides, the X-ray single crystal structure of 1 has been determined.

Introduction

Thin films of the layered perovskite oxide SrBi$_2$Ta$_2$O$_9$ (SBT) have attracted much recent attention as non-volatile ferroelectric computer memories.[1,2] SBT thin films have been deposited by a variety of techniques including: sol–gel, metal–organic decomposition and metal organic chemical vapour deposition (MOCVD). The MOCVD of SBT has been severely restricted by a lack of suitable metal–organic precursors. Conventional precursors include metal alkoxides and β-diketonates which are generally not compatible, having widely differing physical properties and/or decomposition properties.

The most extensively studied heterometallic alkoxides involve titanium or zirconium in combination with other metal ions.[3] In an attempt to improve the range of available precursors, and to deliver both metals in a single source, we have started to develop the chemistry of mixed Sr/Ta alkoxides. Although compounds such as [Sr{Ta(OPr^i)$_6$}$_2$] have been used in combination with [Bi(OBu^t)$_3$] to grow SBT,[4] there exists the possibility that strontium and tantalum alkoxide species will partition during the precursor evaporation and transport stages of the MOCVD process.

The strategy of our research has been to incorporate strontium and tantalum into one molecule. The double alkoxide[5] [SrTa$_2$(OEt)$_{12}$] **2**, and its reaction with nitrogen containing ligands has been investigated. However, the parent alkoxide contains a coordinatively unsaturated strontium centre making them susceptible to attack by moisture and air. The use of donor functional ligands should stabilise such compounds.[6] We have now isolated and characterised a novel bimetallic strontium–tantalum ethoxide from the reaction of the parent ethoxide **2** with the nitrogenous ligand, 1,3-bis(dimethylamino)propan-2-ol. The structure of the parent ethoxide [SrTa$_2$(OEt)$_8$(μ-OEt)$_4$] **2** will be reported elsewhere.

Although some of the chemistry of bimetallic alkoxy derivatives of Ta(V) is well established notably compounds with Cr(III),[7] Fe(II)[8] or Co(II),[9] we find only one reference to any double alkoxides of strontium with tantalum in the literature, and only for the parent alkoxides.[10] Only three double alkoxides of strontium with other metal ions have been characterised structurally to date: [{[Cd(OPr^i)$_3$]Sr[Hf$_2$(OPr^i)$_9$]}$_2$],[11] [SrTi$_4$(OEt)$_{18}$][12] and [{Sr$_2$Ti(OPr^i)$_8$(Pr^{i}OH)$_3$}·2Pr^{i}OH].[12]

The complex [SrTa$_2$(OEt)$_6$(μ-OEt)$_4$(μ-O-bis-dmap)$_2$] **1**† was synthesised from the reaction of [SrTa$_2$(OEt)$_8$(μ-OEt)$_4$] **2** with two equivalents of bis-dmapH in refluxing *n*-hexane. Removal of the solvent *in vacuo* and subsequent vacuum distillation yielded a colourless to pale yellow solution that solidified to a waxy solid on standing. Crystals were obtained by recrystallisation from *n*-hexane and storing at −20 °C for two weeks. The compound is more air stable than the parent ethoxide and can be handled in air for several minutes without notable decomposition.

The complex was characterised by microanalysis, NMR spectroscopy and an X-ray structure determination.‡ In the crystalline state the compound is composed of discrete [SrTa$_2$(OEt)$_6$(μ-OEt)$_4$(μ-O-bis-dmap)$_2$] molecules (Fig. 1). The two dmap ligands are inserted in *cis* positions with respect to the strontium centre, coordinating binuclearly (to tantalum and strontium) *via* oxygen and mononuclearly from nitrogen to strontium leaving in each case the remaining ligand nitrogen non-coordinated, as in related complexes with this ligand.[13] The geometry at strontium is very distorted square antiprismatic, the 'square' faces comprising N(1), O(4), N(11), O(14) and O(21), O(24), O(27), O(30) respectively. The Sr–O distances fall into two groups, with those to the ethoxides [2.547(8)–2.613(7) Å] being shorter than those to the dmap

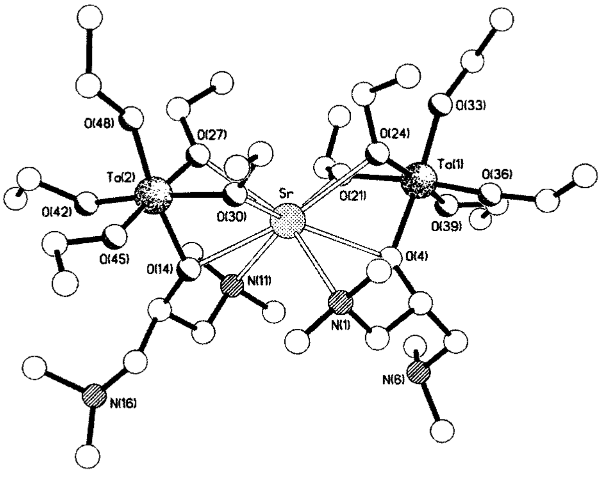

Fig. 1 The molecular structure of **1**. Selected bond lengths (Å); Sr–O(27) 2.547(8), Sr–O(24) 2.565(8), Sr–O(14) 2.595(7), Sr–O(4) 2.613(7), Sr–O(21) 2.654(8), Sr–O(30) 2.669(8), Sr–N(1) 2.744(9), Sr–N(11) 2.762(10), Ta(1)–O(36) 1.870(11), Ta(1)–O(33) 1.884(9), Ta(1)–O(39) 1.898(10), Ta(1)–O(21) 1.989(9), Ta(1)–O(4) 2.006(7), Ta(1)–O(24) 2.032(9), Ta(2)–O(45) 1.880(10), Ta(2)–O(48) 1.890(10), Ta(2)–O(42) 1.906(11), Ta(2)–O(30) 1.983(9), Ta(2)–O(14) 2.015(8), Ta(2)–O(27) 2.029(8).

ligands [2.654(8) and 2.669(8) Å]. Not surprisingly the coordination distances to nitrogen are significantly longer [at 2.744(9) and 2.762(10) Å]. The geometry at each tantalum centre is distorted octahedral with *cis* angles ranging between 82.1(4) and 96.2(4)° at Ta(1) and 82.6(4) and 95.3(3)° at Ta(2). The terminal Ta–O(ethoxide) distances are, as expected, distinctly shorter [1.870(11)–1.906(11) Å] than those to their bridging counterparts [1.983(9)–2.032(9) Å]. The Ta–O(dmap) distances are 2.006(7) [Ta(1)] and 2.015(8) Å [Ta(2)]. The non-bonded Sr···Ta separations are 3.414(1) and 3.415(1) Å to Ta(1) and Ta(2) respectively.

The compound has successfully been used in preliminary growth work[14] of $SrTa_2O_6$. Strontium tantalate thin films (amorphous) were deposited at 400 °C at a growth rate of $>0.2\ \mu m\ h^{-1}$. The full evaluation of this compound as a single source oxide precursor is in hand.

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Notes and references

†*Experimental*: All operations were carried out under a dry dinitrogen atmosphere with exclusion of dioxygen and moisture. 1,3-Bis(dimethylamino)propan-2-ol (bis-dmapH) and d_6-benzene were purchased from Aldrich and used without further purification. Ethanol and *n*-hexane were dried over molecular sieves and distilled prior to use to remove impurities. Strontium metal and tantalum pentaethoxide were supplied by Inorgtech Limited. The preparation of the parent alkoxide $[SrTa_2(OEt)_8(\mu\text{-}OEt)_4]$ **2** was essentially as described in ref. 5 but modified by dissolving the Sr in ethanol and omitting the use of the $HgCl_2$ catalyst. The mixture was refluxed for 1 hour and then solvent removed *in vacuo*. The compound was used for the preparation of **1** without further characterization.

$[SrTa_2(OEt)_6(\mu\text{-}OEt)_4(\mu\text{-}O\text{-bis-dmap})_2]$ **1**: A sample of **2** (16.9 g, 17 mmol) was dissolved in *n*-hexane (500 ml, 99%) and bis-dmapH (5 g, 34 mmol) added with stirring. The mixture was set to reflux for 3 h and the solvent removed *in vacuo*. The pale yellow oil obtained was vacuum distilled at 185–190 °C (0.2 mmHg) to yield a colourless liquid which solidified on standing to a white waxy solid (yield 60%). Crystals were obtained by recrystallisation from *n*-hexane and storing at −20 °C for 2 weeks.

IR (Nujol mull, NaCl plates): 3400s (br), 2900s (br), 1660w (br), 1440s, 1410w, 1380s, 1320m, 1265s, 1150–1050s (v br), 1000m, 910s, 835m and 820m. ^1H (C_6D_6): δ 1.29 (t, CH_3, 30H), 2.18 (m, NCH_3 and NCH_2, 32H) and 4.51 [m, OCH_2CH_3, μ-OCH_2CH_3 and μ-OC*H* (bis-dmap), 22H]. Analysis: Calc. for $C_{34}H_{84}N_4O_{12}SrTa_2$: C, 34.30; H, 7.11; N, 4.71; Found C, 34.12; H, 7.05; N, 4.80%.

‡*Crystal data for* **1**: $C_{34}H_{84}N_4O_{12}SrTa_2$, $M = 1190.6$, monoclinic, space group $P2_1/n$ (no. 14), $a = 20.894(3)$, $b = 9.780(2)$, $c = 25.458(3)$ Å, $\beta = 102.66(1)°$, $V = 5078(1)$ Å^3, $Z = 4$, $D_c = 1.558$ g cm^{-3}, μ(Cu-Kα) = 95.3 cm^{-1}, $F(000) = 2384$, $T = 203$ K; clear blocks, 0.87 × 0.83 × 0.33 mm, Siemens P4/RA diffractometer, ω-scans, 7799 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.072$, $wR_2 = 0.195$ for 6227 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 128°$] and 527 parameters. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/123.

1 T. Ami, K. Hironaka, C. Isobe, N. Nagel, M. Sugiyama, Y. Ikeda, K. Watanabe, A. Machida, K. Miura and M. Tanaka, *Mater. Res. Soc. Symp. Proc.*, 1996, **415**, 195.

2 T. Li, Y. Zhu, S. B. Desu, C. H. Peng and M. Nagata, *Appl. Phys. Lett.*, 1996, **68**, 616.

3 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.

4 Y. Kojima, H. Kodakura, Y. Okahara, M. Matsumoto and T. Mogi, *Ferroelectrics*, 1997, **18**, 183.

5 S. Govil, P. N. Kapoor and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, 1976, **38**, 172.

6 L. G. Hubert-Pfalzgraf, *Chemical Vapor Deposition*, *Proc. 14th Int. Conf. EUROCVD-11*, ed. M. D. Allendorf and C. Bernard, Electrochem. Soc. Proc., 1997, vol. 97, p. 825.

7 S. K. Agarwal and R. C. Mehrotra, *Inorg. Chim. Acta*, 1986, **112**, 177.

8 A. Shah, A. Singh and R. C. Mehrotra, *Indian J. Chem. Sect. A*, 1989, **28**, 392.

9 R. K. Dubey, A. Singh and R. C. Mehrotra, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 983.

10 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978 and references cited therein.

11 M. Veith, S. Mathur, C. Mathur and V. Huch, *J. Chem. Soc., Dalton Trans.*, 1997, 2101.

12 I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, D. M. P. Mingos, J. C. Plakatouras and D. J. Otway, *Polyhedron*, 1998, **17**, 625.

13 A. C Jones, T. Leedham, P. J. Wright, M. J. Crosbie, D. J. Williams amd P. O'Brien, *Mater. Res. Soc. Symp. Proc.*, 1998, **495**, 11.

14 M. J. Crosbie, P. J. Wright, H. O. Davies, A. C. Jones, T. J. Leedham, P. O'Brien and G. W. Critchlow, *Adv. Mater., Chem. Vap. Deposit.*, 1998, in press.

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