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FULL PAPER

Stabilisation of unusual metal co-ordination geometries using an oxo-cubane ligand; syntheses and structures of $[\{Sn_4(N^tBu)_3O\}_3LiCl]\cdot 3thf$ and $[\{Sn_4(N^tBu)_3O\}_3FeCl_2]\cdot 3thf$

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Complexation of LiCl and $FeCl_2$ with the oxo-cubane $[Sn_4(N^tBu)_3O]$ **1** (3 equivalents) gave $[\{Sn_4(N^tBu)_3O\}_3LiCl]\cdot 3thf$ **2** and $[\{Sn_4(N^tBu)_3O\}_3FeCl_2]\cdot 3thf$ **3**, respectively; the co-ordination of three sterically demanding, 'ether-like' $[Sn_4(N^tBu)_3O]$ ligands to the Li^+ and Fe^{2+} centres of **2** and **3** results in unusual geometries for these metals. The geometry in **2** can be described as a distorted trigonal bipyramid with one vertex missing, while in **3** it is trigonal bipyramidal. Model semi-empirical calculations combined with the structural findings stress that although sterically encumbered **1** is a highly effective ligand for oxophilic metals.

Introduction

Despite the current interest in the co-ordination chemistry[1,2] and applications[3] of anionic ligand systems based on p block element imido and phosphinidene frameworks, little attention has been paid to related neutral species. In this regard, Veith and co-workers[4] first prepared the oxo-cubane complex $[Sn_4(N^tBu)_3O]$ **1** from the reaction of the *nido*-cubane fragment $[Sn_3(N^tBu)_4H_2]$ with water–RNH_2. The ability of **1** to behave as a ligand was also demonstrated by its co-ordination to the Lewis acid $AlMe_3$ in the adduct $[Sn_4(N^tBu)_3O]\cdot AlMe_3$.[4] However, although these findings were reported almost twenty years ago no further studies of the co-ordination chemistry of this unusual 'ether-like' ligand have been published. Recently, we showed that **1** is more directly accessible in high yield by a one-pot reaction involving the controlled hydrolysis of the parent imido cubane $[Sn_4(N^tBu)_4]$ with water in a thf–MeCN solvent mixture.[5] Our interests in this ligand are twofold. First, the potential for the elimination of thermodynamically stable oxides and hydroxides makes **1** useful in selective functional group modification. For example, hydrolysis of $[Sn_4(NR)_4]$, followed by reaction of intermediate $[Sn_4(NR)_3O]$ with R′NHLi (with elimination of LiOH) gives a potentially general, direct route to heteroleptic cubanes $[Sn_4(NR)_3(NR')]$.[5] Secondly, **1** is a unique ligand set which combines two normally conflicting properties for such a neutral system. Although sterically encumbered at its periphery, in theory the large development of negative charge on the oxygen centre should make **1** a particularly effective ligand for hard, oxophilic metal ions.

In view of the lack of structural data on complexes containing $[Sn_4(NR)_3O]$ ligands we have recently initiated studies of the co-ordination chemistry of this ligand set with various metals. It was hoped also that these studies would serve as a model for future work on the related Group 15 anions $[Sn_4(NR)_3E]^-$ (E = N or P).[6] We report here the syntheses and structures of the two new tris-solvated complexes $[\{Sn_4(N^tBu)_3O\}_3LiCl]\cdot 3thf$ **2** and $[\{Sn_4(N^tBu)_3O\}_3FeCl_2]\cdot 3thf$ **3**. The unusual geometries of the metal ions found in these species, together with model semiempirical MO calculations, highlight the unique nature of this ligand system.

Discussion

The oxo-cubane **1** was prepared according to the method reported by us previously, by the careful hydrolysis of a dilute solution of $[Sn_4(N^tBu)_4]$ (1 equivalent) in thf with a dilute solution of water (1 equivalent) in MeCN at −78 °C.[5] This method can be performed on the 20 mmol scale. However, yields of **1** from this reaction are in general highly variable (40–80%), with the highest being obtained where the addition of the water–MeCN solution is as slow as possible and where rigorously dried reagents and solvents are used. Samples of **1** are best stored as standardised solutions in thf at −25 °C, as the complex apparently decomposes on prolonged storage of the solid at room temperature (eventually becoming insoluble in organic solvents). The compounds $[\{Sn_4(N^tBu)_3O\}_3LiCl]\cdot 3thf$ **2** and $[\{Sn_4(N^tBu)_3O\}_3FeCl_2]\cdot 3thf$ **3** were obtained in moderate yields (54 and 44%, respectively) by the addition of a thf solution of **1** (3 equivalents) to suspensions of LiCl (1 equivalent) and $FeCl_2$ (1 equivalent), respectively, in thf at 25 °C (Scheme 1).

$$3[Sn_4(N^tBu)_3O] + MX_n \xrightarrow{\text{thf}} [\{Sn_4(N^tBu)_3O\}_3MX_n]\cdot 3thf$$
$$X = Cl, M = Li\ (n = 1)\ (\mathbf{2})\ \text{or}\ Fe\ (n = 2)\ (\mathbf{3})$$

Scheme 1

The products are readily isolated by precipitation with Et_2O, producing material suitable for analytical and spectroscopic studies. Elemental analysis confirmed their basic identities. However, although the later structural characterisation of **2** and **3** revealed that three thf molecules are present in the crystal lattices of both complexes, their isolation under vacuum (10^{-1} atm) prior to analysis produces unsolvated material. Little information could be gleaned from the room-temperature ^1H NMR spectra of **2** and **3**, which exhibit only a singlet resonance for the ^{t}Bu groups of the co-ordinated oxo-cubane ligands. Although the chemical shifts of the ^{t}Bu groups in both complexes are very similar, broadening of this resonance occurs for **3** as a result of its paramagnetic nature.

Crystals of compounds **2** and **3** suitable for X-ray studies were grown by prolonged storage of their thf solutions at

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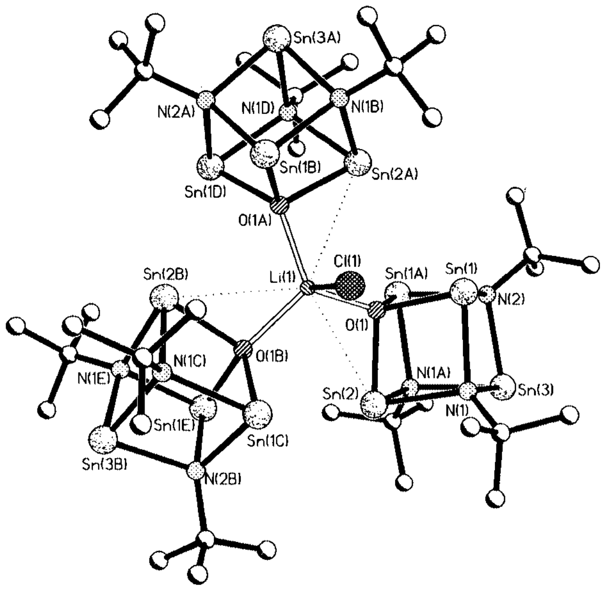

Fig. 1 Structure of compound **2**. The H atoms and lattice-bound thf molecules have been omitted for clarity.

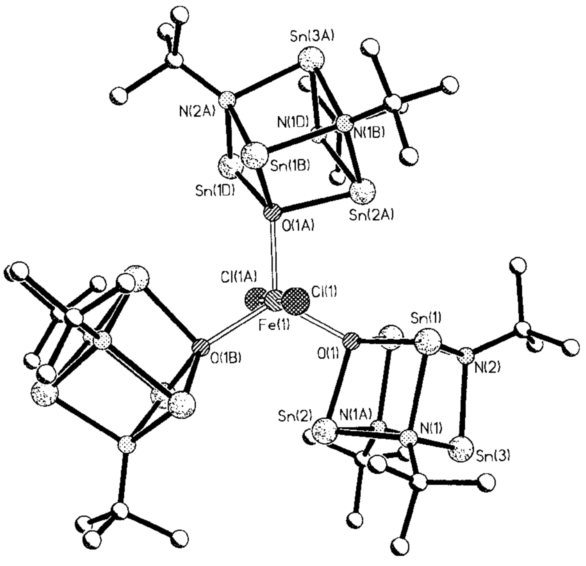

Fig. 2 Structure of compound **3**. Details as in Fig. 1.

Table 1 Key bond lengths (Å) and angles (°) for $[\{Sn_4(N^tBu)_3O\}_3LiCl]\cdot 3thf$ **2** and $[\{Sn_4(N^tBu)_3O\}_3FeCl_2]\cdot 3thf$ **3**

	2 (M = Li)	**3** (M = Fe)
M(1)–Cl(1)	2.19(4)	2.429(3)
M(1)–O(1)	1.94(1)	2.026(7)
Li(1) · · · Sn(2)	3.172(5)	—
Li(1) · · · Sn(1)	3.39(1)	—
Sn(1)–O(1)	2.148(6)	2.165(5)
Sn(2)–O(1)	2.116(9)	2.168(7)
Sn(1)–N(1)	2.21(1)	2.224(9)
Sn(1)–N(2)	2.209(7)	2.206(6)
Sn(2)–N(1)	2.167(9)	2.159(9)
Sn(3)–N(1)	2.185(9)	2.210(9)
Sn(3)–N(2)	2.18(1)	2.19(1)
O(1)–M(1)–O(1A)	115.7(8)	120
O(1)–M(1)–Cl(1)	102(1)	90
Sn–O(1)–M(1) range	102.8(4)–134(1)	101.7(3)–123.5(2)
Sn–O(1)–Sn range	100.4(4)–101.6(3)	101.1(2)–101.7(3)
N–Sn–N mean	81.6	81.2
Sn–N–Sn mean	97.7	98.3
N–Sn–O	mean 79.7	78.8

−15 °C. Table 1 lists key bond lengths and angles for both complexes. The structures of **2** (Fig. 1) and **3** (Fig. 2) are composed of LiCl and $FeCl_2$ units which are co-ordinated at their metal centres by the O atoms of three symmetry-related $[Sn_4(N^tBu)_3O]$ ligands. Both complexes crystallise in the hexagonal system *P*6(3)/*m*, in which the monomer units form a close-packed arrangement in the crystal with thf molecules (three for each monomer) residing within the octahedral and tetrahedral interstice. The steric conflict between the N^tBu groups, resulting from the accommodation of the oxo-cubane donors within the co-ordination spheres of the Li^+ and Fe^{2+} ions, causes the ligands to adopt a 'titled' orientation. This leads to large variations in the associated Sn–O–Li and Sn–O–Fe angles [Sn–O(1)–Li(1) range 102.8(4)–134(1)° in **2**; Sn–O(1)–Fe(1) range 101.7(3)–123.5(2)° in **3**], and to the apparent misalignment of the oxygen lone pairs from the axes of the O–M bonds. However, there is no obvious effect on the strengths of ligand–metal bonding in either complex. Indeed, the Li–O bonds in **2** [1.94(1) Å] are similar to those observed in a variety of species containing neutral oxygen ligands,[7] and the Fe–O bond lengths in **3** [2.026(7) Å] are extremely short for a neutral complex with such a high co-ordination number.[8] The ligand co-ordination mode present in **2** and **3** contrasts with the more regular pattern found in $[Sn_4(N^tBu)_3O]\cdot AlMe_3$ [Sn–O–Al range 117.4(2)–118.7(2)°].[4] One intriguing consequence of this more asymmetric ligand co-ordination in **2** is the promotion of relatively short intramolecular Sn · · · Li contacts [Sn(2) · · · Li(1) 3.172(5), Sn(1) · · · Li(1) 3.39(1) Å]. Although significantly longer than the direct Sn–Li bonds found in monomers of $Ph_3SnLi\cdot PMDETA$ (PMDETA = $\{Me_2NCH_2CH_2\}_2NMe$) (average 2.82 Å),[9] the Sn atoms of the cubane $[Sn(N^tBu)]_4$ are known to co-ordinate various metal centres (*e.g.* in $[Sn(N^tBu)]_4\cdot AlCl_3$).[10] Some evidence in support of Sn · · · Li interaction involving Sn(2) is the shortness of the Sn(2)–O(1) bond [Sn(2)–O(1) 2.116(9) Å; *cf.* 2.148(6) Å for the remaining Sn–O bonds in **2**, mean 2.17 Å in **3** and 2.096(9)–2.168(9) in **1**].

The most obvious impact of the co-ordination of the sterically demanding $[Sn_4(N^tBu)_3O]$ ligands in compounds **2** and **3** is the unusual geometries adopted by the metal centres. There is a large distortion from tetrahedral geometry for the Li^+ cation of **2**, with the metal centre being situated only 0.33 Å out of the plane of the three co-ordinating oxygen centres. While distortion from pure tetrahedral geometry is commonplace in complexes of Li^+, the distortion towards a trigonal bipyramidal arrangement (with one vertex missing) in **2** is reminiscent of crown ether co-ordination to an alkali metal, *e.g.* in [LiCl{12-crown-4}].[11] Also unusual is the discrete molecular structure of **2** itself. Although monomeric complexes of the type $LiX\cdot L_3$ (X = F to I) have been structurally characterised where L is a nitrogen donor,[12] in all examples involving O donors further association of the LiX units occurs as a result of halide bridging.[13] Complex **3** also has an unusual geometry for a monomeric iron(II) complex. Trigonal bipyramidal geometry is relatively uncommon even for monomeric iron(III) complexes[14] and there appear to be no monomeric examples for Fe^{II} involving monodentate ligand sets. This geometry has only been observed where more elaborate cyclic or chain polydentate ligands enforce greater geometric demands, *e.g.* the cations $[FeX(pp_3)]^+$ [X = Br or SH; pp_3 = tris(2-phenylphosphinoethyl)-phosphine],[15] or in a few oligomeric complexes, *e.g.* the tetranuclear complex $[Fe_4Cl_8]\cdot 6thf$.[8c]

In the previous investigation of the adduct $[Sn_4(N^tBu)_3O]\cdot AlMe_3$[4] it was suggested that one possible reason for the Lewis base characteristics of **1** in this complex is the relief from Sn/O lone pair repulsion which accompanies the donation of the oxygen lone pair into the vacant orbital of the Al. At first sight this difference between **1** and Me_3O^+ (in which the O is also three-co-ordinate) provides one explanation as to why the latter is an extremely poor ligand. However, this comparison would clearly undervalue the detrimental effect that the positive

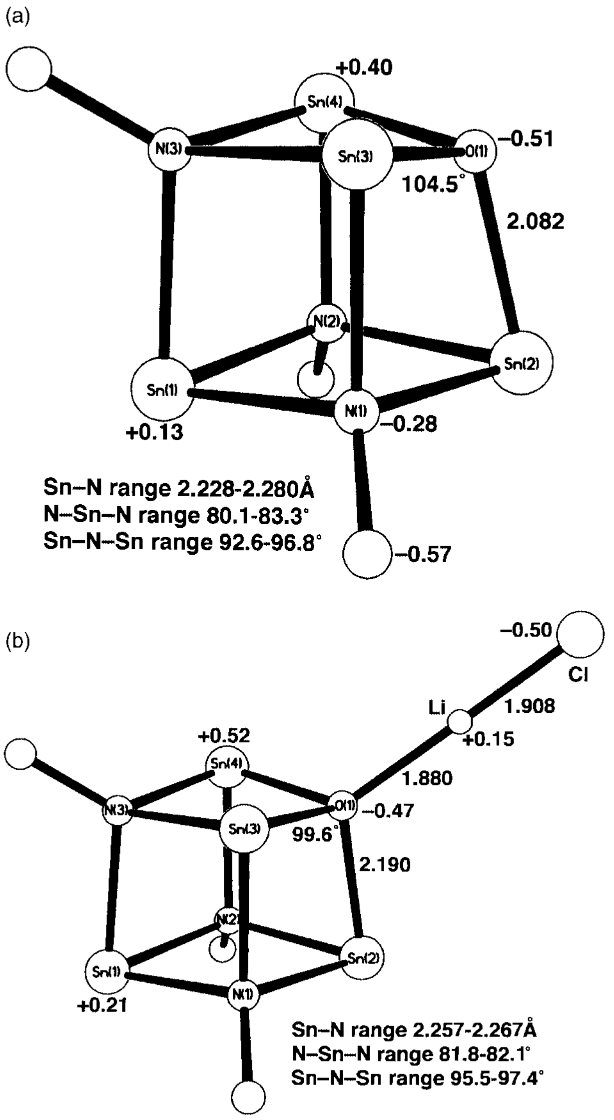

Fig. 3 Geometry optimised structure of (a) $[Sn_4(NMe)_3O]$ and (b) $[Sn_4(NMe)_3O]\cdot LiCl$. Key bond lengths (Å) and angles (°) are shown.

charge of Me_3O^+ has on its ability to co-ordinate electropositive metal centres and the importance of the electronic neutrality of **1**. In order to understand further the reasons for the Lewis base character of **1**, especially in the circumstances which prevail in **2** and **3** where the metal–ligand interactions are highly electrostatic, model semi-empirical PM3 calculations were performed on the complexation of LiCl by the oxo-cubane $[Sn_4(NMe)_3O]$ and, for comparison, the complexation of LiCl by H_2O. The calculated structure of $[Sn_4(NMe)_3O]$ (Fig. 3a) is similar in terms of the key bond lengths and angles to the solid state structure of **1** (Sn–O mean 2.132, Sn–N mean 2.213 Å, Sn–O–Sn mean 101.9, Sn–N–Sn mean 98.1 and N–Sn–N 81.3°). The calculated charges show that there is a high degree of charge separation within the Sn_3O unit of the molecule, resulting in a charge of −0.51e on the O which is significantly greater than on the O in H_2O (−0.36e). The only significant effect of co-ordination to a LiCl monomer is the elongation of the Sn–O bonds and a resulting decrease in the Sn–O–Sn angles within the $[Sn_4(NMe)_3O]$ ligand (from 104.5 to 99.6°) (Fig. 3b). The calculations of the monosolvated model clearly overestimated the magnitude of this effect within the tris-solvated complexes **2** and **3**. The enthalpy of solvation of LiCl by $[Sn_4(NMe)_3O]$ is calculated to be -22.5 kcal mol^{-1}. This value is greater than that calculated for monosolvation of LiCl by H_2O (-13.4 kcal mol^{-1}). Although some care should be taken in attaching too much importance to the absolute values of the charges and enthalpies of formation calculated for these species at this low level, these calculations clearly show that the fundamental reason for the ligand properties of **1** is the high charge carried by its O (making it comparable with H_2O as a donor). Reinforcing this view is the fact that the calculated charges on the O of $[Sn_4(NMe)_3O]$ and H_2O almost directly correlate with the enthalpies of complexation with LiCl (as one might expect for such a predominantly electrostatic situation). In the light of these calculations it is clear why the oxo-cubane **1** can compete effectively for metal co-ordination with thf, as observed in the formation of **2** and **3** in thf solvent.

Conclusion

The results reported suggest that there should be an extensive co-ordination chemistry for $[Sn_4(N^tBu)_3O]$ **1** and related oxo-cubane ligands, and that such ligand systems have unique properties. Although sterically encumbered the high development of the negative charge on the O of **1** should make it suitable for the co-ordination of a broad range of other hard metals.

Experimental

General

Compounds **2** and **3** are air- and moisture-sensitive. They were handled on a vacuum line using standard inert atmosphere techniques and under dry/oxygen-free argon. Diethyl ether and thf were dried by distillation over sodium–benzophenone and MeCN was dried over CaH_2 prior to the reactions. The products were isolated and characterised with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and water internal recirculation system. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and the C, H and N contents were analysed using an Exeter Analytical CE-440 Elemental Analyser. Proton NMR spectra were recorded on a Bruker WM 250 MHz spectrometer in dry deuteriated thf (using the solvent resonances as the internal reference standard). The synthesis of **1** is reported in reference 5.

Syntheses

Compound 2. A solution of compound **1** (1.32 g, 1.87 mmol) in thf (20 ml) was added to a suspension of LiCl (99.9% anhydrous, Aldrich, 0.026 g, 0.61 mmol) at 25 °C. The mixture was stirred for 3 h until all the LiCl had dissolved. The solvent was removed under vacuum until only *ca.* 5 ml remained. Addition of Et_2O (10 ml) gave a yellow precipitate of **2** (0.72 g, 54%). Alternatively, storage of the thf solution at −15 °C (3 weeks) gave yellow crystals of **2** suitable for X-ray diffraction studies. Isolation of **2** under vacuum (10^{-1} atm) leads to loss of the lattice-bound thf. Decomp. >200 °C. ^1H NMR (+25 °C, d_8-thf, 250 MHz): δ 1.40 (s, ^{t}Bu). Found: C, 20.3; H, 3.9; N, 5.9. Calc. for **2** (−3thf): C, 20.1; H, 3.8; N, 5.9%.

Compound 3. A solution of compound **1** (0.70 g, 0.99 mmol) in thf (10 ml) was added to a suspension of $FeCl_2$ (99.99% anhydrous, Aldrich, 0.048 g, 0.38 mmol) at 25 °C. The mixture was stirred for 4 h until all the $FeCl_2$ had dissolved. The brown solution produced was reduced under vacuum to *ca.* 2 ml. Addition of Et_2O (10 ml) gave a brown precipitate of **3** (0.33 g, 44%). Addition of Et_2O (3 ml) to the reduced thf solution and storage at −15 °C (4 weeks) gave brown crystals of **3** suitable for X-ray diffraction studies. Isolation of **3** under vacuum (10^{-1} atm) leads to loss of the lattice-bound thf. Decomp. >200 °C. ^1H NMR (+25 °C, d_8-thf, 250 MHz): δ 1.47 (broad s, ^{t}Bu). Found: C, 19.1; H, 3.0; Cl, 4.0; N, 5.2. Calc. for **3** (−3thf): C, 19.3; H, 3.6; Cl, 3.2; N, 5.6%.

Table 2 Crystal data for [{$Sn_4(N^tBu)_3O$}$_3$LiCl]·3thf **2** and [{$Sn_4(N^tBu)_3O$}$_3FeCl_2$]·3thf **3**

Formula	$C_{48}H_{105}ClLiN_9O_6Sn_{12}$	$C_{48}H_{105}Cl_2FeN_9O_6Sn_{12}$
M	2371.08	2455.44
Crystal system	Hexagonal	Hexagonal
Space group	$P6(3)/m$	$P6(3)/m$
a/Å	16.111(2)	16.302(2)
b/Å	16.111(2)	16.302(2)
c/Å	17.001(2)	16.973(2)
U/Å^3	3821.6(10)	3906.3(11)
Z	2	2
D_c/Mg m^{-3}	2.061	2.088
μ/mm^{-1}	3.924	4.053
Reflections collected	3877	6434
Independent reflections (R_{int})	1741 (0.050)	1761 (0.06)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.043, 0.100	0.040, 0.094
(all data)	0.064, 0.110	0.071, 0.111
Peak and hole/e Å^{-3}	0.611, −0.678	0.716, −0.875

X-Ray crystallographic studies of compounds 2 and 3

Crystals of compounds **2** and **3** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture. X-Ray intensity data for **2** were collected at 180(2) K with a Stoe-Siemens AED diffractometer using a θ–ω scan mode, and for **3** using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least squares on F^2.[16] A semi-empirical absorption correction based on ψ scans was applied in the case of **2**. Although no disorder occurs in the structure of **3**, the LiCl unit of **2** is disordered about the mirror plane of the three co-ordinated oxygen centres, generating another antiparallel LiCl unit with 50 : 50 occupancy for each. Details of the data collection, refinement and crystal data are listed in Table 2.

CCDC reference number 186/1773.

Semi-empirical calculations

PM3 calculations were carried out using VAMP 5.6 (Oxford Molecular)[17] on a Silicon Graphics R4400 workstation. Calculations on [$Sn_4(NMe)_3O$] and [$Sn_4(NMe)_3O$]·LiCl were performed initially in C_{3v} symmetry prior to free refinement with no symmetry constraints (the process resulting in a small lowering in energy). A similar approach was used for LiCl·H_2O. Values of ΔH for formation of calculated geometries (kcal mol^{-1}): H_2O −53.43, LiCl −47.97, LiCl·H_2O −114.79, [$Sn_4(NMe)_3O$] 33.34, [$Sn_4(NMe)_3O$]·LiCl −37.61.

Acknowledgements

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