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Synthesis and Structural Analysis of the Methylindium(III) Binuclear Cation $[(H_2O)Me\overline{In(\mu\text{-mim}_2\text{-pyCO-}N,N',\mu\text{-}O)In}Me(NO_3)]^+$, where the Alkoxide Bridges are formed by Bis(*N*-methylimidazol-2-yl)-(pyridin-2-yl)methanolato-groups

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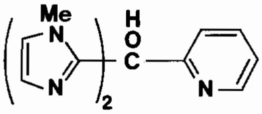
The organometallic cations of the heavier group III elements gallium, indium, and thallium exhibit a rich and diverse coordination chemistry [1]. Of particular interest to us is the lower acceptor properties and pronounced preference for larger C–Tl–C angles in complexes of $Me_2Tl(III)$ compared with $Me_2In(III)$. We have reported studies of the interaction of $Me_2Tl(III)$ with neutral nitrogen donor polydentate ligands [2], and in exploring related $Me_2In(III)$ chemistry we have obtained an unusual binuclear monomethylindium(III) complex involving alkoxide bridges and a new coordination mode for tripodal nitrogen donor ligands. These results are reported here prior to a more extended study of related dimers.

Bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol (mim_2pyCOH) reacts with $Me_2In(NO_3)$ in methanol/water to form a glassy solid on slow evaporation. On dissolution in acetone/methanol, followed by exposure to diethyl ether vapour, colourless crystals were obtained and characterized by structure determination* as $[(H_2O)Me\overline{In(\mu\text{-mim}_2\text{pyCO-}N,N',\mu\text{-O})_2In}Me(NO_3)][NO_3]\cdot H_2O\cdot Me_2CO$ (Fig. 1).



mim_2pyCOH

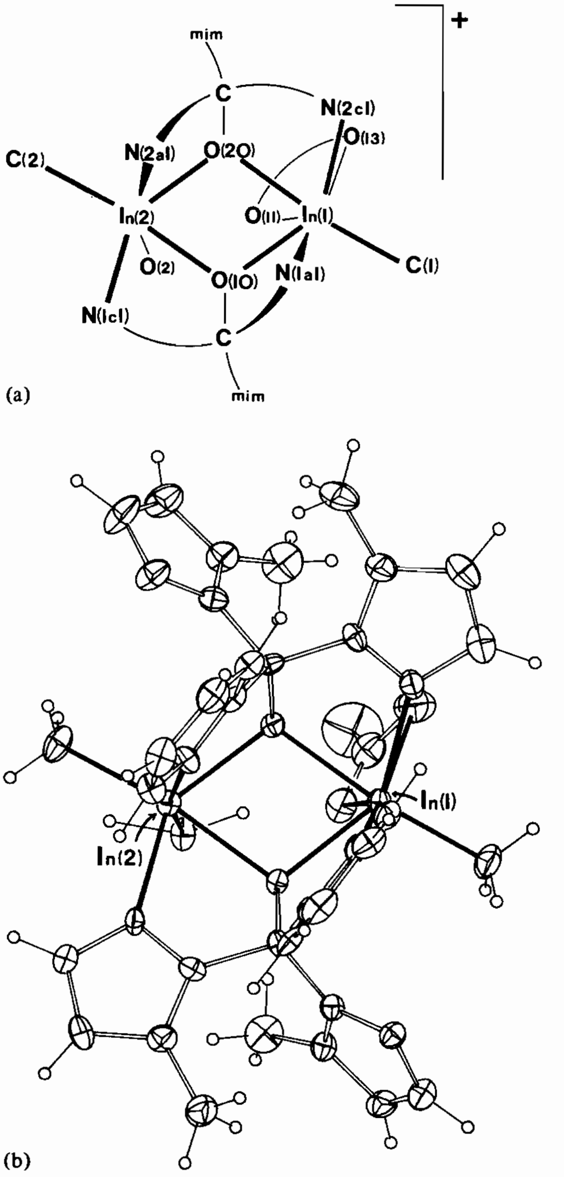


Fig. 1 (a) Idealized structure and (b) ORTEP drawing of $[(H_2O)Me\overline{In(\mu\text{-mim}_2\text{pyCo-}N,N',\mu\text{-O})_2In}Me(NO_3)]^+$ showing selected atom numbering. For In(1): In(1)–C(1), N(1a1, 2c1), O(10,11,13,20), 2.119(11), 2.391(7), 2.259(8), 2.193(6), 2.386(7), 2.802(9), 2.233(6) A, for In(2): In(2)–C(2), N(2a1,1c1), O(2,10,20), 2.153(10), 2.334(7), 2.234(7), 2.300(6), 2.266(6), 2.204(6) A.

The cations have inequivalent methylindium(III) groups bridged by two deprotonated ligands forming alkoxide bridges in an 'In_2O_2' kernel. Each mim_2-$pyCO^-$ group has a py group coordinated to one indium, one mim group coordinated to the other indium, and one uncoordinated mim group, such that each indium has one py and one mim group coordinated to it. Six coordination for In(2), '$InCN_2O_3$',

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*Crystal data: $C_{33}H_{44}N_{12}O_{11}In_2$, space group $P2_1/c$, a = 14.388(6), b = 17.613(10), c = 16.403(10) A, β = 92.18(3)°, Z = 4, R = 0.052 for 3676 observed reflections [$I > 3\sigma(I)$] out of a total of 7165 reflections. Data were collected with a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation (λ = 0.71069 A) and corrected for absorption, with anisotropic thermal parameter refinement for the non-hydrogen atoms.

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is completed by a water molecule, and a nitrate group interacts unsymmetrically with In(1), so that the cation may be formulated as $[(H_2O)MeIn(\mu\text{-mim}_2\text{-pyCo-}N,N',\mu\text{-O})_2InMe(NO_3)]^+$.

The alkoxide bridges are slightly unsymmetrical, with In–O bonds *trans* to methyl groups *ca.* 0.05 Å longer than those *trans* to coordinated mim groups. The nitrate group forms the weakest (semi-bidentate) coordination, with In(1)–O(11) 2.386(7) Å and In(1)–O(13) 2.802(9) Å, longer than the other In–O bonds, 2.205(6)–2.299(6) Å, and In–N bonds, 2.260(8)–2.391(7) Å. The geometry at both indium atoms is irregular, with bond angles 70.5(2)–118.2(3)° for In(1) (excluding O(13)) and 72.0(2)–114.8(3)° for In(2). Except for the orientation of water and nitrate groups, the indium atoms have similar geometry, with analogous donor atoms of the other five groups subtending angles at indium within 2° of each other.

Trimethylindium reacts with alcohols to form alkoxides, e.g. with methanol to form a glassy solid characterized as Me_2InOMe [3], and the dimeric complex reported here presumably results from a similar process. Binding of $\text{mim}_2\text{pyCO}^-$ as a bridging alkoxide represents a new coordination behaviour for the methanols $\text{mim}_n\text{py}_{3-n}\text{COH}$ ($n = 0$–3), with previous structural studies showing nitrogen donor bidentate or tridentate coordination, e.g. for mim_2pyCOH with $Me_2Au(III)$ and MeHg(II), respectively [4, 5], and unidentate coordination with an additional weak Hg•••OH interaction for mim_3COH with MeHg(II) [6].

We are currently investigating the synthesis and properties of related binuclear methylindium(III) cations using the series of methanols $\text{mim}_n\text{py}_{3-n}\text{COH}$.

Supplementary Material

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

Acknowledgements

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