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Tin(II) aminoalkoxides and heterobimetallic derivatives: the structures of $Sn_6(O)_4(dmae)_4$, $Sn_6(O)_4(OEt)_4$ and $[Sn(dmae)_2Cd(acac)_2]_2$

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Tin(II) methoxide reacts with *N,N′*-dimethylaminoethanol (dmaeH) to yield $Sn(dmae)_2$ (1) along with small amounts of the hydrolysis product $Sn_6(O)_4(dmae)_4$ (2). The geometrically more regular iso-structural cage $Sn_6(O)_4(OEt)_4$ (3) was obtained as the only tractable product isolated from reaction of 2 and $Sb(OEt)_3$, while 1 reacted with CdX_2 (X = acac, I) to afford $Sn(dmae)_2Cd(acac)_2$ (4) and $Sn(dmae)_2CdI_2$ (5). The X-ray structures of 2, 3 and 4 are reported. Decomposition of 4 under aerosol-assisted chemical vapour deposition conditions leads to amorphous tin oxide films with no detectable cadmium (i.e. *ca* <2% cadmium), rather than a stoichiometric Sn : Cd oxide. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: tin; cadmium; alkoxide; MOCVD; X-ray

INTRODUCTION

Recent years have seen a rapid rise, in many cases a renaissance, of interest in the chemistry of metal alkoxides.[1,2] Much of the more recent focus in this area has been the synthesis of heterobimetallic alkoxides,[3–6] which have become one of the cornerstones on which advances in new materials have rested. Single-source bimetallic compounds, which deliver both elements of a final material simultaneously, can generate complex ceramic materials in a single step, removing the need to match the reaction rates required of a multi-component precursor mix.[7,8] A typical example, from among many possibilities, is the deposition of $SrTa_2O_6$ directly from $[SrTa_2(OEt)_6(\mu{-}OEt)_4(\mu\text{-bis-dmap})_2]$ [bis-dmapH = 1, 3-bis(dimethylamino)propan-2-ol].[9]

Tin oxide (SnO_2) is one of the most widely studied metal oxides as it plays a central role in various optoelectronic devices, including electrochromic displays, liquid crystal displays and solar cells,[10–15,16–18] or in gas sensors (usually in thick film or nano-particulate form).[19–21] In many instances the functionality of the tin oxide-based material is enhanced by the presence of a second element, e.g. Sb-doped SnO_2 induces enhanced conductivity,[20,21] indium tin oxide (ITO) is widely exploited in displays,[22,23] while doping with a second metal induces selectivity into gas sensors.[24,25] Numerous heterobimetallic alkoxides containing tin are known,[1] which could serve as single-source precursors to M : SnO_2 composites, but these uniformly contain simple alkoxides, e.g. OEt,[26] OBu^t,[27–29] OPr^i,[30,31] and, as a result, could suffer from disproportionation into separate homometallic components at elevated temperatures. To our knowledge, functionalised alkoxides, e.g. $R_2NCH_2CH_2O$, $ROCH_2CH_2O$, which offer greater prospects of stabilizing the Sn–O–M moiety, have not been explored, although they have appeared as components of many other bi-metallic species.[3,32–35] Organotin(IV) aminoalkoxides have, however, previously been reported.[36,37]

In this paper we report on the synthesis of $Sn(dmae)_2$ (dmaeH = $Me_2NCH_2CH_2OH$) and the formation of the bimetallic precursor $[Sn(dmae)_2Cd(acac)_2]_2$ (acacH = 1,

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5-pentane dione). The latter has been assessed as precursor in aerosol-assisted chemical vapour deposition (AACVD) experiments for the production of mixed Sn–Cd oxide thin films. Also reported in this paper are the isolation and characterization of the cage compounds $Sn_6O_4(OR)_4$ (R = dmae, Et), which we obtained indirectly during the course of this work.

Several reports on the synthesis and structural chemistry of group 14 derivatives of dimethylaminoethanol, including the structures of $M(dmae)_2$,[38,39] Li[M(dmae)$_3$][40] and XM(dmae) [M = Ge, Sn; X = Cl, OAc,[41] N_3,[42] $N(SiMe_3)_2$[43]], have appeared in recent years.

RESULTS AND DISCUSSION

$Sn(dmae)_2$ (**1**) (dmaeH = 2-dimethylaminoethanol) has been synthesised by a *trans*-alcoholysis from $Sn(OMe)_2$, following a procedure first outlined by Wakeshima.[44] The reaction was carried out in the absence of solvent at 90 °C; the product, a colourless oil, was obtained in 65% yield after distillation.

$$Sn(OMe)_2 + 2\,HOCH_2CH_2NMe_2 \xrightarrow{-2\,MeOH} \underset{(\mathbf{1})}{Sn(OCH_2CH_2NMe_2)_2} \qquad (1)$$

Zemlyansky has reported the synthesis of **1** by both functional group redistribution between $SnCl_2$ and $Et_3Sn(dmae)$, and alcoholysis of $Sn[N(SiMe_3)_2]_2$. By these routes, crystalline material of low melting point (45–46 °C) was obtained.[38]

The room temperature ^1H NMR of **1** prepared by us is similar to that reported earlier,[38] exhibiting a single set of broad resonances due to the OCH_2 (4.06 ppm) and NCH_2 groups (2.35 ppm), although the latter sharpens to a resolved triplet by 320 K; neither cooling the sample to −50 °C nor heating succeeded in resolving the signal due to the OCH_2 group. The ^{119}Sn NMR is also dominated by a broad resonance (−319 ppm), with additional sharp, weak signals also present at −523 and −561 ppm. Collectively, these data imply a dynamic structure in solution in which the coordination number at tin is at least 3. The solution dynamics are most likely to involve both a mixture of monomers and μ–OR bridged dimers/oligomers, along with dynamic coordination of tin by the donor Me_2N group. Tin(II) alkoxides are either polymeric materials, e.g. $Sn(OCH_2Bu^t)_2$,[45] dimers, e.g. $[Sn(\mu\text{–}OSiMe_3)(OSiMe_3)]_2$,[46] or monomers, e.g. $Sn(OBu^t)_2$,[47] depending on the steric demands of the hydrocarbon groups. The ^{119}Sn NMR shift of such species is often difficult to reconcile with coordination number, and has been variously reported as *ca* −160 and −220 ppm for two- and three-coordinate tin(II) alkoxides, respectively.[46,48] However, the solid-state CPMAS spectrum of four-coordinated $Sn(OCH_2Bu^t)_2$ is at −214 ppm, while in solution the same compound has resonances at −197, −361 and −394 ppm.[45] The authors of this latter paper interpreted these data simply in terms of disruption of the solid-state structure on dissolution. The divalent nature of the tin in **1** is confirmed by the Mössbauer isomer shift of 2.60 mm s^{-1}.

The synthesis of **1** also generates a small number of crystals within the liquid sample, X-ray diffraction of which has shown to be the hydrolysis product $Sn_6(O)_4(dmae)_4$ (**2**). Compound **2** appears in the ^{119}Sn NMR of **1** as a very minor, sharp resonance at *ca* −162 ppm. For comparison, the ^{119}Sn NMR of other $Sn_6(O)_4(OR)_4$ species appear at −128 ($R = CH_2Bu^t$)[45] and −138 ppm ($R = SiMe_3$).[49] The ^1H NMR of **2** includes sharp triplets at 2.29 and 3.75 ppm, while in the ^{13}C NMR, sharp singlets due to CH_2N and CH_2O are seen at 58.7 and 61.5 ppm.

The origin of **2** deserves further comment as oxo-cages of this type, which appear amenable to further exterior elaboration, can afford an entry into the synthesis of models for metals supported on SnO_2 as well as molecular precursors to these materials. Furthermore, its formation was not noted in earlier studies on the preparation of **1** from $Sn(OMe)_2$,[44] nor when **1** was prepared from $Sn[N(SiMe_3)_2]_2$.[38] The latter is easier to purify than $Sn(OMe)_2$, whose preparation can be accompanied by the formation of $Sn_6(O)_4(OMe)_4$,[52] which is a likely intermediate in the formation of **2** by the route we have followed. The formation of small amounts of $Sn_6(O)_4(OMe)_4$ during the preparation of $Sn(OMe)_2$ clearly occurs by way of hydrolysis,[52] with the origin of the water most obviously being the solvent, methanol. However, the methanol used in this study was dried and degassed over activated alumina columns and used immediately after collection from the drying column. We now believe that the formation of $Sn_6(O)_4(OMe)_4$ is a result of partially hydrated $SnCl_2$, and that **2** (and indeed **3**, see below) is a result of trans-alcoholysis of this hydrolysis product with dmaeH. Thus, when an old sample of $SnCl_2$ is used in the preparation of $Sn(OMe)_2$, the resulting product analyses most closely for $Sn_6(O)_4(OMe)_4$ (found: C 6.22, H 1.58%; calculated for $C_4H_{12}O_8Sn_6$: C 5.34, H 1.35%; calculated for $Sn(OMe)_2$, $C_2H_6O_2Sn$: C 16.15, H 4.07%). A partial hydration of $SnCl_2$ would be consistent with the following reaction sequence, which requires 0.66 moles of H_2O per $SnCl_2$:

$$6\,SnCl_2 + 12\,MeOH \xrightarrow[-12[Et_3NH]Cl]{Et_3N} 6\,Sn(OMe)_2$$

$$6\,Sn(OMe)_2 \xrightarrow[-8\,MeOH]{4\,H_2O} Sn_6(O)_4(OMe)_4$$

$$Sn_6(O)_4(OMe)_4 \xrightarrow[-4\,MeOH]{4\,dmaeH} \underset{\mathbf{2}}{Sn_6(O)_4(dmae)_4}$$

TGA analysis of the tin(II) chloride we used in this latter reaction indicates approximately 11% weight loss on heating to 170 °C (compared with a calculated value of 16% for commercially available $SnCl_2{\cdot}2H_2O$), implying an approximate level of hydration of $SnCl_2{\cdot}1.3H_2O$. The excess water this brings to the reaction appears to have little

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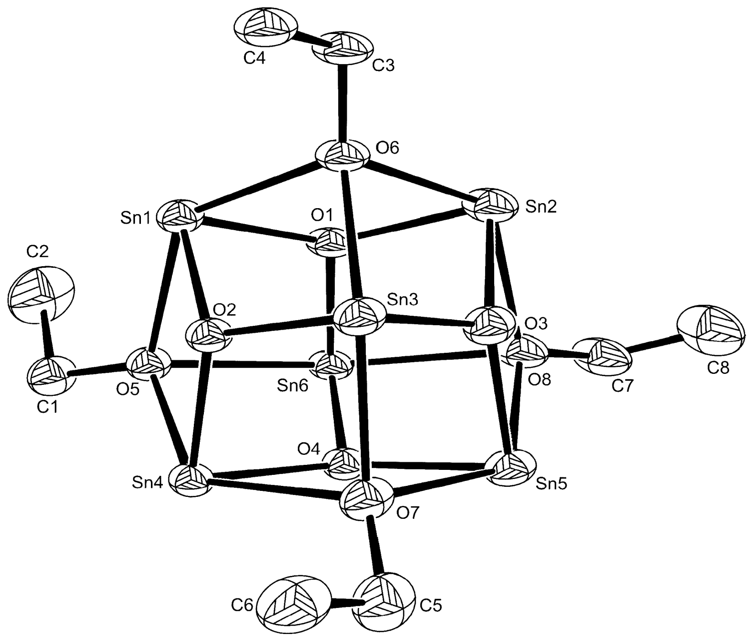

Figure 1. The structure of $Sn_6(O)_4(OEt)_4$ (**3**) showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. Hydrogen atoms have been omitted for clarity.

impact on the formation of $Sn_6(O)_4(OMe)_4$ under the reaction conditions used.

Using the sample of $Sn_6(O)_4(OMe)_4/Sn(OMe)_2$ prepared from partially hydrated $SnCl_2$ as described above, **2** is the only product observed in the subsequent reaction with dmaeH. Compound **2** prepared by this procedure is characterized by a clean ^{119}Sn NMR, $\delta = -157$ ppm, free from any signal due to **1**. The use of hydrated $SnCl_2$ appears a to be reproducible route to $Sn_6(O)_4(OMe)_4$ and hence synthetically useful quantities of $Sn_6(O)_4(dmae)_4$ (**2**).

When **1** was mixed with an equal quantity of $Sb(OEt)_3$[50] a very small amount of crystalline product was isolated from THF and identified by X-ray crystallography as $Sn_6(O)_4(OEt)_4$ (**3**), from a similar alkoxide exchange to that described above and involving the small amount of **2** present in the sample of **1**. No other identifiable products have so far been isolated from this reaction.

The structures of **3** and **2** are shown in Figs 1 and 2, respectively, with a consistent labelling scheme and orientation to facilitate comparison. Selected metrical data are given in Table 2. Compound **3** adopts a regular cage arrangement, which is typical of other members of the structurally characterized $Sn_6(O)_4(OR)_4$ family ($R = H$,[51] Me,[52] Pr^i,[53] $SiMe_3$[49]). The cage comprises two six-membered Sn_3O_3 rings fused by Sn–O links between the two faces. The upper ring (Fig. 1) comprises μ–O bridges, adopts a regular chair conformation and is capped by a μ_3–OEt group. The lower ring, comprising μ–OEt groups, is slightly more flattened and is now capped by a μ_3–O unit. The Sn–O bonds [2.057(7)–2.087(9) Å] are always shorter than the corresponding Sn–OEt linkages [2.339(7)–2.434(8) Å]. The geometry at tin can be described as trigonal bipyramidal with one equatorial site occupied by a lone electron pair, the bond angles about each tin following

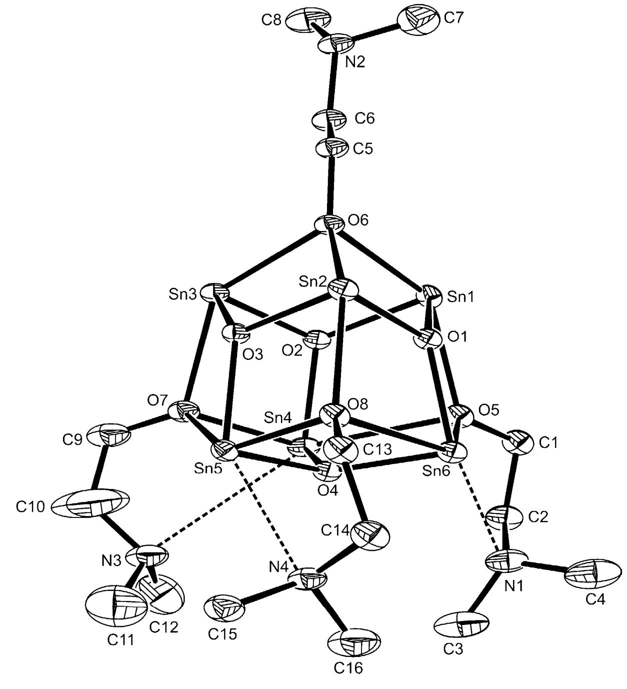

Figure 2. The structure of $Sn_6(O)_4(OCH_2CH_2NMe_2)_4$ (**2**) showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. Only the major component of the disordered grap based on C10 is shown for clarity. Hydrogen atoms have been omitted for clarity.

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a very regular pattern (angles of *ca* 95, 134 and four angles of 75° in all cases). The Sn–O–Sn bond angles at μ_3-O (*ca* 114°) are uniformly less strained than those at the μ_3–OEt groups (*ca* 95°; Table 2).

Compound **2**, while adopting the same general structure as **3**, is far less regular. There are only minor differences between the Sn–O bonds in the top Sn_3O_3 ring of **3** and their analogues in **2**, and here the capping μ_3–dmae group is clearly monodentate [Sn···N2 > 5 Å]. In contrast, in the lower Sn_3O_3 ring, while bonds involving μ_3–O4 are similar to those in **3**, the Sn–O($CH_2CH_2NMe_2$) distances show much greater variability (Table 2). Certain interactions are markedly elongated [Sn4–O5: 2.669(3); Sn5–O7: 2.712(4); Sn6–O8: 2.775(3) Å] and separations of this magnitude have been classed as non-bonding in $Sn_6O_4(OCH_2Bu^t)_4$.[45] The origin of this phenomenon is the coordination mode of the amino groups associated with dmae ligands attached to this lower Sn_3O_3 ring, at least two of which appear to show some weak chelation to tin [N4··· Sn5: 3.007(5); N1···Sn(6): 3.030(5) Å] while the coordination mode of the third dmae group is less clear cut [N3···Sn4: 3.346(5) Å]. In all cases, however, these interactions must be considered to be weak, as $\delta(^{119}Sn)$ for **2** (−161 ppm) is similar to analogous data for $Sn_6(O)_4(OR)_4$ with non-coordinating R groups (see above). The bond angles at tin in the lower Sn_3O_3 ring also show more variability, particularly those O–Sn–O angles *ca* 75° (Table 2).

We have also explored the use of **1** as a reagent for the preparation of heterobimetallic alkoxides in which the chelating dmae ligands aid coordination of the second metal. Mixed Sn/Cd oxide systems, e.g. Cd_2SnO_4, $CdSnO_3$, are transparent wide-bandgap semiconductors with potential applications in solar control and as gas sensing devices.[54–58] It was therefore of interest to develop a single-source precursor to such materials. Previous methods for producing these materials include vacuum evaporation,[57] co-precipitation[55,59] and r.f. sputtering,[60] and one report on a dip-coating procedure employed mixtures of $Sn(OR)_4$ and $Cd(O_2CCH_3)_2$,[61] which other reports have shown contain bi-metallic complexes such as $Cd_4Sn_4(\mu{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}$.[62] Precursors for the deposition of CdO are also of topical interest, with recent reports focussing on the use of adducts $Cd(hfac)_2.L$ (L = TMEDA,[63] polyethers,[64] H_2O[65]) (Hhfac = 1, 1, 1, 5, 5, 5, hexafluoro-2, 4-pentanedione). Indeed, $Cd(hfac)_2(TMEDA)$ has been used, in a dual-source atmospheric pressure CVD process and in conjunction with $Bu_2Sn(O_2CCF_3)_2$, to produce thin films of Cd_2SnO_4.[66] We have thus employed a β-diketonate derivative as the source of the cadmium.

Addition of an equimolar quantity of **1** to a suspension of $[Cd(acac)_2]_m$ in toluene followed by heating to *ca* 60 °C causes dissolution of the latter. A 1 : 1 complex, $Sn(dmae)_2Cd(acac)_2$ (**4**), precipitated on cooling, X-ray quality crystals of which were grown from THF at −20 °C. The room temperature ^1H NMR spectrum of **4** consists of one set of signals associated with each of the two ligand types, but these are broad and are indicative of a dynamic structure in solution. Individual signals arising from the two distinct ligands of each type could not be resolved, even at lower temperatures.

We have prepared the complex $Sn(dmae)_2CdI_2$ (**5**) by a similar route but have so far been unable to obtain definitive structural analysis of this compound, which is markedly less soluble in organic solvents than **4**.

The structure of **4** is shown in Fig. 3 and is centrosymmetric, with an inversion centre at the heart of the central Sn_2O_2 ring. The Sn_2O_2 dimer is held together by μ–OR bridges between tin atoms [Sn1–O6′, 2.270(2) Å]. One dmae group chelates the tin [Sn1–O6, 2.131(2); Sn1–N2, 2.492(3) Å] while the other is monodentate with respect to this metal [Sn1–O5,

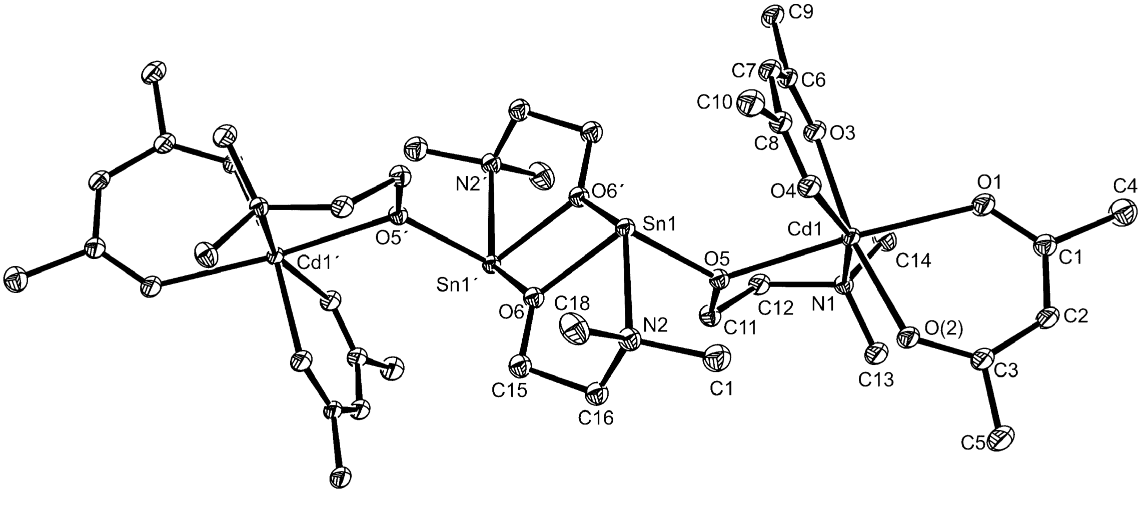

Figure 3. The structure of $Sn(OCH_2CH_2NMe_2)_2Cd(acac)_2$ (**4**) showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. The THF molecule of solvation and all hydrogen atoms have been omitted for clarity. Symmetry operation: 1 − *x*, 2 − *y*, −*z*.

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2.078(2) Å] and has the shortest of the Sn–O bonds; the overall coordination sphere about tin is trigonal bipyramidal, in which one site is occupied by a stereochemically active lone pair. In addition, the dmae group based on O5 acts as a μ–OR bridge to cadmium [Cd1–O5, 2.326(2) Å], supported by chelation from the pendant amino group [Cd1–N1: 2.405(2) Å]. The latter is longer than N: → Cd donor bonds in Cd(hfac)$_2$(TMEDA) [average: 2.351(2) Å][63] and Cd(acac)$_2$(1,10-phenanthroline) [2.368(2) A].[67] Octahedral *cis*-, *cis*-, *cis*-coordination at cadmium is completed by two chelating acac groups, whose Cd–O bonds [2.249(2)–2.273(2) Å] are within the range observed in other Cd(β-diketonate) complexes.[63–65]

As far as we are aware, the only other comparable bi-metallic Sn–Cd species which have been structurally characterized are $Cd_4Sn_4(\mu{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}$,[62] $Cd(I)[Sn_2(\mu_3{-}OPr^i)_2(\mu_2{-}OPr^i)_3(OPr^i)_4]$[68] and $Cd[Sn_2(\mu_2{-}OBu^t)_6]$.[69] Compound **4** has been tested as a possible precursor for the aerosol-assisted CVD of mixed tin/cadmium oxide films. In a typical experiment, 0.5 g of **4** dissolved in toluene (50 ml) was nebulized into a fine mist and transported to the heated substrate (pyrex glass slide heated to 400 or 500 °C) in a flow of N_2 gas (1.0 l min^{-1}). Details of our apparatus are given elsewhere.[70] As deposited at 400 or 500 °C, these films had a brown colouration and were amorphous as determined by X-ray diffraction. Auger analysis indicates a tin to oxygen ratio of 1 : 1, but with 60% carbon incorporation. The films were amorphous by XRD, so no definitive comment can be made as to the nature of the tin oxide. A 1 : 1 ratio is, however, consistent with the divalent nature of the tin precursor. No cadmium was detected in the film by Auger, implying a Cd content of less than 2%, given the thin nature of the film.

The lack of cadmium in the film implies a two-stage decomposition mechanism, the first leading to separate Sn(dmae)$_2$ and Cd(acac)$_2$ components, followed by preferential decomposition of the former. The structural data is relevant here, as the alkoxide which bridges tin centres to hold the dimer together [Sn1–O6′: 2.270(2) Å] is stronger than that which links tin and cadmium [Cd1–O5: 2.326(2) Å]. Furthermore, although the chelation of nitrogen to cadmium [Cd1–N1: 2.405(2) Å] is stronger than that to tin [Sn1–N2: 2.492(3) Å], it is still relatively weak with respect to other N: → Cd interactions (see above). These data suggest that separation of the tin and cadmium components of the precursor is more likely than dissociation of the Sn(dmae)$_2$ dimer.

CONCLUSIONS

Sn(dmae)$_2$ is capable of forming 1 : 1 adducts with unsaturated metal centres such as Cd(acac)$_2$ and CdI$_2$, although Sn(dmae)$_2$Cd(acac)$_2$ fails to act as single-source precursor for mixed Sn–Cd oxide films. It would appear that additional bridging groups are required between the metal centres to maintain the integrity of the precursor with respect to dissociation, in order to generate a mixed metal oxide material. In the synthesis of Sn(dmae)$_2$ some hydrolysis product, Sn$_6$O$_4$(dmae)$_4$, is also produced. This compound is also disposed to coordinate additional metals on the cage periphery, thus acting as a model for metal-supported tin oxide catalysts. Work is in progress to test this assertion.

Table 1. X-ray crystallographic data for **2**, **3** and **4**

	(**2**)	(**3**)	(**4**)
Empirical formula	$C_{16}H_{40}N_4O_8Sn_6$	$C_8H_{20}O_8Sn_6$	$C_{22}H_{42}CdN_2O_7Sn$
Formula weight	1128.66	956.38	677.67
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$	$C2/c$	$P2_1/n$
a, Å	11.2260(1)	19.0210(5)	10.6346(1)
b, Å	11.4870(2)	12.9720(4)	13.7928(2)
c, Å	13.5930(2)	16.9000(4)	19.5561(3)
α, °	99.096(1)		
β, °	101.632(1)	90.803(2)	98.290(1)
γ, °	105.958(1)		
V, Å^3	1607.71(4)	4169.5(2)	2838.53(7)
Z	2	8	4
Reflections collected	28 485	28 039	42 839
Independent reflections	7323 [$R_{\text{int}} = 0.061$]	4759 [$R_{\text{int}} = 0.071$]	6479 [$R_{\text{int}} = 0.064$]
Reflections observed (>2σ)	6202	3400	5563
Final R^1, wR^2 [$I > 2\sigma(I)$]	0.047, 0.116	0.050, 0.128	0.029, 0.070
Final R^1, wR^2(all data)	0.054, 0.123	0.073, 0.147	0.038, 0.074
$\rho_{\max} > 1$ eÅ^3	1.11 (near C10) −2.37(near Sn6)	1.37 (near Sn6) −1.94(near Sn2)	

Table 2. Selected metrical data for **2** and **3**

	(2)	**(3)**		**(2)**	**(3)**
Bond lengths, Å					
Sn1–O1	2.069(3)	2.086(7)	Sn4–O2	2.094(3)	2.079(6)
Sn1–O2	2.081(3)	2.057(7)	Sn4–O4	2.083(3)	2.074(6)
Sn1–O5	2.348(3)	2.393(6)	Sn4–O5	2.669(3)	2.339(7)
Sn1–O6	2.364(3)	2.356(7)	Sn4–O7	2.223(4)	2.429(7)
Sn2–O1	2.063(3)	2.079(8)	Sn5–O3	2.124(3)	2.081(7)
Sn2–O3	2.067(3)	2.087(9)	Sn5–O4	2.089(3)	2.067(6)
Sn2–O6	2.462(3)	2.353(7)	Sn5–O7	2.712(4)	2.373(9)
Sn2–O8	2.294(3)	2.396(7)	Sn5–O8	2.218(3)	2.347(9)
Sn3–O2	2.072(3)	2.088(6)	Sn6–O1	2.088(3)	2.079(6)
Sn3–O3	2.078(3)	2.070(7)	Sn6–O4	2.082(3)	2.088(7)
Sn3–O6	2.357(3)	2.434(8)	Sn6–O5	2.216(3)	2.384(7)
Sn3–O7	2.320(3)	2.365(7)	Sn6–O8	2.775(3)	2.377(8)
Bond angles at Sn, °					
O1–Sn1–O2	92.5(1)	95.0(3)	O2–Sn4–O4	93.5(1)	94.5(2)
O1–Sn1–O5	73.1(1)	73.8(2)	O2–Sn4–O5	70.0(1)	75.0(2)
O1–Sn1–O6	75.6(1)	74.6(3)	O2–Sn4–O7	74.9(1)	73.9(3)
O2–Sn1–O5	77.2(1)	74.2(2)	O4–Sn4–O5	70.8(1)	74.9(2)
O2–Sn1–O6	74.7(1)	75.7(3)	O4–Sn4–O7	82.3(1)	73.2(3)
O5–Sn1–O6	136.4(1)	133.5(2)	O5–Sn4–O7	133.6(1)	132.9(3)
O1–Sn2–O3	92.7(1)	94.4(3)	O3–Sn5–O4	93.0(1)	94.7(2)
O1–Sn2–O6	73.5(1)	74.8(2)	O3–Sn5–O7	69.2(1)	73.8(3)
O1–Sn2–O8	79.5(1)	74.0(3)	O3–Sn5–O8	75.1(1)	75.3(3)
O3–Sn2–O6	73.4(1)	74.7(3)	O4–Sn5–O7	71.1(1)	74.6(2)
O3–Sn2–O8	74.5(1)	74.1(3)	O4–Sn5–O8	82.2(1)	75.1(3)
O6–Sn2–O8	136.5(1)	133.3(2)	O7–Sn5–O8	133.4(1)	134.1(3)
O2–Sn3–O3	94.6(1)	93.7(3)	O1–Sn6–O4	90.7(1)	94.3(3)
O2–Sn3–O6	75.0(1)	73.4(2)	O1–Sn6–O5	75.6(1)	74.1(2)
O2–Sn3–O7	73.2(1)	75.2(2)	O1–Sn6–O8	68.3(1)	74.5(3)
O3–Sn3–O6	75.5(1)	73.2(3)	O4–Sn6–O5	81.0(1)	73.7(2)
O3–Sn3–O7	78.4(1)	74.1(3)	O4–Sn6–O8	69.7(1)	74.1(3)
O6–Sn3–O7	136.7(1)	132.4(2)	O5–Sn6–O8	132.4(1)	132.4(2)
Bond angles at μ_3–O, °					
Sn1–O1–Sn2	117.1(2)	114.4(3)	Sn2–O3–Sn3	116.8(1)	116.8(3)
Sn1–O1–Sn6	112.7(1)	116.4(3)	Sn2–O3–Sn5	110.5(1)	115.0(3)
Sn2–O1–Sn6	121.5(2)	116.1(3)	Sn3–O3–Sn5	120.0(2)	116.1(4)
Sn1–O2–Sn3	114.7(1)	116.3(3)	Sn4–O4–Sn5	115.8(1)	117.2(3)
Sn1–O2–Sn4	120.4(2)	115.5(3)	Sn4–O4–Sn6	116.0(2)	115.2(3)
Sn3–O2–Sn4	112.3(1)	115.9(3)	Sn5–O4–Sn6	117.6(2)	115.0(3)
Bond angles at μ_3–OEt, °					
Sn1–O5–Sn4	92.2(1)	95.3(2)	Sn3–O7–Sn4	99.2(1)	94.9(3)
Sn1–O5–Sn6	98.6(1)	95.6(2)	Sn3–O7–Sn5	92.3(1)	96.0(3)
Sn4–O5–Sn6	92.2(1)	96.2(3)	Sn4–O7–Sn5	90.9(1)	94.8(3)
Sn1–O6–Sn2	93.8(1)	96.1(2)	Sn2–O8–Sn5	99.5(1)	95.6(3)
Sn1–O6–Sn3	95.5(1)	94.6(2)	Sn2–O8–Sn6	90.7(1)	95.3(3)
Sn2–O6–Sn3	94.2(1)	95.4(2)	Sn5–O8–Sn6	90.5(1)	95.8(3)

EXPERIMENTAL

Elemental analyses were performed using an Exeter Analytical CE 440 analyser. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker Avance 300 MHz FT-NMR spectrometer, using saturated C_6D_6 solutions at room temperature; chemical shifts are in ppm relative to either Me_4Si or Me_4Sn. Details of our Mössbauer spectrometer

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and related procedures are given elsewhere.[71] $Sn(OMe)_2$ and $Sb(OEt)_3$ were prepared by a literature procedures.[50,72] All reactions were carried out under an inert atmosphere. Solvents were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology solvent purification system (SPS).

Synthesis of $Sn(dmae)_2$ (1)

Compound **1** was prepared by the method of Wakeshima and purified by vacuum distillation (130–132 °C/10 mmHg; 3.83 g, 65%).[44] Analysis, found (calcd for $C_8H_{20}N_2O_2Sn$): C 31.1(32.5), H 6.60(6.77), N 9.58(9.49)%. ^1H NMR: 2.13 (s, 6H, CH_3N), 2.35 (br, 2H, CH_2N), 4.06 (br, 2H, CH_2O). ^{13}C NMR: 41.3 (CH_3), 57.9 (CH_2N), 58.7 (CH_2O). ^{119}Sn NMR: −319 (br). ^{119}Sn Mössbauer (mm s^{-1}): i.s. 2.60, q.s. 2.20.

Synthesis of $Sn_6O_4(dmae)_4$ (2)

Addition of an excess of MeOH (60 ml) to $SnCl_2 \cdot 1.3H_2O$ (estimated from TGA weight loss in the range 25–170 °C; 10.48 g, 49.2 mmol) generated a cloudy solution. To this a slight excess of Et_3N (16.96 ml, 121.6 mmol) was added, resulting in an exothermic reaction and giving a dense white precipitate. Stirring was continued for 1 h and the precipitate allowed to settle. The solid was isolated by filtration washed with MeOH until the washings appeared colourless (3 × 50 ml). The product (7.24 g) appears to be largely $Sn_6(O)_4(OMe)_4$ by microanalysis (found: C 6.22, H 1.58%; calculated for $C_4H_{12}O_8Sn_6$: C 5.34, H 1.35%; calculated for $Sn(OMe)_2$, $C_2H_6O_2Sn$: C 16.15, H 4.07%).

$Sn_6(O)_4(OMe)_4$ as prepared above (3.00 g, 3.3 mmol) was heated to 90 °C in the presence of excess dmaeH (2.95 g, 33.2 mmol) and stirred for 1 h. The resulting volatiles were then pumped off *in vacuo* leaving **2** as a white solid (3.24g, 86%; m.p. 74–78 °C). Analysis, found (calcd for $C_{16}H_{40}N_4O_8Sn_6$): C 18.1(17.0), H 3.99(3.54), N 4.11(4.96)%. ^1H NMR: 2.04 (s, 18H, NCH_3), 2.29 (t, 8H, CH_2N), 3.75 (t, 8H, CH_2O). ^{13}C NMR: 43.7 (br, CH_3), 58.7 (CH_2N), 61.5 (CH_2O). ^{119}Sn NMR: −157.

Synthesis of $Sn_6O_4(OEt)_4$ (3)

Compound **1** (0.30 g, 1 mmol) was reacted with $Sb(OEt)_3$ (0.26 g, 1 mmol) in toluene (10 ml). The resulting white suspension cleared on heating at 60 °C over a 3–4 h period. Toluene was evaporated *in vacuo* to leave a yellow mass; crystallization from THF at *ca* −20 °C yielded a very small amount of crystals which were identified as (**3**) by X-ray crystallography.

Synthesis of $Sn(dmae)_2Cd(acac)_2(THF)$ (4)

Compound **1** (0.29 g, 1 mmol) was heated at *ca* 60 °C with $[Cd(acac)_2]_m$ (0.31 g, 1 mmol) in toluene (5 ml) for 45 min, during which time the solid had almost completely dissolved, leaving a clear orange-yellow solution. This was filtered to remove traces of solid residue and allowed to cool. The resulting white solid was isolated by canula filtration and crystallized from THF at −20 °C (0.59 g, 87%). ^1H NMR: 1.75 (br, 10H, CH_3C, CH_2CH_2O), 2.10 (br, 6H, CH_3N), 2.30 (br, 2H, CH_2N), 3.61 (br, 2H, CH_2O), 3.70 (s, 4H, CH_2CH_2O), 5.00 (br, 2H, CH). ^{13}C NMR: 24.6 (CH_2CH_2O), 27.8 (br, CH_3C), 44.4 (NCH_3), 56.3 (CH_2N), 59.8 (CH_2O), 66.9 (CH_2CH_2O), 98.1 (CH), 191.1 (CO). ^{119}Sn NMR: −423. Mössbauer (mm s^{-1}): i.s. = 2.86, q.s. = 1.96.

Synthesis of $Sn(dmae)_2CdI_2$ (5)

Compound **1** (0.29 g, 1 mmol) was heated with CdI_2 (0.34 g, 1 mmol) in toluene (5 ml) overnight, during which time the CdI_2 dissolves. Compound **5** precipitated on cooling and was washed with hexane, THF and ethanol (0.30 g, 45%); m.p. 208 °C dec. Analysis, found (calcd for $C_8H_{20}CdI_2N_2O_2Sn$): C 14.1(14.5), H 2.95(3.02), N 3.98(4.23)%. ^1H NMR (DMSO): 2.20 (s, 6H, NCH_3), 2.40 (t, 2H, CH_2N), 3.50 (br, 2H, CH_2O). ^{13}C NMR: 45.8 (CH_3), 58.2 (CH_2O, CH_2N).

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic study of complexes **2**–**4** are given in Table 1. Data were collected up to $\theta_{max} = 27.5°$ on a Nonius Kappa CCD at 150 K using Mo-Kα radiation ($\lambda = 0.71073$ Å). The refinement method was full-matrix least-squares on F^2. In each case a semi-empirical absorption correction from equivalents was made. Hydrogen atoms were included at calculated positions. For **2**, the components of the ethanolamine chain including C10, N3, C11 and C12 were found to be disordered over two sites in a 55 : 45 ratio, of which only the major component is shown in Fig. 2. In the case of **4** the electron density associated with the solvent of crystallization (one molecule of THF per asymmetric unit) appeared very smeared and was refined using a split atom model in the ratio of 60 : 40.

Table 3. Selected metrical data for **4**[a]

Bond lengths, Å			
Sn1–O5	2.078(2)	Sn1–O6	2.131(2)
Sn1–O6′	2.270(2)	Sn1–N2	2.492(3)
Cd1–O1	2.251(2)	Cd1–O2	2.249(2)
Cd1–O3	2.273(2)	Cd1–O4	2.249(2)
Cd1–O5	2.326(2)	Cd1–N1	2.405(2)
Bond angles, deg			
O5–Sn1–O6	95.82(8)	O6–Sn1–O6′	68.61(8)
O5–Sn1–O6′	88.51(8)	O6–Sn1–N2	72.50(8)
O5–Sn1–N2	82.39(9)	O6′–Sn1–N2	138.83(9)
O1–Cd1–O2	82.53(8)	O2–Cd1–N1	93.52(8)
O1–Cd1–O3	88.49(8)	O3–Cd1–O4	82.50(7)
O1–Cd1–O4	104.60(9)	O3–Cd1–O5	91.99(8)
O1–Cd1–O5	168.89(8)	O3–Cd1–N1	89.94(8)
O1–Cd1–N1	93.64(9)	O4–Cd1–O5	86.45(7)
O2–Cd1–O3	170.56(8)	O4–Cd1–N1	159.98(8)
O2–Cd1–O4	96.91(8)	O5–Cd1–N1	75.27(7)
O2–Cd1–O5	97.38(7)		

[a] Symmetry operation for primed atoms: $-x, 2-y, -z$.

The software used was SHELXS 86,[73] SHELXL 97[74] and ORTEX.[75] CCDC reference numbers are 265429–265431 for **2**–**4**, respectively.

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REFERENCES

1. Mehrotra RC, Singh A, Sogani A. *Chem. Rev.* 1994; **94**: 1643.
2. Bradley DC. *Chem. Rev.* 1989; **89**: 1317.
3. Hubert-Pfalzgraf LG. *Inorg. Chem. Commun.* 2003; **6**: 102.
4. Veith M, Mathur S, Mathur C. *Polyhedron* 1998; **17**: 1005.
5. Herrmann WA, Huber NW, Runte O. *Angew. Chem., Int. Edn Engl.* 1995; **34**: 2187.
6. Hubert-Pfalzgraf LG. *Appl. Organomet. Chem.* 1992; **6**: 627.
7. Jones AC. *J. Mater. Chem.* 2002; **12**: 2576.
8. Hubert-Pfalzgraf LG. *Polyhedron* 1994; **13**: 1181.
9. Davies HO, Jones AC, Leedham TJ, O'Brien P, White AJP, Williams DJ. *J. Mater. Chem.* 1998; **8**: 2315.
10. Fillard JP, Manifacier JC. *Jpn. J. Appl. Phys., Part 1* 1970; **9**: 1012.
11. Tatsuyama C, Ichimura S. *Jpn. J. Appl. Phys., Part 1* 1976; **15**: 843.
12. Hass G, Heaney JB, Toft AR. *Appl. Opt.* 1979; **18**: 1488.
13. Brinker DJ, Wang EY, Wadlin WH, Legge RN. *J. Electrochem. Soc.* 1981; **128**: 1968.
14. Chopra KL, Major S, Pandya DK. *Thin Solid Films* 1983; **102**: 1.
15. Das SK, Morris GC. *J. Appl. Phys.* 1993; **73**: 782.
16. Ferrere S, Zaban A, Gregg BA. *J. Phys. B: Atom. Mol. Opt. Phys.* 1997; **101**: 4490.
17. Ford WE, Wessls JM, Rodgers MAJ. *J. Phys. Chem.* 1997; **101**: 7435.
18. Laverty SJ, Feng H, Maguire P. *J. Electrochem. Soc.* 1997; **144**: 2165.
19. Moseley PT. *Meas. Sci. Technol.* 1997; **8**: 223.
20. Lin Y-J, Wu C-J. *Surf. Coat. Technol.* 1996; **88**: 239.
21. Haneko H, Miyake K. *J. Appl. Phys.* 1992; **53**: 3629.
22. Granqvist CG, Hultaker A. *Thin Solid Films* 2002; **411**: 1.
23. Granqvist CG. *Appl. Phys. A Mater. Sci. Process.* 1993; **57**: 19.
24. Gopel W, Schierbaum KD. *Sensors Actuators B* 1995; **26**: 1.
25. Williams DE, Mosely PT. *J. Mater. Chem.* 1991; **1**: 809.
26. Hampden-Smith MJ, Smith DE, Duesler EN. *Inorg. Chem.* 1989; **28**: 3399.
27. Veith M, Hill S, Huch V. *Z. Anorg. Allg. Chem.* 2001; **627**: 1495.
28. Veith M, Kunze K. *Angew. Chem., Int. Edn Engl.* 1991; **30**: 95.
29. Veith M, Hans J, Stahl L, May P, Huch V, Sebald A. *Z. Naturforsch. B* 1991; **B46**: 403.
30. Veith M, Mathur S, Mathur C, Huch V. *Organometallics* 1998; **17**: 1044.
31. Veith M, Mathur S, Huch V. *J. Chem. Soc., Chem. Commun.* 1997; 2197.
32. Daniele S, Tcheboukov D, Hubert-Pfalzgraf LG, Lecocq S. *Inorg. Chem. Commun.* 2002; **5**: 347.
33. Daniele S, Tcheboukov D, Hubert-Pfalzgraf LG. *J. Mater. Chem.* 2002; **12**: 2519.
34. Limberg C, Hunger M, Habicht W, Kaifer E. *Inorg. Chem.* 2002; **41**: 3359.
35. Becker R, Weiss J, Winter M, Merz K, Fischer RA. *J. Organomet. Chem.* 2001; **630**: 253.
36. Gaur DP, Srivastava G, Mehrotra RC. *Z. Anorg. Allg. Chem.* 1973; **398**: 72.
37. Mehrotra RC, Bachlas BP. *J. Organomet. Chem.* 1970; **22**: 121.
38. Zemlyansky NN, Borisova IV, Kuznetsova MG, Khrustalev VN, Ustynyuk YA, Nechaev MS, Lunin VV, Barrau J, Rima G. *Organometallics* 2003; **22**: 1675.
39. Khrustalev VN, Borisova IV, Zemlyansky NN, Ustynyuk YA, Antipin MY. *Cryst. Rep.* 2002; **47**: 616.
40. Khrustalev VN, Antipin MY, Zemlyansky NN, Borisova IV, Ustynyuk YA, Lunin VV, Barrau J, Rima G. *J. Organomet. Chem.* 2004; **689**: 478.
41. Zemlyansky NN, Borisova IV, Khrustalev VN, Antipin MY, Ustynyuk YA, Nechaev MS, Lunin VV. *Organometallics* 2003; **22**: 5441.
42. Khrustalev VN, Portnyagin IA, Zemlyansky NN, Borisova IV, Ustynyuk YA, Antipin MY. *J. Organomet. Chem.* 2005; **690**: 1056.
43. Khrustalev VN, Portnyagin IA, Zemlyansky NN, Borisova IV, Nechaev MS, Ustynyuk YA, Antipin MY, Lunin V. *J. Organomet. Chem.* 2005; **690**: 1172.
44. Wakeshima I, Kijima I. *Chem. Lett.* 1972; 325.
45. Boyle TJ, Alam TM, Rodriguez MA, Zechmann CA. *Inorg. Chem.* 2002; **41**: 2574.
46. Sita LR, Babcock JR, Xi R. *J. Am. Chem. Soc.* 1996; **118**: 10912.
47. Fjeldberg T, Hitchcock PB, Lappert MF, Smith SJ, Thorne AJ. *J. Chem. Soc., Chem. Commun.* 1985; 939.
48. Teff DJ, Minear CD, Baxter DV, Caulton KG. *Inorg. Chem.* 1998; **37**: 2547.
49. Sita LR, Xi R, Yap GPA, Liable-Sands LM, Rheingold AL. *J. Am. Chem. Soc.* 1997; **119**: 756.
50. Brill TB, Campbell NC. *Inorg. Chem* 1973; **12**: 1884.
51. Howie RA, Moser W. *Nature* 1968; **219**: 373.
52. Harrison PG, Haylett BJ, King TJ. *J. Chem. Soc., Chem. Commun.* 1978; 112.
53. Sasaki Y, Miyazawa N. *Kinki Daigaku Rikogakubu Kenkyu Hokoku* 1992; **28**: 237.
54. Zhang T, Shen Y, Zhang RF, Liu X. *Mater. Lett.* 1996; **27**: 161.
55. Bowden ME. *J. Mat. Sci. Lett.* 1990; **9**: 735.
56. Cardile CM, Bowden ME, Koplick AJ, Buckley RG. *Thin Solid Films* 1990; **186**: L11.
57. Hashemi T, Al-Dhhan ZT, Hogarth CA. *J. Mater. Sci.* 1989; **24**: 615.
58. Xiangfeng C, Zhiming C. *Sensors Actuators B* 2004; **98**: 215.
59. Zhang T, Yusheng S, Qiang D, Huajun F. *J. Mater. Sci. Lett.* 1994; **13**: 1647.
60. Blackmore JM, Cattell AF. *Thin Solid Films* 1990; **185**: 97.
61. Cardile CM, Koplick AJ, McPherson R, West BO. *J. Mater. Sci. Lett.* 1989; **8**: 370.
62. Chandler C, Fallon GD, West BO. *J. Chem. Soc., Chem. Commun.* 1990; 1063.
63. Babcock JR, Wang A, Metz AW, Edleman NL, Metz MV, Lane MA, Kannewurf CR, Marks TJ. *Chem. Vapor Depos.* 2001; **7**: 239.
64. Gulino A, Dapporto P, Rossi P, Fragalà I. *Chem. Mater.* 2002; **14**: 4955.
65. Gulino A, Castelli F, Dapporto P, Rossi P, Fragalà I. *Chem. Mater.* 2002; **14**: 704.
66. Metz AW, Lane MA, Kannewurf CR, Poeppelmeier KR, Marks TJ. *Chem. Vapor Depos.* 2004; **10**: 297.
67. Bustos L, Green JH, Hencher JL, Khan MA, Tuck DG. *Can. J. Chem.* 1983; **61**: 2141.
68. Veith M, Mathur S, Huch V. *J. Chem. Soc., Dalton Trans.* 1996; 2485.
69. Veith M, Hans J, Stahl L, May P, Huch V, Sebald A. *Z. Naturforsch. B* 1991; **B 46**: 403.
70. Edwards DA, Harker RM, Mahon MF, Molloy KC. *J. Mater. Chem.* 1999; **9**: 1771.
71. Molloy KC, Purcell TG, Quill K, Nowell I. *J. Organomet. Chem.* 1984; **267**: 237.

72. Gsell R, Zeldin M. *Inorg. Nucl. Chem.* 1975; **37**: 1133.
73. Sheldrick GM. SHELX 86S, A Computer Program for Crystal Structure Determination. University of Gottingen, Gottingen, 1986.
74. Sheldrick GM. SHELX 97L, A Computer Program for Crystal Structure Refinement. University of Gottingen, Gottingen, 1997.
75. McArdle P. *J. Appl. Crystallogr.* 1994; **27**: 438.

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