An E_4O_4 heterocubane structure with a trivalent element of group 13 realized in $In_4O_4[C(SiMe_3)_3]_4$

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The tetrahedral indium(I) compound $In_4[C(SiMe_3)_3]_4$ **1** reacts with the oxygen donor *o*-nitrosotoluene to form the extremely hygroscopic $In_4O_4[C(SiMe_3)_3]_4$ **2** in moderate yield, which exhibits a distorted In_4O_4 molecular center with normal In–O bond lengths, but short intracage In···In and O···O distances.

Although heterocubane type compounds $X_4(ER)_4$ with E a group 13 element, X a chalcogen atom and R an alkyl or aryl group have been known for several years with a continually increasing number of X = S, Se or Te,[1–4] no information concerning the properties or structure of the oxygen analogues is available from literature. Recently, a new method for the synthesis of such derivatives was developed by the treatment of tetrahedral element(I) clusters like $In_4[C(SiMe_3)_3]_4$ **1**[3,5] with elemental sulfur, selenium or tellurium, which gave the heterocubane compounds in high yields.[3,4] Their formation and structure can be described by the occupation of all tetrahedral faces of the cluster by chalcogen atoms. Dry oxygen and **1** gave no isolable products and, as previously reported,[5] moist air yielded the compound $In_4O(OH)_6[C(SiMe_3)_3]_4$[6] upon partial hydrolysis. Therefore, we searched for a suitable oxygen donor to oxidize **1** under mild conditions and to synthesize the up to now unknown In_4O_4 derivative.

Phosphane oxides or trimethylamine *N*-oxide did not react with **1**, and mixtures of unknown products resulted with bis(trimethylsilyl)peroxide. *p*-Nitrotoluene gave the In_4O_4 product **2** in a low yield, but the reaction was not well reproducible. The best result was obtained with *o*-nitrosotoluene (Scheme 1),† which formed, upon transfer of its oxygen atom to **1**, the corresponding dark red diazobenzene derivative identified by IR, NMR and UV–VIS spectroscopy. Mixed crystals of both products were isolated from hexane, in which the diazo compound was so strongly disordered that the structure could not be refined satisfactorily. Treatment with toluene to dissolve the more readily soluble diazo compound and recrystallization from hexane gave the colorless In_4O_4 derivative **2** in a yield of 24%. Compound **2** is hygroscopic and forms $In_4O(OH)_6[C(SiMe_3)_3]_4$[6] upon hydrolysis, which can be separated from the less soluble **2** by recrystallization. Crystal-
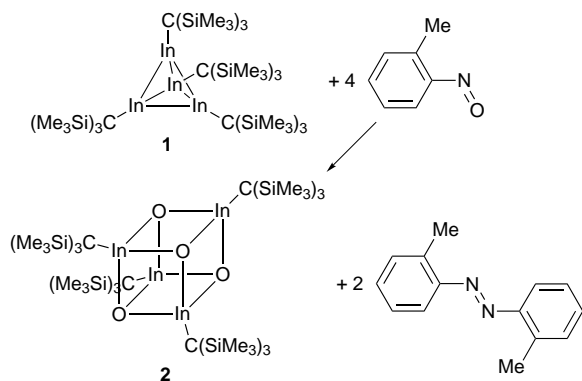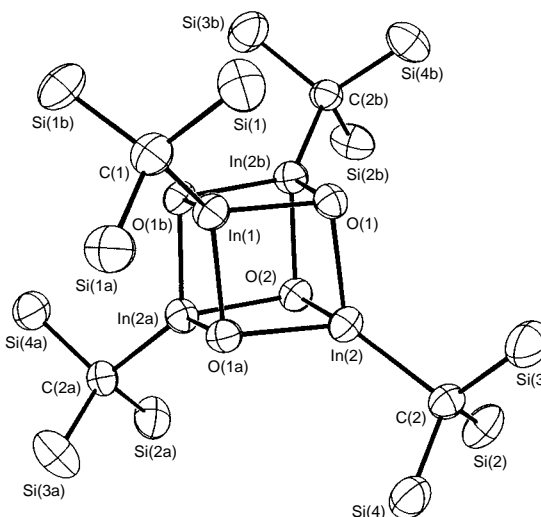
Fig. 1 Molecular structure of **2**. Selected bond lengths (pm) and angles (°): In(1)–O(1) 214.3(5), In(2)–O(1) 213.3(5), In(2)–O(1a) 214.0(5), In(2)–O(2) 213.8(5), In(1)–C(1) 222(1), In(2)–C(2) 216.5(7); O–In–O 84.4(2)–84.8(2), In–O–In 95.0(3)–95.3(2).

line **2** decomposes at 390 °C and is thermally more stable than its analogues with heavier chalcogens, for which decomposition points gradually decrease (330 °C for X = Te).[3,4] The molecule does not dissociate in benzene, as shown by the cryoscopically determined molar mass.

The structure of **2** (Fig. 1) shows a distorted In_4O_4 heterocubane in the molecular center with normal In–O bond lengths [213.3(5)–214.3(5) pm] and each In atom bound to a terminal alkyl group.‡ To the best of our knowledge, similar structures have not been observed before. The compounds $[MeIn(OH)(O_2PPh_2)]_4\cdot4py$ (py = pyridine) and Ga_8-$(pz)_{12}O_4Cl_4$ (pz = pyrazolate) exhibit an $In_4(OH)_4$ or a Ga_4O_4 cube,[7] but due to the coordination number of four at the oxygen atoms and the bridging of faces or edges of the cages they are not comparable to the $E_4X_4R_4$ compounds discussed here. Also, the thallium(I) alcoholates with $Tl_4(OR)_4$ heterocubanes,[8] μ_3-OR groups and no alkyl substituents at the Tl atoms belong to another class of compounds. The series of the tetrachalcogen derivatives of **1** is completed with the synthesis of **2**. Comparison of important structure parameters in Table 1 shows that, with the exception of the oxygen compound **2**, the sum of

Scheme 1

Scheme 1

Table 1 Comparison of important structure parameters of the heterocubane molecules $In_4X_4R_4$ [X = chalcogen, R = $C(SiMe_3)_3$, $\Sigma r(X)$ = sum of the van der Waals radii of the chalcogen atoms,[9] $\Sigma r(In)$ = 380 pm]

	In–X/ pm	In–X– In/°	X–In– X/°	In···In/ pm	X···X/ pm	$\Sigma r(X)$/ pm
$In_4O_4R_4$	214.0	95.1	84.6	315.7	287.9	300
$In_4S_4R_4$	254.9	86.8	93.1	350.4	370.0	360
$In_4Se_4R_4$	267.1	85.4	94.4	362.1	392.1	380
$In_4Te_4R_4$	286.4	83.7	95.6	382.9	425.2	420

the van der Waals radii[9] is exceeded between the chalcogen atoms, which may be caused by the charge distribution in the cage and a strong electrostatic repulsion between the more electronegative atoms. In contrast, the In–In distances are equal to (X = Te) or smaller (X = S, Se) than the sum of the van der Waals radii (380 pm). The difference between the intramolecular In$\cdots$In and X$\cdots$X distances increases from 20 pm for X = S to 42 pm for X = Te with the smallest distance always between the In atoms. The situation changes with the oxygen derivative **2**, where the In$\cdots$In distance (315.7 pm) is larger than the O$\cdots$O distance (287.9 pm). Both are smaller than the sum of the van der Waals radii, and the In$\cdots$In distance approaches the bond length in the indium(I) compound **1** (300.2 pm)[3] indicating a considerable steric stress in the molecule. The inverse ratio of the homoatomic intracage distances leads to quite different bond angles. The most acute angles ($< 90°$) of **2** are observed at the In atoms, while with X = S, Se and Te they occur at the chalcogen atoms. The largest distortion of the cube is observed for the Te derivative, it decreases gradually to X = S and is reversed between X = S and O. The bond angles in **2** are in good agreement with values predicted by Barron and coworkers from a relation between intracage bond angles in known E_4X_4 cubane molecules and the ratio of the covalent radii of the elements.[2]

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Notes and References

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† Compound **1** (200 mg, 0.145 mmol) was treated under argon with 20 ml (0.579 mmol) of a solution of sublimed *o*-nitrosotoluene in *n*-hexane (stored over molecular sieve, $c = 3.5$ mg l^{-1}), the mixture was warmed to 50 °C for 36 h, during which it changed from violet to brown–red. After concentration and cooling to -50 °C, red crystals were isolated which were washed with toluene and recrystallized from hexane. Yield: 56 mg (24%); decomp. 390 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 0.49. ^{13}C NMR (75.5 MHz, C_6D_6): δ 29.7 (InC), 6.3 (SiMe$_3$). IR (paraffin, cm^{-1}): 1260m, 1250m (δCH$_3$); 1169vw, 1154vw, 1017vw; 858vs, 766s, 721m (ρCH$_3$); 671m, 654w, 615w (νSiC); 520w, 496w, 466w, 426w, 399w (νInC), (νInO); 362 (δSiC). FD-MS: *m/z* 1448.9 (M$^+$). Molar mass (cryoscopically in benzene): obs. 1375, calc. 1449.6 g mol^{-1}.

‡ *Crystal data*: single crystals from *n*-hexane; two solvent molecules included; $C_{40}H_{108}In_4O_4Si_{12}\cdot 2C_6H_{14}$, cubic, space group $Pa\bar{3}$ (no. 205), $a = 25.536(2)$ pm, $U = 16\ 652(2)$ Å^3; $Z = 8$; $D_c = 1.271$ g cm^{-3}; crystal dimensions $0.5 \times 0.4 \times 0.4$ mm, $T = 293$ K; μ(Mo-Kα) = 1.299 mm^{-1}; ω–2θ scan, range $3 < 2\theta < 50°$, $0 \leq h \leq 20$, $0 \leq k \leq 21$, $2 \leq l \leq 30$; STOE STADI4 diffractometer; 4774 independent reflections; 2555 reflections with $F > 4\sigma(F)$; structure solved by direct methods and refined with all independent structure factors based on F^2;[10] 239 parameters; $R1 = 0.079$, $wR2 = 0.113$; max., min. residual electron density 0.548, -0.394. The molecule is located on a crystallographic threefold rotation axis across the atoms C(1), In(1) and O(2). The hexane molecules are disordered; their carbon atoms were refined isotropically; hydrogen atoms were not considered. CCDC 182/728.

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