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Gallium and Indium Alkoxides with Hydride, Cyclopentadienediide and Copper(I) *tert*-Butoxide as further Components

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Dedicated to Prof. Arndt Simon on the Occasion of his 80th Birthday

Abstract. Gallium hydride stabilized by the base quinonuclidine reacts with acetone under addition of the Ga-H function to the carbon–oxygen double bond yielding $(HGa)_5(OiPr)_8O$ (**1**) as isolable compound. $(HGa)_5(OiPr)_8O$ may be formally split in to four entities of $HGa(OiPr)_2$ and one entity HGaO. The inner atomic skeleton of **1** is a novel Ga_5O_9 heterocluster with gallium atoms occupying the corners of a distorted trigonal bi-pyramid, an oxygen atom in the center and the remaining alcoholate oxygen atoms bridging eight of the nine edges of the bi-pyramid (X-ray diffraction analysis). Potassium indium alkoxide $KIn(OtBu)_4$ has been used to synthesize several new compounds like $In_4(OtBu)_8(C_5H_4)_2$ (**2**), $(py)_2CuIn(OtBu)_4$ (**3**), and $[CuIn(OtBu)_4]_2$ (**4**) by reaction with $TiCl_2cp_2$ (**2**) and CuCl (**3**, **4**). All compounds were characterized by spectroscopic means and by X-ray structure analyses revealing novel polycyclic structures.

Introduction

Materials based on oxides of gallium and indium have since several years attracted high attention due to their use in advanced physics: so β-Ga_2O_3 is actually studied as a wide bandgap semiconductor[1] or for use as ultra-high power rectifier.[2] Indium oxide since many years is used as basic material for TCOs (Transparent Conducting Oxides) especially in combination with other metal oxides.[3] For the syntheses of these materials molecular precursors are often very useful as they allow simple processing specifically shown for ITO (Indium-Tin-Oxide).[4,5] In the present study we describe new possible precursors for Ga_2O_3, and for indium/metal oxides.

In view of our experience with alkoxi-hydrides of aluminum, which are, among others, precursors for Al/Al_2O_3 nano composites,[6] we were interested to extend our studies also to the corresponding compounds of gallium.[7] One way to obtain gallium oxide with defect structures could be the thermolysis of precursors of the type $H_xGa(OR)_{3-x}$ (x = 1, 2). Although some gallium hydrides with *tert*-butoxi ligands have been described,[8] not much is known about isopropoxi gallium hydrides.[9] Indeed only few gallium alkoxi hydrides with or without further auxiliary ligands have been fully characterized.[10–12]

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On the same line, looking for precursors for materials with indium oxide as main component, especially in the context of TCOs (Transparent Conducting Oxides), different combinations between indium and other metallic elements, for example Ti and In (ITiO, indium titanium oxide, used for near IR transparency)[13] or Cu and In ($CuInO_2$, delafossit, used as p- or n-conductor)[14] are of high interest. In order to assemble the two metallic elements in a molecular compound, which could be used as a precursor, we again used alkoxides as ligands.

We here describe our results concerning first our attempts to obtain isopropylates of gallium hydride, which led to the unprecedented formation of a new gallium oxide cluster $((HGa)_5(OiPr)_8O$ (**1**)), followed by those with different indium/metal combinations using *tert*-butanolates as bridging units between the different metallic elements. In the Ti/In case we could not isolate a bimetallic compound, but instead an alkoxi/organyl indium compound of composition $In_4(OtBu)_8(C_5H_4)_2$ (**2**), which has a novel remarkable polycyclic structure. Contrarily, in the Cu/In case the desired compounds $(py)_2CuIn(OtBu)_4$ (**3**) and $[CuIn(OtBu)_4]_2$ (**4**) could be obtained, and are compared with the corresponding aluminum compounds (In replacing Al).[15]

Results and Discussion

After fruitless attempts to synthesize isopropylates of gallium hydride by reaction of GaH_3*OEt_2 with isopropanol (under hydrogen elimination) resulting in powders with high tendency to decompose (see also a report on iPr-$OGaH_2$ and $(iPr$-$O)_2GaH)$,[9] we switched to another method, which was first described by *H. Schmidbaur* et al.: here acetone is used instead of iso-propanol allowing an addition of the Ga–H bond to the C=O double bond.[16] In order to avoid side reactions we replaced the thermo-labile etherate $GaH_3 \cdot OEt_2$ by the more

stable quinonuclidine adduct of GaH$_3$, which can be isolated and purified in a crystalline form (see also Experimental Section), prior to be used in the reaction [Equation (1)].[17]

$$5\ GaH_3 \cdot N(CH_2CH_2)_3CH + 10\ O=C(CH_3)_2 \rightarrow$$
$$(HGa)_5(OiPr)_8O\ (1) + 5\ N(CH_2CH_2)_3CH\ \ (1)$$
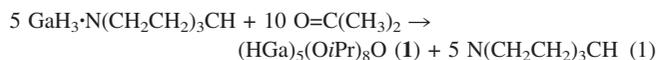
We have performed the reaction at –78 °C in toluene as solvent. As can be seen from Equation (1) the isolable product **1** is not a simple iso-propoxi gallane but formally a tetramer of H-Ga(O-iPr)$_2$, which includes HGaO. The source of the oxygen presumably comes from traces of water in the reaction mixture, but could also be generated from diisopropyl ether as one further possible side product. The composition of **1** follows from X-ray diffraction analysis of single crystals which form in the concentrated solution at –15 °C. When the solvent is completely separated from the colorless product, the obtained solid residue is thermally unstable and turns into a grey powder.

The reaction (1) can be followed by ^{1}H and ^{13}C NMR spectroscopy showing the disappearance of the signals due to acetone and the appearance of signals due to iso-propanylate groups (no quantitative measurement has been performed). In the IR spectrum a strong band at 1811 cm^{-1} is found which we attribute to Ga–H stretching vibration (the corresponding wave number for Ga–H in [H–Ga(O–tBu)$_2$]$_2$ is found at 1945 cm^{-1}[8]). The lower value for Ga–H in **1** indicates a weakening of the bond compared to [H–Ga(O–tBu)$_2$]$_2$, which is due to a increase of the coordination numbers at the gallium atoms. There are only signals for one type of isopropylate group in the ^{1}H and ^{13}C NMR spectra, suggesting that the molecule in solution is fluctuating.

As a result of the X-ray diffraction analysis on single crystals of (HGa)$_5$(OiPr)$_8$O (**1**) the molecule is depicted in Figure 1. The point symmetry of the molecule in the crystal is C_1 with a minor deviation (neglecting the isopropyl groups) from C_{2v} (the pseudo twofold axis passing through O1–Ga1–H1). The inner polycyclic skeleton can be described in two ways: either 1) as a square Ga$_5$ pyramid with Ga2–Ga5 occupying the base and the Ga1 the top of the pyramid, all alkoxide groups bridging the edges while the single oxygen atom connects Ga2 and Ga3 severely destroying the fourfold symmetry or 2) as a trigonal Ga$_5$ bi-pyramid, centered by oxygen atom O1, with alkoxide groups bridging the edges apart the one between Ga2 and Ga3. In both descriptions all gallium atoms display a terminal hydrogen bond. Indeed, using the geometry index τ_5 a value of 0.44 can be calculated for **1**, which is in-between the two arrangements.[18]

From the gallium atoms present in **1** Ga1 is six-coordinate, Ga2 and Ga3 are five-coordinate, and Ga4 and Ga5 four-coordinate. These differences in coordination numbers are reflected in the Ga–O bonding distances which are the smallest for Ga4 and Ga5 (mean: 1.875, 1.877 Å) followed by Ga2 and Ga3 (mean: 1.983, 1.984 Å) and finally Ga1 (mean: 2.080 Å) (compare also legend of Figure 1). The oxygen atom O1 not only displays the shortest bonds, but also is in an almost planar coordination sphere [sum of angles: 360.0(1)°]. As stated
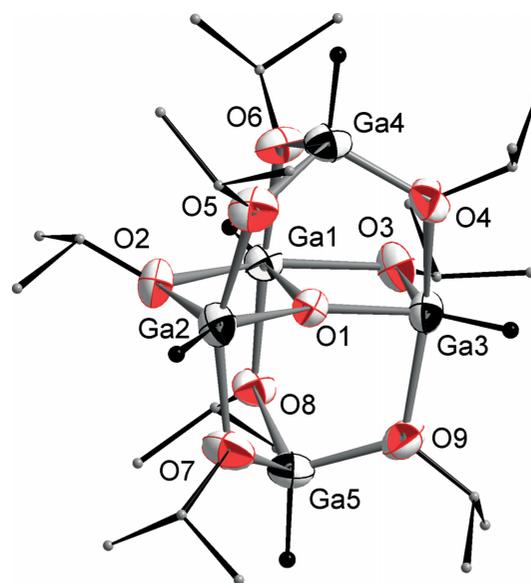
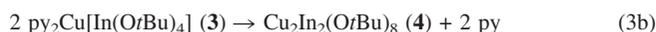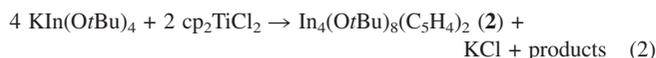**Figure 1.** Graphical representation of the structure of (HGa)$_5$(OiPr)$_8$O (**1**). The carbon atoms of the isopropyl groups are presented in a simplified ball and stick manner while the hydrogen atoms attached to them are omitted for clarity, ellipsoids at 50 % level. Some important bond lengths and angles (Å, °): Ga1–O1 1.936(3), Ga1–O2 2.148(3), Ga1–O3 2.142(3), Ga1–O6 2.066(3), Ga1–O8 2.070(3), Ga2–O1 1.867(3), Ga2–O2 1.898(3), Ga2–O5 2.090(3), Ga2–O7 2.076(4), Ga3–O1 1.870(3), Ga3–O3 1.900(4), Ga3–O4 2.074(3), Ga3–O9 2.093(3), Ga4–O4 1.865(3), Ga4–O5 1.881(4), Ga4–O6 1.879(3), Ga5–O7 1.871(4), Ga5–O8 1.880(3), Ga5–O9 1.881(3); O1–Ga1–O2 76.0(1), O1–Ga1–O3 76.1(1), O2–Ga1–O3 152.1(1), O6–Ga1–O8 171.5(1), O1–Ga2–O2 84.1(1), O5–Ga2–O7 157.3(1), O1–Ga3–O3 83.8(1), O4–Ga3–O9 157.1(2), O4–Ga4–O5 108.2(2), O4–Ga4–O6 105.0(2), O5–Ga4–O6 103.0(2), O7–Ga5–O8 104.3(2), O7–Ga5–O9 108.4(2), O8–Ga5–O9 103.3(2), Ga1–O1–Ga2 104.3(1), Ga1–O1–Ga3 104.3(1), Ga2–O1–Ga3 151.4(2). Mean values: Ga–H 1.46(1), Ga–O(4–9)–Ga 116.7(5).

above, the origin of the oxygen atom O1 is most probably due to partial hydrolysis of HGa(OiPr)$_2$.

The gallium compound **1**, with respect to its composition, is very similar to (HAl)$_5$(O-C$_5$H$_9$)$_8$O, which has aluminum in the place of gallium and cyclopentanolate in the place of isopropylate groups.[19] Structurally, they are different as the oxygen atom in (HAl)$_5$(O–C$_5$H$_9$)$_8$O is five-coordinate (the Al$_5$ subunit forms an almost ideal quadratic pyramid (including the central oxygen atom the τ_5 value is 0.01[18]), whereas it is three-coordinate in **1**.[19] In a simplified picture (not considering the different ionic parts in the Al-O, respectively Ga–O bonds) the atomic and ionic radii of aluminum (1.43, 0.39 Å) are shorter than those of gallium (1.53, 0.47 Å) ,[20] which could explain that the mean Al–O(R) distances in (HAl)$_5$(O–C$_5$H$_9$)$_8$O with 1.85(8) Å are in general smaller than those in (HGa)$_5$(OiPr)$_8$O (**1**) with 1.99(8) Å. This means that the Al$_5$O$_8$ cage (ignoring O1) is distinctly smaller than the corresponding Ga$_5$O$_8$ cage, allowing four bonding contacts of O1 with the metal atoms in the basal plane [mean Al2,3,4,5–O1 = 2.09(3) Å], whereas there are only two in the gallium derivative [mean Ga2,3–O1 = 1.869(2) Å, mean Ga4,5···O1 = 2.79(1) Å]. Of course also the stronger polarizing capability of the aluminum atom has to be considered in this comparison.

Some years ago we have described another metal-oxygen cluster $Sn_3(InCl)(tBuO)_6O$, which in many respects resembles **1**: it has a Sn_3In trigonal pyramidal metal arrangement with an oxygen atom in the middle and six *tert*-butoxi groups bridging all the edges of the pyramid.[21] Although this compound, at a first glimpse, seems to be quite different from $(HAl)_5(OC_5H_9)_8O$ and $(HGa)_5(OiPr)_8O$ (**1**), there are remarkable similarities: all compounds can be formally split in a cyclic metal alcoholate oligomer with the ring external OR groups pointing in one direction, serving as "host" and an OM-X entity serving as "guest". In $(HAl)_5(OC_5H_9)_8O$ and $(HGa)_5(OiPr)_8O$ (**1**) a tetrameric $[HAl(OC_5H_9)_2]_4$ or $[HGa(OiPr)_2]_4$ unit connecting the metal atoms through four alcoholate groups can be cut out, in which either a OAl–H or OGa–H unit is inserted, whereas in $Sn_3(InCl)(tBuO)_6O$ a trimeric $[Sn(OtBu)_2]_3$ unit serves in a similar way as "basket" towards OIn–Cl. Interestingly, in the tin-indium cluster one of the bridging *tert*-butoxi groups has a further bonding contact to the indium atom allowing the rise of the coordination number at indium to six.[21] From the three-atomic units OAl–H, OGa–H and OIn–Cl only OAl–H has been obtained separately in a molecular form: at ambient temperatures it is a glassy solid with a polymeric structure.[6]

For the synthesis of the bimetallic Ti/In, respectively Cu/In compounds we have used the potassium alkoxi-indate $KIn(OtBu)_4$ as indium source and either cp_2TiCl_2 or CuCl as reaction partner [Equation (2) and Equation (3a)]. Compound **4** is generated, when **3** is sublimed at 130 °C losing the pyridine ligands [Equation (3b)].

$$4\ KIn(OtBu)_4 + 2\ cp_2TiCl_2 \rightarrow In_4(OtBu)_8(C_5H_4)_2\ (\mathbf{2}) +$$
$$KCl + products \quad (2)$$

$$KIn(OtBu)_4 + CuCl + 2py \rightarrow py_2Cu[In(OtBu)_4]\ (\mathbf{3}) + KCl \quad (3a)$$

$$2\ py_2Cu[In(OtBu)_4]\ (\mathbf{3}) \rightarrow Cu_2In_2(OtBu)_8\ (\mathbf{4}) + 2\ py \quad (3b)$$

The compounds **2**, **3**, and **4** are obtained from their solutions by crystallization. The ^1H NMR spectrum for **2** shows one signal for the tertiary butyl groups and a broad singlet for the cyclopentadiendiide entity with 9:1 integral ratio. In the ^{13}C NMR spectrum the tertiary butyl groups again are represented by one signal for the primary and the tertiary carbon atoms, whereas the five atoms of the cyclopentadiendiide entity are found at 76, 129, and 130 ppm indicating one of the atoms being bonded to a metal atom and the four other ones being engaged in π-bonding. By qualitative analysis we could find no titanium in the compound, suggesting that a transfer of the cyclopentadienyl group from titanium to the indium atom had taken place together with a formal proton abstraction from $C_5H_5^-$ (considering the integrals in the ^1H NMR spectrum). Transformations of $C_5H_5(E)$ (E = mono-valent metal centered substituent) into $C_5H_4(E)_2$, $C_5H_4(E)(E')$ or $C_5H_4(E')(E')$ (E' = main group metal centered substituent) have been investigated in view of the synthesis of ansa –metallocenes and can be performed with lithium organyls or even metal-alkoxides followed by salt eliminations:[22,23] an instructive example is the formation of $C_5H_4(SiMe_2-SiMe_2)_2C_5H_4$, which has some resemblance to **2** (see below).[24] Interestingly the bridging C_5H_4

groups in this exemplary compound may connect in 1,1-, 1,2- and 1,3-positions of the ring due to 1,5-sigmatropic shifts of the silyl groups, whereas only the 1,1-bridge is active in **2**.[24] In the reaction leading to **2** [Equation (2)], apart the scrambling of ligands (Cl⁻, *t*Bu-O⁻, Cp⁻ [or Cp²⁻]) between Ti and In, presumably the potassium *tert*-butoxide, present in solution, could have acted as proton acceptor.

In Figure 2 the result of the X-ray structure of the tricyclic **2** is shown: two formal di-cations $(tBuO)In(OtBu)_2In(OtBu)^{2+}$, both displaying a four membered InO_2In ring, are connected by two formal di-anions $C_5H_4^{2-}$ in such a way that all cycles (the pentacyclic C_5H_4, and the tetracyclic $(InOtBu)_2(OtBu)_2$) are almost parallel to one and another. On connecting the indium atoms to the carbon atom C17 and C17' a six membered In_4C_2 cycle (with non-bonding indium-indium contacts) can be constructed, which is totally planar and to which the four and five membered cycles are perpendicular (deviation less than 2°). The crystal point symmetry of **2** is C_i (–1), but the deviation from D_{2h} (2/m 2/m 2/m) is only minor, suggesting the free molecule having this symmetry.
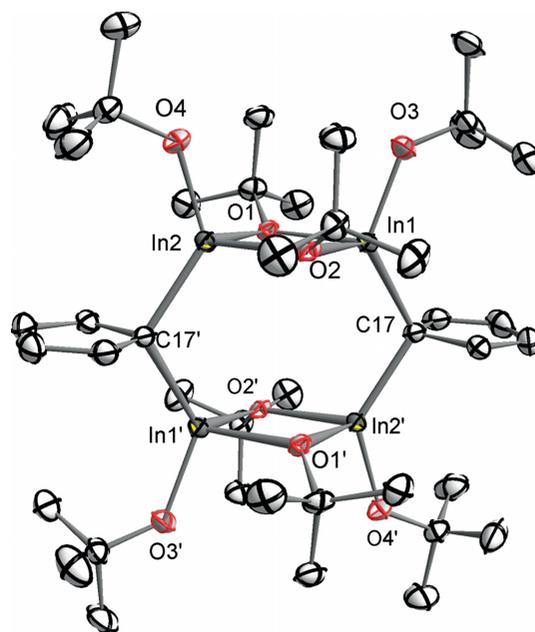
Figure 2. Representation of the structure of $In_4(OtBu)_8(C_5H_4)_2$ (**2**). The hydrogen atoms are omitted for clarity, ellipsoids at 50 % level. Some important bond lengths and angles (Å, °): In1–O1 2.138(4), In1–O2 2.127(4), In2–O1 2.140(4), In2–O2 2.120(4), In1–O3 1.994(4), In2–O4 1.992(4), In1–C17 2.159(5), In2–C17 2.168(5), In1···In2 3.3096(6); In1–C17–In2' 116.2(2), O1–In1–O2 78.1(1), O1–In1–C17 115.3(2), O2–In1–C17 114.9(2), O1–In2–C17 114.9(2), O2–In2–C17 114.9(2), In1–O1–In2 101.3(2), In1–O2–In2 102.4(2), C17–In1···In2 122.0(2), C17'–In2···In1 121.8(1).

So far no indium compounds with C_5H_4 groups in the special arrangement found for **2** have been reported although alkoxi-cyclopentadienyl indanes are known like the dimeric $(cp_2InOtBu)_2$ which has a $In_2(OtBu)_2$ part in common with **2**.[25] Main group metals may bond to $C_5H_4^{2-}$ and arrange in a fashion similar to **2** with perpendicular orientation of $C_5H_4^{2-}$ to the main ring (Sn_3C_3) as found for $[Me_2Sn(C_5H_4)]_3$, which can be described as a trimer of a stanna fulvene.[26] There is

another molecule which should be compared to **2**: this is the dimeric tri(*tert*-butoxi)indane.[27] On substituting two *tert*-butoxi groups in $(tBuO)_2In(OtBu)_2In(OtBu)_2$ by $C_5H_4^{2-}$ followed by dimerization, $In_2(OtBu)_6$ can be formally transformed to **2**. Indeed, the whole structural entity $(tBuO)In(OtBu)_2In(OtBu)$ is very similar in both compounds, with the exception that the bridging alkoxi groups are pushed outside the center of the molecule **2** due to the repulsion from the C_5H_4 groups.

A closer look to the bond lengths and angles within **2** reveals that In–O distances can be divided in shorter ones when the O*t*Bu group is terminal and longer ones if it is bridging, similarly as found in $In_2(OtBu)_6$ (see also caption of Figure 1).[27] As typical for dienes the bond lengths in the two $C_5H_4^{2-}$ groups are alternating [1.36(1), 1.44(1), 1.35(1) Å] with C17 displaying two almost equal values to the adjacent carbon atoms [1.483(8) and 1.488(8) Å]. The carbon atom C17 must therefore considered to have a double negative charge introducing a high polarity in the C17–In(1,2) bonds. The In–C bond lengths compare well with those of $InPh_3$ [2.13(2) Å], but are clearly shorter than those found in $InCp_3$ [2.30(3) Å], both compounds displaying intermolecular contacts in the crystal.[28,29]

The molecule **2** in solution must fluctuate as on the NMR time scale we cannot distinguish between the bridging and the terminal alkoxi groups as in the crystal.

Whereas the titanium could not be included in a molecule together with indium [Equation (2)], the analogous reaction of potassium tetra(*tert*-butoxi)indate with copper(I) chloride [Equation (3a)] runs smoothly. When using pyridine we could easily crystallize $py_2Cu[In(OtBu)_4]$ (**3**) after separation of the potassium chloride from the solution. The copper in this molecule must have a d^{10} electron configuration as the ^1H and ^{13}C NMR spectra of **3** could be obtained without difficulty. As in the case of **2** and **4** (see below) the alkoxi-ligands seem to exchange between bridging and terminal positions in solution in agreement with a simple resonance found for the *tert*-butyl groups in the spectra. The di-metallic compound **3** is a heavier congener of $py_2Cu[Al(OtBu)_4]$, which we have isolated some years ago and which undergoes, as in the aluminum case, dimerization under pyridine abstraction resulting in molecule **4**, when heated under reduced pressure [Equation (3b)].[15] The molecule **4** shows one single resonance for tertiary-butyl in the NMR spectra and can be obtained by crystallization from the solution.

In Figure 3 and Figure 4 the results of the X-ray structure analyses of compounds **3** and **4** can be seen together with the most relevant bond lengths and angles in the captions. The molecule **3**, which has almost a mirror plane passing through N1, N2, Cu, In, O3 and O4, can be described as a py-Cu-py$^+$ cation to which a $In(OtBu)_4^-$ anion is coordinated through O1 and O2 alkoxide bridges thus creating a four-membered CuO_2In cycle. In the centro-symmetric **4** two $In(OtBu)_4^-$ entities are connected by two copper(I) cations to form a eight-membered $In_2O_4Cu_2$ cycle with almost linear O–Cu–O bridges.
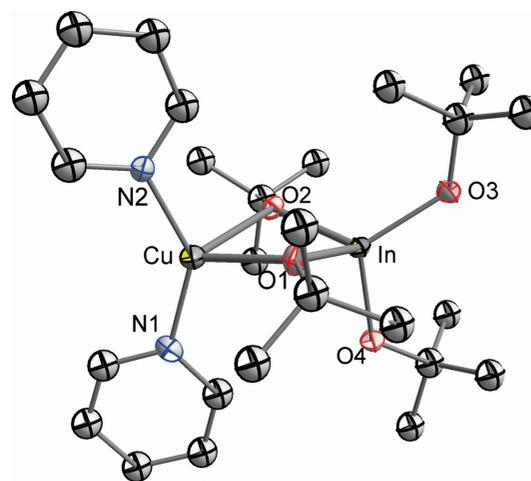
Figure 3. The molecular structure of $py_2Cu[In(OtBu)_4]$ (**3**). The hydrogen atoms are omitted for clarity, ellipsoids (isotropic values for C) at 50 % level. Some important bond lengths and angles (Å, °): In–O1 2.047(4), In–O2 2.057(4), In–O3 2.016(4), In–O4 2.021(4), Cu–N1 1.959(8), Cu–N2 1.971(7), Cu–O1 2.195(8), Cu–O2 2.262(9), Cu···In 3.213(1); N1–Cu–N2 139.2(2), O1–Cu–O2 75.1(1), O1–In–O2 82.95(6), O3–In–O4 112.3(1).
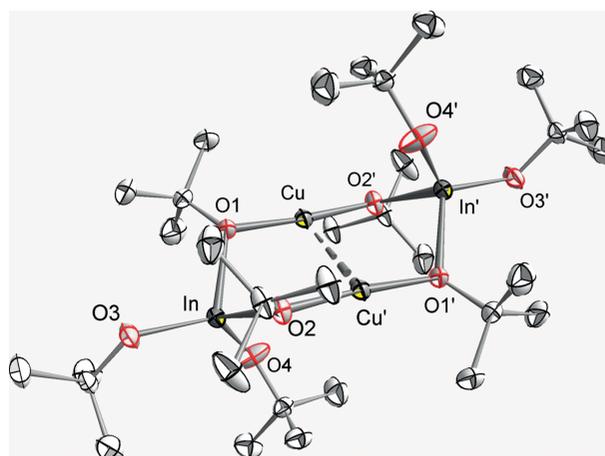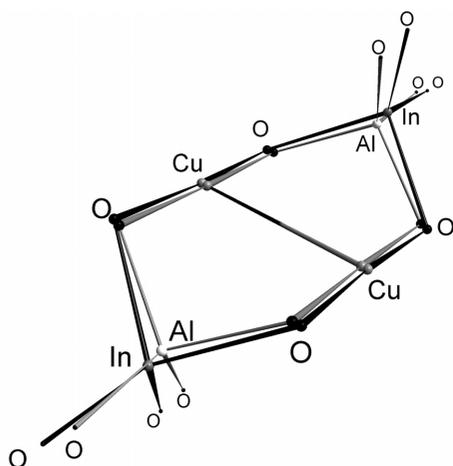

Figure 4. The molecular structure of $Cu_2In_2(OtBu)_8$ (**4**). The hydrogen atoms are omitted for clarity, ellipsoids at 50 % level. Some important bond lengths and angles (Å, °): In–O1 2.092(3), In–O2 2.087(3), In–O3 1.999(4), In–O4 1.998(4), Cu–O1 1.861(4), Cu–O2' 1.858(4), Cu···Cu' 2.884(2); O1–In–O2 93.7(1), O1–In–O3 112.2(1), O1–In–O4 100.5(1), O2–In–O3 110.0(1), O2–In–O4 110.4(1), O3–In–O4 125.3(1), O1–Cu–O2' 174.6(1), In–O1–Cu 108.3(2), In–O2–Cu' 114.7(2).

As already stated, both molecules **3** and **4** are structurally very similar to the aluminum analogues.[15] We therefore confine our discussion to the most striking similarities and differences between the corresponding structures. As the ionic radius of In^{3+} is 0.23 Å larger than that of Al^{3+} [20] and the atom is softer than aluminum there should be consequences with respect to the strain in the cycles. So in **3** the O1–In–O2 angle (83.0°) is by 9.6° smaller than the O1–Al–O2 angle in $py_2Cu[Al(OtBu)_4]$ allowing the O1–Cu–O2 angle in **3** to be less acute than that in $py_2Cu[Al(OtBu)_4]$ (69.2°). As in $py_2Cu[Al(OtBu)_4]$ the four-membered cycle in **3** is not planar

(the "envelope" angle dividing the CuO$_2$In cycle by a line through Cu and In is 172°) and the distances of Cu to oxygen and nitrogen are almost equal within standard deviations in the two molecules.

The most remarkable difference between molecule **4** and its aluminum analogue Cu$_2$Al$_2$(OtBu)$_8$ (both having a crystallographic inversion center) is the distinctly longer Cu··Cu distance in **4** [2.884(1) Å] compared to 2.687(1) Å in the aluminum derivative. The d^{10}–d^{10} interaction between copper(I) centers, which is assumed to be responsible to explain their approach towards one and another, seems (on a pure structural basis) to be less important in **4**.[30] Indeed, the Cu··Cu distance found in **4** is almost equal to that which is expected for the sum of the van-der-Waals radii (2.80 Å), although it should be noted that both atoms have a formal charge of +1. Nevertheless we had a closer look to Cu$_2$Al$_2$(OtBu)$_8$ and Cu$_2$In$_2$(OtBu)$_8$ (**4**) in order to learn more about the different geometries in the two structures.

In Figure 5 the two molecules Cu$_2$Al$_2$(OtBu)$_8$ and **4** (approximate point symmetries C_{2h}, crystallographic point symmetry C_i) are superimposed using the inversion center, the Cu–Cu axis and the planes with the two O–Cu–O motives as common reference (the deviations of the 6 atoms from these planes are negligible in both molecules with 0.005 Å as a maximum). As can be easily deduced from Figure 5, the indium derivative forms a larger ring compared to the aluminum derivative, which is not surprising as the atom radius of indium is larger than aluminum.[20] There are clearly structural similarities between the two molecules. For example, the eight-membered Al$_2$O$_4$Cu$_2$ and In$_2$O$_4$Cu$_2$ cycles show the same sort of chair conformation with similar angles between the central Cu$_2$O$_4$ planes and the adjacent AlO$_2$, respectively InO$_2$ planes (122.4° [Al] and 125.7° [In]).

On the other hand, there are also remarkable differences between Cu$_2$Al$_2${OtBu}$_8$ and **4**. The bite-angle of the Al(OtBu)$_4$ tetrahedron for the Cu$_2$ dumbbell with 101.0(1)° is less strained than the corresponding angle for the In(OtBu)$_4$ tetrahedron [93.6(1)°], which is a consequence of the longer In–O compared to the Al–O bond. Another distinction can be found by comparing the non-bonding O···O distances in the ring and those between terminal alkoxide groups (values assembled in the caption of Figure 5): in the aluminum case the difference between these non-bonding interactions amounts to 6 %, while in the indium case the value is 14 %. Comparing with the aluminum derivative the Cu–Cu distances are elongated in the indium derivative by 7.4 %, which is less than the trans-annular O···O distance (9.6 %, values see caption of Figure 5). From this it must be concluded that the Cu–Cu interactions seem still to be binding also in the indium derivative: on the same line the O–Cu–O angles are even more acute in the indium case [174.6(1)°] than in the aluminum case [176.5(1)°].

Conclusions

In summary four novel molecular structures for gallium and indium mixed alkoxides (**1 – 4**) have been determined. The comparison between Al$_2$Cu$_2$(OtBu)$_8$ and In$_2$Cu$_2$(OtBu)$_8$ (**4**) reveals two major findings: (1) The Cu–Cu interaction is influenced by the "chelating capacity" of the bonded tetra-alkoxides: more the oxygen atoms in the tetra-alkoxide M(OtBu)$_4$ (M = Al, In) are close, more the Cu–Cu bond is short. Even, if, as in the indium derivative, the distance between the copper atoms is increasing, the d^{10}–d^{10} interaction (which should be verified by quantum chemical calculations) is still structurally apparent. (2) The elongation of the Cu–Cu bond in **4** is somewhat compensated by a smaller and stronger Cu–O bond as can be seen by comparing these bonds in the two compounds.

Experimental Section

All manipulations were performed under exclusion of oxygen and water using a nitrogen atmosphere. Solvents were purified prior to use by distillation and have been kept over sodium wire. NMR spectra in benzene/toluene solution were obtained from a Bruker AC 200 F (^{1}H, ^{13}C). The data sampling for X-ray structure analyses was performed on a STOE Image Plate (**1**) or a X8 Apex diffractometer using Mo-K_α radiation. The structures were solved using the SHELX-system.[31] The drawings of the structures have been made using the Diamond program.[32]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1954243 (**1**), CCDC-1954244 (**2**), CCDC-1954245 (**3**), and CCDC-1954246 (**4**), (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

(HGa)$_5$(μ_2-OiPr)$_8$(μ_3-O) (1): The quinonuclidine adduct of GaH$_3$ [GaH$_3$·N(CH$_2$CH$_2$)$_3$CH] was prepared following a published route[17] and sublimed at 70 °C·per 0.1 atm forming colorless crystalline prisms. C$_7$H$_{16}$GaN (184.00): calcd. C 45.7, H 8.8, N 7.6 %; found

Figure 5. Superposition of the central rings of Cu$_2$Al$_2$(OtBu)$_8$[15] (grey) and Cu$_2$In$_2$(OtBu)$_8$ (**4**) (black) using the inversion centers, the Cu–Cu line and the Cu$_2$O$_4$-planes as reference (see also text). Some important angles and mean bond lengths as well as trans-annular distances (Å, °): Al$_2$Cu$_2$(OtBu)$_8$: Cu–O 1.886(2), Cu–Cu 2.686(2), O···O$_{(ring)}$ 2.780(6), O···O$_{(exo)}$ 2.956(6), O–Cu–O 176.5(1): In$_2$Cu$_2$(OtBu)$_8$, **4**: Cu–O 1.860(3), Cu–Cu 2.884(2), O···O$_{(ring)}$ 3.048(6), O···O$_{(exo)}$ 3.550(6), O–Cu–O 174.6(1).

C 46.1, H 8.7, N 7.7%. Immediately after synthesis 0.486 g (0.00264 mol) of this freshly sublimed adduct were dissolved in 50 mL toluene to which at –78 °C 0.195 mL of a solution of 1 volume of acetone (0.0026 Mol) to 10 volumes of toluene was slowly added whilst stirring. The solution was warmed up to 0 °C and most of the solvent was eliminated by condensation in a cold trap. Caution: do not eliminate the solvent until a solid residue is formed, as this product is not stable and decomposes forming a grey powder! Instead the solution, being reduced in volume to 1/4, is kept at –15 °C for 2 d, from which 0.02 g (5%) colorless crystals of **1** formed. $C_{24}H_{61}Ga_5O_9$ (842.33): No analytical data available for high reactivity reasons. **^{1}H NMR**: δ = 0.94 {d [^{3}J(H/H) = 6.1 Hz], 48 H, –CH(CH_3)$_2$}, 3.74 {sept [^{3}J(H/H) = 6.1 Hz], 8 H, CH(CH$_3$)$_2$}, 5.08 (broad, 5 H, Ga-H). **^{13}C NMR**: δ = 25.3 [s, –CH(CH$_3$)$_2$], 63.1 [s, –CH(CH$_3$)$_2$]. **IR**: $\tilde{\nu}$ = 1811 cm^{-1} (broad, Ga–H).

X-ray Data for 1: (293 K) Triclinic, $P\bar{1}$, a = 12.330(2), b = 12.449(2), c = 12.682(3) Å, α = 98.04(3), β = 96.84(3), γ = 97.51(3) °, V = 1892.2(6) Å^3, Z = 2. Structure refinement: 5506 independent reflexions (Θ-limits: 2.74–24.04°); refinement method: full-matrix least-squares on F^2; 361 parameters (no restraints); final R indices [$I > 2\sigma(I)$]: R_1 = 0.037, wR_2 = 0.0928; R indices (all data): R_1 = 0.0498, wR_2 = 0.0983; largest diff. peak and hole: 0.658 and –0.626l e·Å^{-3}.

In$_4$(μ_2-OtBu)$_4$(OtBu)$_4$(μ_2-1,1-C$_5$H$_4$)$_2$ (2): 2.56 g (0.0057 mol) of potassium tetra(*tert*-butoxi)indate [KIn(OtBu)$_4$] were dissolved in 85 mL toluene under heating and then added drop wise to a suspension of 0.718 g (0.0029 mol) bis(cyclopentadienyl)titaniumdichloride (cp$_2$TiCl$_2$) in 10 mL toluene. The suspension turned from red to brown when heated up to 110 °C during 24 h. Potassium chloride and other solids were filtered off and the solution was reduced in volume to 10 mL by condensation of toluene in a cold trap. After three days 0.729 g (0.00062 Mol, 44%) colorless needles of **2** were formed by crystallization. $C_{42}H_{80}In_4O_8$ (1172.35) calcd. C 43.03, H 6.88%; found C 43.11, H 6.47%. **^{1}H NMR**: δ = 1.27 [s, 36 H, -C(CH_3)$_3$], 6.26 (s, 4 H, C$_5$H$_4$). **^{13}C NMR**: δ = 32.02 [s, –C(CH$_3$)$_3$], 69.64 [s, –C(CH$_3$)$_3$], 76.14 (C_α, C$_5$H$_4$), 129.48 (C_β, C$_5$H$_4$), 132.39 (C_γ, C$_5$H$_4$).

X-ray Data for 2·2C$_7$H$_8$: (122 K) Monoclinic, $C2/c$, a = 23.871(2), b = 12.407(1), c = 23.341(2) Å, β = 115.39(2)°, V = 6245.4(8) Å^3, Z = 4. Structure refinement: 8536 independent reflexions (Θ-limits: 1.90–29.3°); refinement method: full-matrix least-squares on F^2; 346 parameters (no restraints); final R indices [$I > 2\sigma(I)$]: R_1 = 0.0497, wR_2 = 0.1275; R indices (all data): R_1 = 0.075, wR_2 = 0.141; largest diff. peak and hole: 2.35 and –1.23 e·Å^{-3}.

Bis(pyridin)copper(I)tetra(*tert*-butoxi)indate, py$_2$Cu[In(OtBu)$_4$] (3): 1.775 g (0.004 mol) potassium tetra(*tert*-butoxi)indate [KIn(OtBu)$_4$] dissolved in 80 mL toluene were dropped slowly to a suspension of 0.393 g (0.004 mol) of copper(I) chloride. After 24 h reflux at 120 °C the solution was separated from the formed potassium chloride by filtration. The volume of the solution was reduced to approximately 8 mL by condensation of the solvent and stored at –30 °C. Within 3 d 1.824 g (0.0029 mol, 72%) of yellow needles formed by crystallization. The compound is very oxygen and moisture sensitive (effecting analytical data). $C_{26}H_{46}CuInN_2O_4$ (629.01) calcd. C 49.65, H 7.37%; found C 51.6, H 7.02%. **^{1}H NMR**: δ = 1.59 [s, 36 H, –C(CH_3)$_3$]. **^{13}C NMR**: δ = 35.36 [s, –C(CH$_3$)$_3$], 71.21 [s, –C(CH$_3$)$_3$].

X-ray Data for 3: (134 K) Triclinic, $P\bar{1}$, a = 9.7129(5), b = 11.1875(5), c = 15.531(1) Å, α = 78.67(1), β = 82.27(1), γ = 66.56(1)°, V = 1515.2(2) Å^3, Z = 2. Structure refinement: 17988 independent reflexions (Θ-limits: 1.34–39.6°); refinement method: full-matrix least-squares on F^2; 319 parameters (no restraints); final R indices

[$I > 2\sigma(I)$]: R_1 = 0.0577, wR_2 = 0.1384; R indices (all data): R_1 = 0.079, wR_2 = 0.15; largest diff. peak and hole: 1.40 and –1.68 e·Å^{-3}.

Copper(I)tetra(*tert*-butoxi)indate Dimer, {Cu[In(OtBu)$_4$]}$_2$ (4): 1.122 g (0.002 mol) of compound **2** were sublimed at 130 °C and 10^{-2} mbar in a glass vessel connected to a tube. The yellow sublimate formed in the tube was dissolved in 2 mL toluene and crystallized at –30 °C yielding 0.17 g (0.0002 Mol, 10%) yellow cube shaped crystals. The compound is very oxygen and moisture sensitive (effecting analytical data). $C_{32}H_{72}Cu_2In_2O_8$ (941.62) calcd. C 40.82, H 7.71%; found C 38.87, H 7.32%. **^{1}H NMR**: δ = 1.59 [s, 72 H, –C(CH_3)$_3$]. **^{13}C NMR**: δ = 32.27 [s, –C(CH$_3$)$_3$], 73.89 [s, –C(CH$_3$)$_3$].

X-ray Data for 4: (153 K) Triclinic, $P\bar{1}$, a = 9.330(1), b = 10.352(1), c = 11.395(1) Å, α = 97.12(1), β = 101.54(1), γ = 94.97 (1) °, V = 1063.0(2) Å^3, Z = 1. Structure refinement: 11366 independent reflexions (Θ-limits: 1.84–38.0°); refinement method: full-matrix least-squares on F^2; 211 parameters (no restraints); final R indices [$I > 2\sigma(I)$]: R_1 = 0.0227, wR_2 = 0.0499; R indices (all data): R_1 = 0.031, wR_2 = 0.053; largest diff. peak and hole: 0.70 and –0.53 e·Å^{-3}.

Acknowledgements

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