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Synthesis and crystal structure of a novel μ_4-oxygen-bridged tetranuclear organoindium complex $(InEt_2)_4$(di-2-pyridyl-amido)$_2$(μ_4-O)

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Abstract

Reaction of di-2-pyridylamine with **3** equivalent of $InEt_3$ in benzene results in a novel μ_4-oxo-bridged tetranuclear organoindium complex [$(InEt_2)_4(dpa)_2(\mu_4$-O)] (dpa = di-2-pyridylamido) which has been determined by X-ray crystallography. In the molecule there exist two unusual five-coordinate and two usual four-coordinate indium atoms in distorted trigonal bipyramidal and tetrahedral environments, respectively.

Keywords: Indium; μ_4-oxo-bridged; di-2-pyridylamido; Tetranuclear complex; Crystal structure

1. Introduction

The chemistry of organoaluminum and organogallium compounds which contain either group 15 or group 16 elements have been under investigation for many years due to their rich structural chemistry and as possible precursors to semiconductor material [1–3]. The organometallic complexes of group 13 metals aluminum, gallium, and indium have been for many years dominated by tetrahedral coordination mode [4]. Stimulated by efforts to clarify the steric and electronic effects on both the structure and the reactivity of group 13 organometallic species, there has been a recent increase of interest in the preparation of alkyl complexes of these metals having uncommon coordination geometries. In contrast to an increase in the number of polynuclear and monomeric five-and six-coordinate organoaluminum complexes [5–8], structurally characterized five- and six-coordinate organometallic complexes of indium have been rarely reported [9–12]. The use of the 2-(benzylamino)pyridine anion as a bidentate ligand in the organometallic chemistry of indium leads to a five-coordinate complex of MeIn[2-$N(CH_2C_6H_5)NC_5H_4]_2$ in which the structural analysis revealed a molecular core with the metal center in an unusual distorted square-based pyramidal environment consisting of the four nitrogen atoms of the two ligands with an apical methyl group completing the coordination sphere [9]. The interaction of $InMe_3(3,5\text{-}Me_2Py)$ with one and two equivalents of 1,3-diphenyltriazine (Hdpt) yielded the five- and six-coordinate indium alkyls $InMe_2$(dpt)(3,5-Me_2py) and $InMe(dpt)_2$ (3,5-Me_2py), respectively [10]. The trimethylindium adduct of *N*,*N*′,*N*″-triisopropyl-1,3,5-triazacyclohexane, $Me_3In(Pr_iNCH_2)_3$, represents the rare example of a six-coordinate indium (III) complex in which the indium atom lies in the crystallographic mirror plane and above the six-membered triazane ring [11]. Previously we have reported that the reaction of di-2-pyridylamine (dpa) with trimethylaluminum and trimethylgallium yielded the compounds Me_2M(dpa) (M = Al, Ga) in which the depronated form of dipyridylamine formed bidentate chelating complexes with dimethylaluminum and dimethylgallium [13], here we report the different reaction product—a novel oxygen-bridged tetranuclear organoindium complex containing two five-coordinate indium atoms in distorted trigonal bipyramidal envi-

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ronments and two four-coordinate indiums in the same molecule, from the reaction of di-2-pyridylamine with $InEt_3$. Organometallic oxo compounds of the transition elements in which the oxo ligand occurs in five different modes of bonding: terminal [M=O], doubly bridging [$M(\mu_2\text{-O})_nM$], triply bridging [$M_3(\mu_3\text{-O})$], and in interstitial quadruply and quintuply bridging forms have been reported [14–16]. However, to our knowledge, the title complex represents the first structurally characterized μ_4-oxo bridge with different coordination environments compound for heavier group 13 element in addition to representing rather unusual example of containing two five-coordinate indium atoms.

2. Experimental details

2.1. General procedures

All experiments were performed in a HE-493 Dri-Train Drybox under nitrogen atmosphere, solvents were carefully dried by distillation from sodium and diphenyl ketone under nitrogen prior to use. ^{1}H-NMR spectra were obtained on a Bruker AM500 spectrometer in C_6D_6 using $SiMe_4$ as internal reference. Mass spectra were obtained on a ZAB-MS instrument. Microanalyses (C, H, N) were performed on a Perkin–Elmer 240C elemental analyzer. Trimethylgallium was provided by the Special Gas Institute of Nanjing University. Di-2-pyridylamine was purchased from Aldrich and used as received.

2.2. Preparation of $(InEt_2)_4$(di-2-pyridylamido)$_2(\mu_4$-O)

Triethylindium (2.8 cm^3, 17.5 mmol) was added to a solution of di-2-pyridylamine (1 g, 5.84 mmol) in benzene (20 cm^3) at 25°C. The exothermic reaction was stirred at 25°C until the evolution of gas ceased and then heated at 40°C in an oil bath for 5 h. The solvent was removed in vacuo. After recrystallization from benzene/petroleum ether (2:1), colorless transparent crystals suitable for X-ray determination were obtained. (2.4 g, 80%) (Found: C, 41.11; H, 5.05; N, 7.89%. Calc. for $C_{36}H_{56}In_4N_6O$: C, 41.25; H, 5.38; N, 8.01%). ^{1}H-NMR (500 MHz, solvent C_6D_6): δ 0.96–1.04 (8H, m, 4InCH_2); 1.19–1.21 (8H, m, 4InCH_2); 1.34–1.69 (12H, m, 4CH_2CH_3); 1.70–1.77 (12H, m, 4CH_2CH_3); 6.14 (4H, d, 4C_5H_4N-$^{\gamma}H$); 6.80 (4H, 4C_5H_4N-$^{\beta}H$); 6.92 (4H, 4C_5H_4N-$^{\beta}H$); 7.78 (4H, 4C_5H_4N-$^{\alpha}H$). MS (% intensity, m/e): 342.7 (1.89, dpaInEt_2), 313.7 (100.00, dpaInEt), 284.8 (64.16, dpaIn), 172.8 (22.76, InEt_2), 170.9 (33.01, dpa-H), 143.8 (5.73, InEt), 114.8 (99.44, In).

2.3. X-ray structure determination of [$(InEt_2)_4$(di-2-pyridylamido)$_2(\mu_4$-O)]

A transparent colorless single crystal was mounted in a Lindemann glass capillary and then flame-sealed under an nitrogen atmosphere. Data were collected at 294 K on a Siemens P4 four-circle diffractometer with monochromated Mo–K_α ($\lambda = 0.71703$ Å) radiation using $\theta/2\theta$ scan mode with a variable scan speed 5.0–50.0 min^{-1} in ω. The data were corrected for Lorentz and Polarization effects during data reduction using XSCANS. The structure was solved by direct method and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0. A total of 12694 reflections measured, 10727 independent reflections were used in the refinement. Final R_1 and wR_2 values were 0.0688 and 0.1425 respectively for 849 parameters and goodness-of-fit = 0.630 [$I > 2\sigma(I)$], and $wR_2 = 0.2520$ (all data). The weighting scheme was $w^{-1} = \sigma_2(F_0^2)$, $wR = [\Sigma\, w(F_0^2 - F_c^2)^2/\Sigma\, w(F_0^2)^2]^{1/2}$. All non-H atoms were refined ansiotropically. All H atoms were added at calculated positions using a C–H bond length of 0.95

Table 1
Crystal data and structure refinement for $(InEt_2)_4$(di-2-pyridylamido)$_2(\mu_4$-O)

Empirical formula	$C_{36}H_{56}In_4N_6O$
F_w	1048.15
Temperature (K)	293(2)
Radiation (wavelength, Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.042(2)
b (Å)	11.503(2)
c (Å)	38.331(14)
α (°)	82.50(2)
β (°)	87.16(3)
γ (°)	61.553(11)
V (Å^3)	5890(6)
$D_{calc.}$ (g cm^{-3})	1.640
Z	4
Abs. coeff. (mm^{-1})	2.179
F(000)	2072
Crystal dimensions (mm)	$0.21 \times 0.33 \times 0.45$
Crystal habitat	Colorless columnar
θ range for data collection (°)	2.03–22.50
No. of refections collected	12 694
Indepdent reflections	10 727 ($R_{int} = 0.0373$)
Observed reflections [$I>2\sigma(I)$]	4380
Data/restraints/parameters	10686/16/849
Goodness-of-fit on F^2	0.630
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0688$ $wR_2 = 0.1425$
R indices (all data)	$R_1 = 0.1340$ $wR_2 = 0.2520$
Extinction coefficient	0.0 00091(12)
Largest difference peak and hole (e Å^{-3})	0.913, −1.182

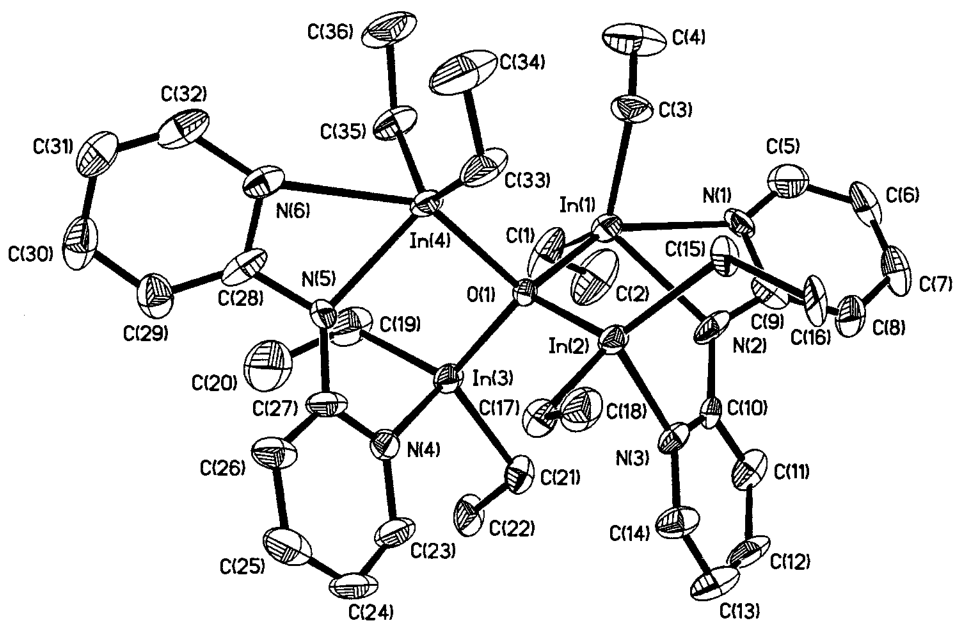


Fig. 1. Molecular structure of $(InEt_2)_4$(di-2-pyridylamido)$_2$(μ_4-O) (one of the two independent molecules) showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Å, and were included in the structure-factor calculation. All computations were carried out on a PC-586 computer using SHELXTL-PC program package. Crystal data and details on refinement are presented in Table 1. Additional data, including ansiotropic displacement coefficient and hydrogen atom coordinates, and a list of observed and calculated structure factors are available from the authors.

3. Results and discussion

3.1. Synthesis and characterization

Triethylindium reacted with di-2-pyridylamine in a 3:1 ratio to afford a colorless crystalline complex. This complex is less air-sensitive than free $InEt_3$. The elemental analyses (C, H, N) of this complex show that the reaction of $InEt_3$ with di-2-pyridylamine resulted in a new complex rather than the expected product $InEt_2$(dpa), analogous to the compounds Me_2M(dpa) (M = Al, Ga) as we found in the reaction for Me_3Al and Me_3Ga under similar mild conditions. The compounds Me_2M(dpa) (M = Al, Ga) have been fully characterized previously [13]. The complex shows no parent molecular ion $[M]^+$. Only fragments $[dpaInEt_2]^+$, $[dpaInEt]^+$, $[dpaIn]^+$ can be found in the EI mass spectra.

The complex was soluble in benzene and the ^{1}H-NMR spectra was obtained in deuterated benzene to account for the ratio of $InEt_3$ protons vs the aromatic protons. The ^{1}H-NMR spectra of the complex is characterized by two groups of resonances, one group in the region δ 6.14–7.78 ppm attributable to the protons of dipyridylamido and the other complicated series of multiplets in the region δ 0.96–1.77 ppm assigned to In–Et. Compared to the ^{1}H-NMR chemical shift data of $InEt_3$ with a quartet at δ 0.53 for CH_2 group and a triplet at δ 1.42 for CH_3 group [17], ethyl signals of the complex are shifted downfield, resulting from the deshielding and anisotropic effect of the aromatic pyridyl rings. In addition, the chemical shifts of the protons on the dipyridylamido are shielded in the complex and shifted upfield relative to the free ligand.

3.2. X-ray crystal structure of $(InEt_2)_4$(di-2-pyridylamido)$_2$(μ_4-O)

The structure was determined by X-ray crystallography. The complex crystallized in the triclinic space group $P\bar{1}$ with two chemically identical, crystallographically independent, and conformable only slightly different molecules in the asymmetric unit. There are no short intermolecular contacts. The molecular structure and atom-numbering scheme of one of the two independent molecules is shown in Fig. 1. Since the geometrical parameters of the two independent molecules are very similar, only the selected bond lengths and angles of one of them are given in Table 2. This structure is just consistent with the elemental analyses and ^{1}H-NMR spectra.

To our surprise, the molecule exhibits a μ_4-oxygen atom, that is, an oxygen bridging four indium atoms in a tetrahedral array. The In···In separation of 3.504 and 3.788 Å for In(1)···In(2) and In(1)···In(4), respectively, are not indicative of significant metal–metal

Table 2
Selected bond lengths (Å) and angles (°) for $(InEt_2)_4$(di-2-pyridylamido)$_2$(μ_4-O) (one of the two independent molecules) with estimated standard deviations in parentheses

In(1)–C(1)	2.14 5(6)	In(1)–C(3)	2.172(6)
In(1)–O(1)	2.25 2(3)	In (1)–N(2)	2.361(4)
In(1)–N(1)	2.43 1(5)	In(2)–C(15)	2.129(5)
In(2)–O(1)	2.160(3)	In(2)–C(17)	2.183(4)
In(2)–N(3)	2.240(4)	In(3)–C(19)	2.162(3)
In(3)–O(1)	2.175(4)	In(3)–C(21)	2.205(4)
In(3)–N(4)	2.230(5)	In(4)–C(33)	2.112(6)
In(4)–C(35)	2.182(4)	In(4)–O(1)	2.273(3)
In(4)–N(5)	2. 299(6)	In(4)–N(6)	2.546(5)
N(2)–C(9)	1.331(9)	N(2)–C(10)	1.428(8)
N(5)–C(27)	1.393(7)	N(5)–C(28)	1.403(7)
C(1)–In(1)–C(3)	131.2(2)	C(1)–In(1)–O(1)	102.3 (2)
C(3)–In(1)–O(1)	100.7(2)	C(1)–In(1)–N(2)	106.5(2)
C(3)–In(1)–N(2)	115.3(2)	O(1)–In(1)–O(1)	91.6(2)
C(1)–In(1)–N(1)	94.8(2)	C(3)–In(1)–N(1)	90.1(2)
O(1)–In(1)–N(1)	145.07(12)	N(2)–In(1)–N(1)	54.1(2)
C(15)–In(2)–O(1)	118.3(2)	C(15)–In(2)–C(17)	118.6(2)
O(1)–In(2)–C(17)	110.73(14)	C(15)–In(2)–N(3)	104.3(2)
O(1)–In(2)–N(3)	95.84(14)	C(17)–In(2)–N(3)	105.1(2)
C(19)–In(3)–O(1)	116.4(2)	C(19)–In(3)–C(21)	118.0(2)
O(1)–In(3)–C(21)	114.09(12)	C(19)–In(3)–N(4)	105.0(2)
O(1)–In(3)–N(4)	95.5(2)	C(21)–In(3)–N(4)	103.4(2)
C(33)–In(4)–C(35)	129.1(2)	C(33)–In(4)–O(1)	104.69(14)
C(35)–In(4)–O(1)	101.8(2)	C(33)–In(4)–N(5)	110.8(2)
C(35)–In(4)–N(5)	110.7(2)	O(1)–In(4)–N(5)	92.1(2)
C(33)–In(4)–N(6)	92.1(2)	C(35)–In(4)–N(6)	88.2(2)
O(1)–In(4)–N(6)	147.3(2)	N(5)–In(4)–N(6)	55.4(2)
In(2)–O(1)–In(3)	120.0(2)	In(2)–O(1)–In(1)	1 05.1(2)
In(3)–O(1)–In(1)	107.56(14)	In(2)–O(1)–In(4)	105.94(14)
In(3)–O(1)–In(4)	104.85(14)	In(1)–O(1)–In(4)	113.67(14)

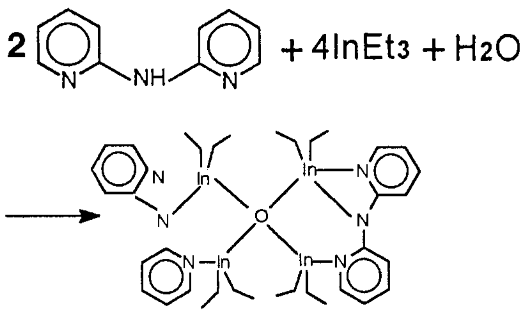
interaction. The two five-coordinate indium atoms with In(1)–O(1) [2.252(3) Å] and In(4)–O(1) [2.273(3) Å] distances are significantly longer than the sum of the covalent radii (2.11 Å) for In (1.45 Å) and O (0.66 Å) [18,19] whereas the In(2)–O(1) [2.160(3) Å] and In(3)–O(1) [2.175(4) Å] are slightly longer than that. All the In–O bond distances are significantly shorter than the sum of the Van der Waals radii (r(In) = 1.58 Å, r(O) = 1.52 Å, S = 3.10 Å) indicating a strong interaction between In and O. The In–O bond lengths in the present complex are very close to values for the In–OH bonds in the tetrameric cluster [InMe(OH)$(O_2PPh_2)]_4(py)_4$ which contains a distorted cubane core of four indium atoms and four μ_3-OH groups [20]. In the latter, the In–OH bond lengths consist of two long [In–O(1), 2.288(5) Å and In–O(1a), 2.285(6) Å] and a short [In–O(1b), 2.163(6) Å].

The conformation of the dipyridylamido ligand in the title complex is significantly different from that observed for Me_2Ga(dpa) complex [13]. The complex Me_2Ga(dpa) contains the ligand in an *anti–anti* configuration, where *anti–anti* refers to the relation of the pyridyl nitrogens to the amine hydrogen. By use of similar nomenclature, dipyridylamido ligands of the title complex are in an unusual *syn–syn* configuration. Each tridentate ligand is nonplanar with an average dihedral angle of 47.9° between the pyridyl rings. Both pyridyl rings of the ligands undergo rotation around the C–N (amido) bond to the *syn–syn* conformation, which allows all three nitrogens to coordinate to the tetrahedral array of indium atoms. The *syn–syn* conformation has also been found in linear trinuclear copper complex [$Cu_3(dpa)_4Cl_2$] [21] and nickel complex [$Ni_3(dpa)_4Cl_2$] [22]. The short average C–N (amido) distances [1.40 Å], which are significantly shorter than the normal C–N single bond length of 1.472 Å [23] imply a delocalization of the p-electrons between the amido nitrogen and the pyridyl rings.

Both In(1) and In(4) are five-coordinate with two ethyl groups, two nitrogen atoms of the same di-2-pyridyl-amido ligands and one oxygen atom. The environment of In(1) is a distorted trigonal-bipyramidal configuration, where the equatorial plane is defined by C(1), C(3) and N(2) (ΣX–In–Y = 353.0°), and N(1) and O(1) occupy the pseudoaxial positions [O(1)–In(1)–N(1) = 145°]. The environment of In(4) is similar to In(1). Both In(2) and In(3) are four-coordinate with two ethyl groups, one nitrogen atoms of ligands and the oxygen atom and in an usual distorted tetrahedral environment. Both In(1) and In(4) show that In–N (amido) distances are slightly shorter than In–N (pyridyl) distances, which is consistent with those reported in the literature [9,10,24]. This would be expected from a consideration of the relative s and p character of In atoms in the respective In–N bonds. The In(2)–N(3) [2.240 (4) Å] and In(3)–N(4) [2.230(5) Å] bond distances are close to the sum of the covalent radii [2.10 Å]. This implies the presence of normal single In–N bonds. The separation of 3.248 and 3.172 Å for In(2)···N(2) and In(3)···N(5), respectively, indicate that there are little interactions between the corresponding indium atoms and nitrogen atoms. In–C(ethyl) distances range from 2.112(6) to 2.205(4) Å [average 2.161(5) Å] are similar to the reported values for five-coordinate indium complexes [9,10].

It is noteworthy to compare the environments and bond distances of the two types of indium. The bond distances of five-coordinate indium atoms In(1) and In(4), with In(1)–O(1) [2.252(3) Å] and In(4)–O(1) [2.273(3) Å] are significantly longer than the four-coordinate indium atoms In(2) and In(3), with In(2)–O(1) [2.160(3) Å] and In(3)–O(1) [2.175(4) Å]. The In(1)–N(1) [2.431(5) Å] and In(4)–N(6) [2.546(5) Å] are also longer than In(2)–N(3) [2.240(4) Å] and In(3)–N(4) [2.230(5) Å]. The corresponding bond distances involving five-coordinate indium are significantly longer than those of four-coordinate indium.

Smith and coworkers [25] reported that higher reaction temperature resulted in intermolecular condensation when alumminum alkyls react with amines. We also observed the formation of gas (C_2H_6) due to the hydrogenolysis of In–Et bonds by di-2-pyridylamine during the course of the reaction. However, a total of four ethyl groups were eliminated from four triethylindium units (one from each of $InEt_3$) while only two aza-hydrogen atoms were eliminated from the two di-2-pyridylamine ligands. We postulate that traces of H_2O present in the reaction medium may eliminate two hydrogen atoms to form a μ_4-oxygen, as hydrolysis is the most important method to prepare transitional organometallic oxo complexes [26]. Thus we deduce that the reaction equation would be:



Further investigations of the reaction mechanism are in progress.

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