A Penta-Indium Oxo Alkoxide Cluster with a Central 5-Co-ordinate Oxygen. Preparation and *X*-Ray Crystal Structure of $(InOPr^i)_5(\mu_2\text{-}OPr^i)_4(\mu_3\text{-}OPr^i)_4(\mu_5\text{-}O)$

Donald C. Bradley,* Halina Chudzynska, Dario M. Frigo, Michael B. Hursthouse,* and Muhammed A. Mazid

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

The *X*-ray crystal structure of $(InOPr^i)_5(\mu_2\text{-}OPr^i)_4(\mu_3\text{-}OPr^i)_4(\mu_5\text{-}O)$ reveals a square-pyramidal arrangement of indium atoms about a central oxygen; five of the alkoxo groups are terminal, four are μ_2 about the basal metals, and four are μ_3 about the triangular faces of the pyramid; the geometry about each metal is highly distorted octahedral.†

The alkoxide chemistry of indium consists mainly of the simple homoleptic compounds $In(OR)_3$, [R = Me, Et, Pr^i, Bu^n, Bu^s, Bu^t, $Pent^n$][1] mixed metal alkoxides, *e.g.* $In[M(OPr^i)_4]_3$ (M = Al, Ga)[2] and some dialkylindium alkoxides R_2InOR', [R = Me, R′ = Me,[3] Bu^t,[4] $CMe(CF_3)_2$;[5] R = Bu^t, R′ = Et[6]]. Crystal structures are limited to $(Bu_2{}^tInOEt)_2$[6] and a substituted methoxo-bridged dinuclear compound.[7] Indium has been shown to cluster *via* OH bridges, *e.g.* $[L_4In_4(OH)_6](S_2O_6)_3\cdot 4H_2O$[8] and to form the oxygen-centred cluster $O[(Me_3Si)_3CIn]_4(OH)_6$.[9]

We report here the preparation and *X*-ray crystal structure‡ of $(InOPr^i)_5(\mu_2\text{-}OPr^i)_4(\mu_3\text{-}OPr^i)_4(\mu_5\text{-}O)$, Figure 1, in which an oxygen-centred square pyramid of indium atoms is bridged by four μ_2-alkoxo groups around the equator and four μ_3-alkoxo groups on the triangular faces of the pyramid; the cluster possesses virtual C_{4v} symmetry and the geometry about each indium is highly distorted octahedral. Besides being an indium cluster of unusual symmetry and the first structurally determined indium oxo-alkoxo compound, only one other μ_5-O system is known, the structurally similar organometallic $(CpY)_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe_4)(\mu_5\text{-}O)$ (Cp = η-C_5H_5).[10] This structural type may be of great significance as an intermediate in the decomposition of group III metal alkoxides to the corresponding metal oxide, either by metal-organic chemical vapour deposition[11] or by sol-gel deposition.[12]

There is clearly no M–M bonding in the structure, the average distances base–base and base–apex being 3.16 and 3.26 Å respectively (the covalent radius of indium is *ca.* 1.4 Å). The basal indium atoms are virtually planar and have a mean distance to the central oxygen of 2.24 Å as compared with 2.21 Å for the apical indium. The central oxygen is only 0.16 Å above the quasi-plane formed by the basal indiums. The mean terminal In–O distance is 1.96 Å; the μ_2-alkoxo bridges are symmetrical with a mean In–O distance of 2.14 Å, as compared with 2.15 and 2.17 Å found in $(Bu_2{}^tInOEt)_2$.[6] The μ_3-alkoxo bridges are highly asymmetrical about the trianguular faces of the pyramid, the distances to the apical metal being on average 0.12 Å shorter than to the basal indium atoms.

The title compound was synthesised as follows: a commercial sample of 'anhydrous' $InCl_3$ (subsequently shown to be partially hydrated) was dissolved in isopropanol and added slowly to a solution of $NaOPr^i$ prepared by dissolving the requisite amount of sodium in isopropanol/benzene (1 : 4 vol. mixture). The mixture was refluxed for 2 hours and allowed to cool to room temperature. The white precipitate was filtered off and the filtrate concentrated *in vacuo* to give large colourless crystals of $[In_5O(OPr^i)_{13}]$ in 44% yield based on indium. [M.p. 158 °C, decomp.; satisfactory elemental analyses obtained; ^{1}H n.m.r. (C_6D_6, 80 MHz) δ 4.57 (13H, m, CH) 1.65 (48H, d, *J* 6 Hz, Me from μ_2- and μ_3-OPr^i) 1.49 (30H, d, *J* 6 Hz, Me from terminal OPr^i)]. The doublet due to the terminal OPr^i groups remained essentially unchanged to −80 °C ($C_6D_5CD_3$, 400 MHz) whilst that due to the bridging alkoxo groups collapsed at around −30 °C (250 MHz) and had split into two broad peaks of equal intensity flanking the terminal signal by −60 °C (250 MHz). Since the separation of these peaks is 0.24 p.p.m. this implies the $\Delta G^\ddagger$ for exchange between μ_2- and μ_3-bridging sites lies in the range 43—49 kJ mol^{-1}. Since the terminal signal does not split to −80 °C (into 4 : 1, basal : apical) then either the fluxionality must be extremely facile or the chemical shift difference very small.

The title compound is clearly a partial hydrolysis product and its possible formation from $In(OPr^i)_3$ and water (5 : 1 molar ratio) is now under investigation.

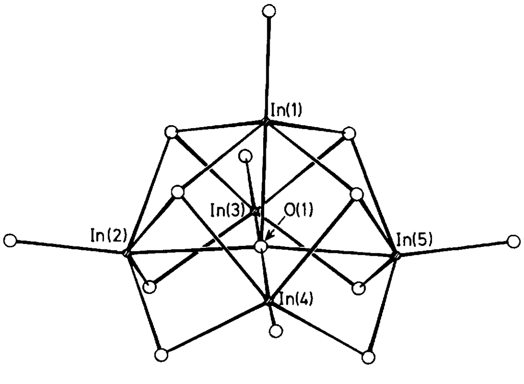

Figure 1. Structure of the In_5O_{14} unit in $O(InOPr^i)_5(\mu_2\text{-}OPr^i)_4(\mu_3\text{-}OPr^i)_4$. Selected bond lengths (Å): In(1)–O(1), 2.211(9); mean basal In–O(1), 2.24 ± 0.02; mean terminal In–O, 1.96 ± 0.013; mean basal In–μ_2-O 2.14 ± 0.014; mean In(1)–μ_3-O, 2.22 ± 0.01; mean basal In–μ_3-O, 2.34 ± 0.025. Selected bond angles (°): mean basal In–O(1)–In(1), 94.2 ± 0.6; mean basal In–O(1)–basal In : *trans*, 171.5 ± 1.1, *cis*, 89.7 ± 0.7.

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† In attempting to prepare $M(OPr^i)_3$ (M = Y and Yb) from the MCl_3 and $LiOPr^i$ under stringently anhydrous conditions we have obtained the compounds $M_5O(OPr^i)_{13}$ which appear to be analogous to the indium compound (satisfactory elemental analyses have been obtained). Unlike the indium compound which we have been unable to sublime, the yttrium and ytterbium compounds were sublimed at *ca.* 200 °C/10^{-2} mm Hg and gave mass spectra which confirmed that the integrity of these clusters was maintained in the vapour.

‡ *Crystal data* for $C_{39}H_{91}O_{14}In_5$, M = 1358.25, monoclinic, space group P_21/n, a = 12.665(2), b = 21.305(2), c = 20.910(6) Å, β = 90.70(2)°, U = 5641.68 Å^3, D_c = 1.598 g cm^{-3}, Z = 4, $F(000)$ = 2668, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 18.99 cm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares analysis. Anisotropic thermal parameters were assigned for all atoms included. The isopropyl groups showed large thermal motion and C–O and C–C distances were fixed at 1.40 and 1.50 Å respectively. The refinement converged with R = 0.057 and R_w = 0.062 for 4680 observed reflections with $F_o \geqslant 3\sigma(F_o)$. The weighting scheme used was $w = 1/[\sigma^2(F_o) + gF_o{}^2]$ where g = 0.0035. Data were collected on a CAD4 diffractometer using θ–2θ scan for $1.5 \geqslant \theta \geqslant 23.0°$ and corrected for absorption empirically. Structure and refinement were performed using the SHELXS-86 and SHELX-76 programs. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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