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Synthesis of Two New Group 13 Benzoato-Chloro Complexes: A Structural Study of Gallium and Indium Chelating Carboxylates

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Abstract

Two new heteroleptic chelated-benzoato gallium (III) and indium (III) complexes have been prepared and structurally characterized. The molecular structures of $[GaCl_2(4\text{-Mepy})_2(O_2CPh)]$•4-Mepy (1) and $[InCl(4\text{-Mepy})_2(O_2CPh)_2]$•4-Mepy (2) have been determined by single-crystal x-ray diffraction. The gallium compound (1) is a distorted octahedron with *cis*-chloride ligands co-planar with the chelating benzoate and the 4-methylpyridines *trans* to each other. This is the first example of a Ga(III) structure with a chelating benzoate. The indium compound (2) is a distorted pentagonal bipyramid with two chelating benzoates, one 4-methylpyridine in the plane and a chloride *trans* to the other 4-methylpyridine. The indium *bis*-benzoate is an unusual example of a seven-coordinate structure with classical ligands. Both complexes, which due to the chelates, could also be described as pseudo-trigonal bipyramidal, include a three-bladed motif with three roughly parallel aromatic rings that along with a solvent of crystallization and electron-withdrawing chloride ligand(s) stabilize the solid-state structures.

1.0 Introduction

In recent years, there has been an intense and ongoing interest in the study of gallium and indium complexes for use as potential precursors for electronic materials via chemical spray pyrolysis or chemical solution deposition (Refs. 1 to 4). Ideally, such precursors should be readily prepared from inexpensive starting materials, be easily handled or preferably air-stable, and decompose cleanly for chemically-driven processing to be economically viable (Refs. 5 and 6). In our on-going research, we are preparing derivatives of gallium and indium chlorides with chalcogenide ligands, determining their single-crystal structures and studying further reactions to produce new precursors for solid-state materials (Refs. 6 to 9). For example, oxidative addition of lower-valent Ga and In chlorides (or metal) via addition of carboxylate (RCO_2^-) or dithiocarbamate ($S_2C\text{-}NR_2^-$) ligands by reaction with the respective

chalcogenide-bonded dimers affords compounds that are amenable to characterization, particularly complexes that are stabilized by pyridine-like ligands (Refs. 1 to 10). Use of 4-methylpyridine or γ-picoline solvent (ligands) has yielded complexes that most readily provide single crystals suitable for x-ray diffraction studies. Previously, reaction of sodium benzoate with Ga_2Cl_4 in 4-methylpyridine resulted in isolation and structural characterization of the first oxo-centered main group trinuclear carboxylate, $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-}MeC_5H_5N)_3](GaCl_4]$ (Ref. 9). Similarly, oxidation of indium powder with benzoyl peroxide produced the first example of a mononuclear eight-coordinate indium (III) benzoate, $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}MeC_5H_5N)_2$ (Ref. 10). In this report, we detail two further examples of structurally characterized examples of mixed-ligand chelated-benzoato complexes prepared by this straightforward synthetic approach with classical ligands. We discuss the structures and compare them to other molecular and metal-organic framework structures of indium and gallium.

2.0 Experimental

2.1 Materials and Methods

All manipulations were performed either in an MBRAUN Labmaster 130 drybox or utilizing standard Schlenk techniques under an atmosphere of nitrogen. All solvents were distilled from sodium benzophenone ketyl just prior to use. Celite was purchased from ACROS and heated under vacuum for 24 hr prior to use. All glassware used was flame-dried and stored in an oven prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Gallium (II) chloride (99.999 percent) and indium (I) chloride (99.995 percent) (both from Alfa Aesar) were purchased in argon-filled ampoules and transferred in an inert atmosphere glove box. Benzoyl peroxide ($(C_6H_5CO_2)_2$ - Aldrich) was deaerated under vacuum at room temperature prior to use.

2.2 Preparation of $[GaCl_2(4\text{-}Mepy)_2(O_2CPh)]\bullet 4\text{-}Mepy$ (1)

Gallium (II) chloride (0.302 g, 0.996 mmol) and a 2:1 excess of benzoyl peroxide (0.480 g, 1.98 mmol) were added to a Schlenk flask charged with a stirbar in a drybox. The flask was sealed with a septum, removed from the drybox, and taken to a fume hood where the flask was placed under nitrogen. 4-methylpyridine (10 mL) was slowly added via cannula with rapid stirring. The solution immediately turned a deep crimson red color and the solution was allowed to stir at room temperature for 48 hr. During the course of the reaction, the solution gradually changed from crimson red to orange in color. The reaction mixture was then filtered through a pad of Celite. An equal amount of hexanes was layered on the filtrate via cannula. Colorless single crystals, suitable for x-ray diffraction studies were observed at the solvent interface after standing for 72 hr at room temperature.

2.3 Preparation of $[InCl(4\text{-}Mepy)_2(O_2CPh)_2]\bullet 4\text{-}Mepy$ (2)

Indium (I) chloride (0.150 g, 0.998 mmol) and benzoyl peroxide (0.240 g, 0.998 mmol) were added to a Schlenk flask charged with a stirbar in a drybox. The flask was sealed with a septum, removed from the drybox and taken to a fume hood where the reaction flask was placed under nitrogen. 4-methylpyridine (10 mL) was slowly added via cannula with rapid stirring, and a cloudy solution was evident. The solution was allowed to stir for 7 days at room temperature. The reaction mixture was filtered through a pad of Celite to yield a colorless solution. An equal amount of hexanes was layered on the filtrate via cannula. Colorless single crystals, suitable for x-ray diffraction studies were isolated from the resulting filtrate after standing for 3 weeks at room temperature.

2.4 X-Ray Crystallographic Study of 1 and 2

X-ray intensity data from previously described single crystals were measured at 300 K on a Bruker SMART1000 (Bruker AXS, Inc.) CCD-based x-ray diffractometer system using Mo Kα (λ = 0.71073 Å). Crystals used for data collection were cemented to a quartz fiber with epoxy glue. Data were measured using ω scans of 0.3° per frame for 10 seconds for both **1** and **2** so that a hemisphere (1271 frames) was collected with a final resolution of 0.75 Å. No decay was indicated by the recollection of the first 50 frames at the end of data collection. The frames were integrated with the Bruker SAINT (Bruker AXS, Inc.) software package (Ref. 11) using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS (Refs. 12 and 13) supplied by George Sheldrick (Ref. 14). Structures were solved and refined using the Bruker SHELXTL (Bruker AXS, Inc.) (version 5.1) software package (Refs. 14 and 15) in space groups of *P*-1bar (**1**) and $P2_1/n$ (**2**). All non-hydrogen atoms were derived from the direct method solution. With all non-hydrogen atoms being anisotropic and hydrogen atoms being isotropic, the structure was refined to convergence by least squares method on F^2, SHELXL-97, incorporated in SHELXTL.PC V 5.03 (Ref. 14). Crystallographic data are given in Table 1, selected bond lengths and angles are given in Table 2.

TABLE 1.—SUMMARY OF X-RAY DIFFRACTION DATA

Compound	1	2
Empirical Formula	$C_{25}H_{26}Cl_2GaN_3O_2$	$C_{32}H_{31}ClInN_3O_4$
Molecular Weight	541.11	671.87
Crystal System	Triclinic	Monoclinic
Space Group	*P*-1(bar) (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.5987 (13)	13.1565 (13)
b, Å	11.3705 (15)	8.2116 (8)
c, Å	12.6660 (17)	28.796 (3)
α, deg.	104.525 (2)	90
β, deg.	101.976 (3)	94.460 (2)
γ, deg.	111.981 (2)	90
V, Å^3	1290.7 (3)	3101.6 (5)
Z	2	4
D_{calc}, g cm^{-3}	1.392	1.439
μ, mm^{-1}	1.30	0.89
$\tilde{F}$	556	1368
Crystal size, mm	0.38 by 0.23 by 0.09	0.31 by 0.14 by 0.08
θ range for collection, deg.	2.2 to 22.3	2.5 to 22.2
No. collected	6882	15267
No. ind. (R_{int})	4505 (0.029)	5462 (0.054)
T_{max}, T_{min}	1.000, 0.537	1.000, 0.580
R [$F^2 > 2\sigma(F^2)$]	0.044	0.053
$wR(F^2)$	0.084[a]	0.119[b]
Largest diff. peak and hole, e Å^{-3}	0.48, –0.41	1.17, –0.47
Goodness of fit (GOF) on F^2	1.000	0.999
CCDC deposit no.	753437	753438

[a] $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

[b] $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE 2.—SELECT BOND DISTANCE (Å) AND ANGLES (°) FOR COMPOUNDS 1 AND 2

Ga(1)-O(1)	2.099(2)	In(1)-O(1)	2.274(3)
Ga(1)-O(2)	2.102(3)	In(1)-O(2)	2.292(4)
		In(1)-O(3)	2.212(3)
		In(1)-O(4)	2.417(4)
Ga(1)-N(1)	2.099(3)	In(1)-N(1)	2.312(4)
Ga(1)-N(2)	2.111(3)	In(1)-N(2)	2.286(4)
Ga(1)-Cl(1)	2.2455(11)	In(1)-Cl(2)	2.4132(15)
Ga(1)-Cl(2)	2.2365(11)	O(1)-C(13)	1.261(6)
O(1)-C(1)	1.288(4)	O(2)-C(13)	1.259(6)
O(2)-C(1)	1.271(4)	O(3)-C(20)	1.248(6)
		O(4)-C(20)	1.249(6)
O(1)-Ga(1)-N(1)	85.47(10)	O(3)-In(1)-O(1)	162.40(15)
O(1)-Ga(1)-O(2)	62.83(10)	O(3)-In(1)-N(2)	82.98(14)
N(1)-Ga(1)-O(2)	87.21(11)	O(1)-In(1)-N(2)	83.94(14)
O(1)-Ga(1)-N(2)	86.64(11)	O(3)-In(1)-O(2)	134.10(14)
N(1)-Ga(1)-N(2)	171.04(12)	O(1)-In(1)-O(2)	56.99(12)
O(2)-Ga(1)-N(2)	85.43(11)	N(2)-In(1)-O(2)	140.78(14)
O(1)-Ga(1)-Cl(2)	159.73(8)	O(3)-In(1)-N(1)	86.83(14)
N(1)-Ga(1)-Cl(2)	93.01(9)	O(1)-In(1)-N(1)	81.50(14)
O(2)-Ga(1)-Cl(2)	96.92(8)	N(2)-In(1)-N(1)	90.28(15)
N(2)-Ga(1)-Cl(2)	92.92(10)	O(2)-In(1)-N(1)	81.33(14)
O(1)-Ga(1)-Cl(1)	95.30(8)	O(3)-In(1)-Cl(2)	97.07(11)
N(1)-Ga(1)-Cl(1)	92.62(10)	O(1)-In(1)-Cl(2)	95.43(11)
O(2)-Ga(1)-Cl(1)	158.09(8)	N(2)-In(1)-Cl(2)	93.44(11)
N(2)-Ga(1)-Cl(1)	92.32(10)	O(2)-In(1)-Cl(2)	93.60(10)
Cl(2)-Ga(1)-Cl(1)	104.96(4)	N(1)-In(1)-Cl(2)	174.91(10)
O(2)-C(1)-O(1)	117.6(4)	O(3)-In(1)-O(4)	55.57(13)
		O(1)-In(1)-O(4)	135.57(13)
		N(2)-In(1)-O(4)	138.45(14)
		O(2)-In(1)-O(4)	79.23(13)
		N(1)-In(1)-O(4)	85.11(14)
		Cl(2)-In(1)-O(4)	94.37(10)
		O(2)-C(13)-O(1)	119.6(5)
		O(4)-C(20)-O(3)	120.2(5)

3.0 Results and Discus0sion

3.1 Synthesis of Compounds 1 and 2

The synthesis of both compound **1** and **2** can be simply described as oxidative addition, see (1) and (2) respectively, below, with the cleavage of the peroxide bond and subsequent electron transfer producing benzoate ligands and oxidizing the In and Ga centers to produce trivalent metal complexes.

$$Ga_2Cl_4 + H_5C_6C(O)O\text{-}OC(O)C_6H_5 \rightarrow 2\ GaCl_2(4\text{-Mepy})_2(O_2CC_6H_5) \quad (1)$$

$$InCl + H_5C_6C(O)O\text{-}OC(O)C_6H_5 \rightarrow InCl(4\text{-Mepy})_2(O_2CC_6H_5)_2 \quad (2)$$

The starting material for reaction (1) is actually more accurately described as a Ga(I)Ga(III) species: $Ga^{+}[GaCl_4]^{-}$. The reaction most likely proceeds through an intermediate ethane-like formally Ga(II) complex, $Ga_2Cl_4(\gamma\text{-pic})_2$ (**3**). An unsuccessful attempt to produce a gallium basic carboxylate (Ref. 9), resulted in the isolation and structural characterization of the Ga(II) dimer (Ref. 7). In the same study, an

attempt to produce a mixed-metal Ga-Ni species resulted in the isolation of the solvated mixed-oxidation state salt, $[GaCl_2(\gamma\text{-pic})_4]^+[GaCl_4]^-$ (**4**) (Ref. 7). The isolation and structural characterization of **1** brings to five the number of related structures from the reaction of benzoate-containing reagents and Ga_2Cl_4 in γ-picoline, reinforcing the utility of Ga_2Cl_4 as an extremely versatile entry into Ga coordination chemistry.

The oxidizing potential of benzoyl peroxide is amply demonstrated in reaction (2). We had previously exploited this chemistry when we prepared the first example of an eight-coordinate indium benzoate, $In(O_2CC_6H_5)_3(4\text{-Mepy})_2$, by oxidation of indium metal powder with a 3:2 excess of benzoyl peroxide in γ-picoline (Ref. 10). The use of the indium (I) chloride starting material provides a site for further chemistry to be utilized for preparation of mixed-metal complexes or clusters (Refs. 5 and 6).

3.2 Structural Features of Compound 1

A key structural feature of **1** is the chelating benzoate ligand; compound **1** (shown in Fig. 1) is the first example of such a structurally characterized gallium benzoate. A recent review of mononuclear six-coordinated Ga compounds did not include a single example of a homoleptic, tris-bidentate or chelating carboxylate structure (Ref. 16). A structural and theoretical study by Barron *et al.* demonstrated that chelated-group 13 carboxylate structures (particularly Al) are not energetically favorable, relative to bridged on mono-dentate coordination (Ref. 17). A very thorough discussion of coordination of metal carboxylates can be found in a classic monograph (Ref. 18).

The angle formed by the chelating benzoate in 1, O1-Ga-O2, is 62.83(10)°, and is significantly larger than the average angle for compound **2** of 56.28(13)° but is comparable to an average angle of 62.6(1)° for three structurally characterized chelating carboxylates previously reported (Refs. 19 to 21); a more thorough consideration of indium carboxylate-chelate bonding angles is given below. The previously reported chelating carboxylates include a four-coordinate doubly-chelating dicarboxylate organometallic complex (Ref. 19) and two compounds stabilized by chelating hetrocyclic ligands, one with (pyrazolyl)borate (Ref. 20) and the other with benzoxazole (Ref. 21).

Previously, we prepared a trimeric basic carboxylate (compound **5**) with *syn-syn* bridging benzoates (Ref. 18) obtained through a similar reaction involving sodium benzoate instead of benzoyl peroxide (Ref. 9); see reaction (3). The source of the central oxygen atom is likely water from the sodium benzoate.

$$2\ Ga_2Cl_4 + 6\ NaCO_2C_6H_5 \rightarrow [Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3][GaCl_4] \quad (3)$$

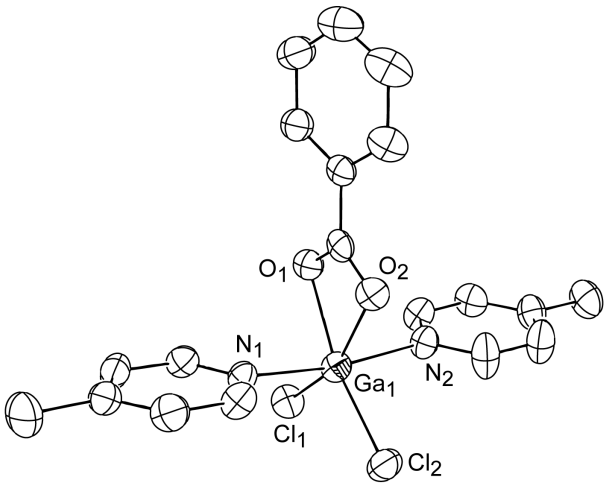

Figure 1.—ORTEP diagram and atomic labeling scheme of first coordination sphere of $[GaCl_2(O_2CPh)(4\text{-Mepy})_2]\bullet 4\text{-Mepy}$ (1) (hydrogen atoms and the co-crystallized picoline not shown for clarity).

The Ga-O bond distances of the bridging benzoates in **5** ranged from 1.959 (5) to 2.006 (9) Å, with an average distance of 1.985(6) Å (Ref. 9). This is shorter than the average Ga-O bond distance for the chelating benzoate found in **1** of 2.101(3) Å. These intermolecular distances are comparable to those found in the three chelating carboxylates (Refs. 19 to 21) that range from 2.042(2) to 2.127(3) Å, with the four-coordinate organometallic compound having the shortest average bond length (2.049(2) Å) (Ref. 19). Of the four structurally characterized chelating gallium carboxylates, only the (pyrazolyl) borate compound had asymmetrical coordination of the carboxylate moiety (ΔGa-O = 0.079(3) Å) (Ref. 20).

This can be contrasted to the surprisingly complex structure of methylgallium diacetate, H_3C-$Ga(O_2CCH_3)_2$ (Ref. 22). This structure includes dative, bridging, and monodentatę acetate coordination resulting in Ga-O bond distances ranging from 1.873(3) to 2.219(3) Å. As noted previously (Ref. 17), several reports of related organometallic indium compounds, dimethyl (Ref. 23) and diethyl (Ref. 24) acetate include simultaneously bridging and chelating acetate coordination. A much more straightforward Ga acetate monodentate interaction is found in a neutral acetato tetraphenylporphyrin complex (Ga(OAc)(tpp) with Ga-O bond length of 1.874(4) Å (Ref. 25), very similar to the mondentate Ga-O bond length of 1.873(3) Å (Ref. 22).

A further example of a lengthened M-O bond for a chelating versus bridging carboxylate group is demonstrated by a series of silver complexes $(AgO_2CR)_2$ where a dimer (R = C(Me)=C(Me)H) with bridging carboxylates is stabilized as a monomer by the addition of triphenylphosphine ligands: $[AgO_2CR(PPh_3)_2]$ (R = CH_2CN, CH_2CH_2=C(H)CH_2, and C(Me)=C(Me)H) with a subsequent average increase of 0.235(3) Å for a chelated versus bridging Ag-O bond length (Ref. 26).

The carboxylate moiety in **1** is fairly symmetrical with an average C-O bond length of 1.280(4) Å. This is comparable to an average C-O bond length of 1.274(5) Å for the bridging acetates of methylgalliumdiacetate (Ref. 22), 1.25(2) Å for the bridging benzoates of compound **5** (Ref. 9), 1.255(2) Å for the chelating acetate of the benzoxazole (Ref. 21), and 1.254(6) Å for compound **2** of this study. A recent study of solvent-free synthesis of a bismuth carboxylate reported a C-O bond range of 1.249(2) Å to 1.301(2) Å for dimeric substituted benzoates with multiple coordination modes (Ref. 27).

The 2.105(3) Å average Ga-N bond length for the ligated picolines is comparable to 2.105(5) Å for **4** (Ref. 7) and 2.085(9) Å for **5** (Ref. 9). This is slightly longer than Ga-N bond length of 2.058(4) Å for the (pyrazolyl)borate (Ref. 20) and 2.034(2) Å for the benzoxazole (Ref. 21) compounds. It is longer than the Ga-N (picoline) bond length of 2.005 (6) Å of the Ga(II) complex, **3** (Ref. 7). Finally, the Ga-Cl average bond length of 2.2410(11) Å is comparable to Ga-Cl bond lengths determined for compounds **3** (2.195(2) Å) and **4** (cation – 2.320(2) Å; anion – 2.157(3) Å)) (Ref. 7), **5** (anion – 2.126(12) Å) (Ref. 9), and 2.2827(16) Å averaged for $[GaCl_2(\gamma\text{-pic})_2(S_2CNR_2)]$ (R = Me (Ref. 8), Et (Ref. 7)).

The N1-Ga-N2 angle is 171.04(12)°; as expected the picoline rings tilt towards the chelated benzoate. The three aromatic rings are roughly parallel; giving the complex a semi-paddlewheel appearance, more typically associated with bridging carboxylate structures (Refs. 9 and 28). The narrow angle of the benzoate results in a larger Cl2-Ga-Cl1 angle of 104.96(4)°. The O2-C1-O1 angle of 117.6(4)° is slightly smaller than the 120° expected for an sp^2 hybridized RCO_2^- moiety; this is likely due to the steric hindrance of the chelated benzoate bonding to a Ga(III) center. For the less-constrained six bridging benzoates in complex **5**, the CO_2^- angle ranged from 123° to 128° (Ref. 9). In $CH_3Ga(OAc)_2$, the average bridging CO_2^- bonding angle was 120.3(3)°; the monodentate acetate had a 122.0(5)° CO_2^- bonding angle (Ref. 19); and the monodentate acetate of (Ga(OAc)(tpp) had a 122.9(5)° CO_2^- bonding angle (Ref. 22). The other chelating carboxylates (Refs. 19 and 21) had more narrow O-C-O angles of approximately 118°, expected for the wider O-Ga-O chelate.

3.3 Structural Features of Compound 2

As has been noted previously, bidentate chelating In (III) carboxylate bonding has not frequently been observed (Refs. 17 and 18). Compound **2** (shown in Fig. 2) had In-O bond distances ranging from 2.212(3) Å to 2.417(4) Å with one symmetrical benzoate, like complex **1**, with an average In-O distance of 2.283(4) Å, the other unsymmetrical with a 0.205 Å ΔIn-O bond length. A review of In-O bond lengths in

chelating In carboxylates exhibits a range from 2.142(5) to 2.875(8) Å from (nearly) symmetrical to asymmetrical (Refs. 4, 10, 29 to 36). In our previously reported eight-coordinate In benzoate complex, one benzoate was symmetrical with an In-O bond distance of 2.286(5) Å, and the other two were asymmetrical with distances of 2.225(6) Å and 2.413(5) Å (Ref. 10). Asymmetrical bonding of chelating carboxylate groups to an In(III) center has been observed for other eight-coordinate carboxylates: $In(O_2CMe)_3L$ (L = phen, ΔIn-O = 0.157(7) Å and 0.198(7) Å ; L = bipy, ΔIn-O = 0.172(6) Å) (Ref. 37). A related but simpler, cis-dichloro chelating-benzoato octahedral complex with two trans pyridine ligands had similar, nearly symmetrical In-O bond lengths of 2.246(4) Å and 2.280(4) Å (Ref. 32). Another octahedral benzoate compound with a tetradentate N_2S_2 bis(aminoethanethiol) chelate had a significantly more asymmetric benzoate coordination with In-O bond lengths of 2.247(3) Å and 2.390(3) Å (Ref. 30). Another seven-coordinate carboxylate with a terpyridine and two azide ligands had a slightly less asymmetric carboxylate with In-O bond lengths of 2.274(2) Å and 2.354(2) Å (Ref. 4). A similar degree of asymmetry is observed for a series of trinuclear and tetranuclear metal cluster butyrates containing In, and Co or Ni atoms (Ref. 31).

An unsymmetrical acetate is found in a $(TPP)In(O_2CCH_3)$ (TPP = tetraphenylporphinato) complex with In-O bond lengths of 2.215(4) Å and 2.322(4) Å (Ref. 33). A pair of related tetra-arylporphyrinato indium acetates $(TRP)In(O_2CCH_3)$ (R = py, 4-pyridyl; mp, 4-methoxyphenyl) resulted in nearly symmetrical (R = py, In-O range from 2.24(1) to 2.34(1) Å) and unsymmetrical (R = mp, In-O = 2.185(6) Å and 2.412(6) Å) acetates (Ref. 34). An asymmetrically-bound acetate is also found in an $(OEP)In(O_2CCH_3)$ (OEP = octaethylporphyrinato) complex with In-O bond lengths of 2.60(2) Å and 2.14(1) Å (Ref. 35). Two related ylide-containing halide compounds had In-O coordination that varied from slightly (< 0.1 Å) to moderately asymmetric (> 0.25 Å) (Ref. 29). Finally, the most asymmetric bidentate chelate is found in a dimeric μ-oxo bridged neutral seven-coordinate complex $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\bullet 2NaClO4$ (L = 1,4,7-triazacyclononane) with each In(III) bound to a monodentate and chelating acetate group; significantly different average In-O bond lengths in the chelating groups of 2.142(5) Å and 2.863(7) Å (Ref. 36) are present.
The In-Cl bond length in **2** is 2.4132(15) Å and similar to the related octahedral chloro-benzoato compound, 2.391(2) Å (Ref. 32). It is also comparable to the *cis*-In-Cl bond length in *mer*-$InCl_3(4\text{-Etpy})_3$ of 2.41 Å but shorter than the *trans*-In-Cl bond length of 2.46 Å (Ref. 38). The *cis*- (2.471(1) Å) and *trans* (2.476(2) Å) In-Cl bond lengths in *mer*-$InCl_3(py)_3\bullet py$ (Ref. 39) are practically equal within experimental error. The ylide compound with chloride ligands has an In-Cl bond length that ranges from 2.26(1) to 2.49(1) Å (Ref. 29).

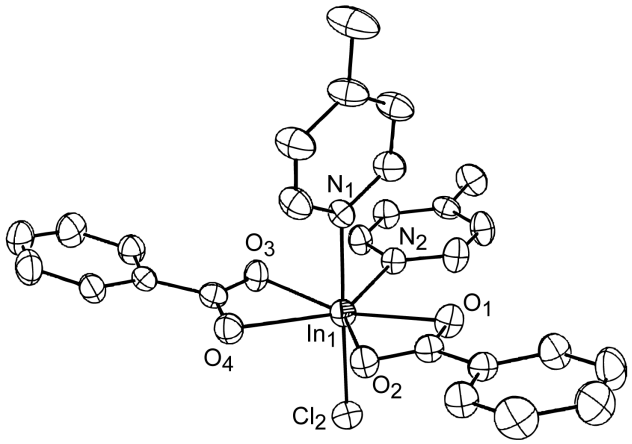

Figure 2.—ORTEP diagram and atomic labeling scheme of first coordination sphere of $[InCl(O_2CPh)_2(4\text{-Mepy})_2]\bullet 4\text{-Mepy}$ (2) (hydrogen atoms and the co-crystallized picoline not shown for clarity).

The In-N bond lengths are unremarkable but slightly unsymmetrical; there is a slight lengthening of the In-N bond *trans* to the Cl (2.312(4) Å versus 2.286(4) Å in the plane). The two In-N bond lengths for the trans pyridines in the related octahedral compound are (2.250(5) and 2.300(6) Å (Ref. 32). This is typically not observed in the family of *mer*-$InX_3(Rpy)_3$ (R = H, X = I, Br; R = Et; X = Cl; R = Me, X = I) complexes where the average In-N bond length is 2.31 Å (Refs. 38 to 41). There is some asymmetry in *mer*-$InCl_3(py)_3$•py where there is a some lengthening of the In-N bond *trans* to a Cl (2.377(21) Å) versus 2.302(7) Å (for trans pyridines). The In-N bond lengths were similar for the two seven-coordinate compounds with terpyridine (2.292(2) – 2.341(2) Å) and azide (2.203(3) Å) ligands (Ref. 4) and the triazacyclononane chelate (2.271(5) to 2.324(5) Å) (Ref. 36). The tetradentate bis(aminoethanethiol) octahedral compound (2.298(3) and 2.367(3) Å) was also similar (Ref. 30). The In-N bond lengths for the porphyrin compounds were shorter and ranged from 2.16 to 2.18 Å (Refs. 33 to 35).

The Cl(2)-In(1)-N(1) bond angle is 174.91(10)°, the apical Cl atom is inclined away from the other five coordinated atoms in the InO_4N plane at angles from 93.44(11)° (N(2)-In(1)-Cl(2)) to 97.07(11)° (O(3)-In(1)-Cl(2)). The two In-N bonds are nearly perpendicular forming a (N(2)-In(1)-N(1) angle of 90.28(15)°. The four In-O bonds are bent towards the apical N(1) forming O-In(1)-N(1) angles that vary from an average of 81.42(14)° for In-O(1) and In-O(2) to 86.83(14)° for In-O(3). Steric factors can be invoked to explain this structural feature. As with the gallium complex above, the two chelating benzoates and the apical picoline are roughly parallel and form a semi-paddlewheel structure.

The benzoate chelates contain smaller angles of 56.99(12)° and 55.57(13)° for (O(1)-In(1)-O(2)) and (O(3)-In(1)-O(4)), respectively in the indium complex (**2**) than the gallium complexes (**1**) and (Refs. 19 to 21). The individual nearest-neighbor atoms in the InO_4N plane form five angles that add up to approximately 359°; the non-chelated atoms form average angles of 82°. The larger size of the In(III) center results in less steric strain for the chelates and a nearly symmetrical RCO_2^- average bond angle of 119.9(5)°. The closely-related eight-coordinate *tris*-benzoato *bis*-picoline indium (III) complex had quite similar O-In-O angles of 56.5(3) ° and 55.9(2)° (Ref. 10). The eight-coordinate complex also had a nearly symmetrical RCO_2^- average bond angle of 119.5(8)°. The octahedral benzoato complex, isostructural with compound **1**, had a similar RCO_2^- angle (118.9(6)°), with a wider O-In-O angle of 57.5(1)° (Ref. 32), similar to the larger of the two angles of compound **2**, but significantly less than the O-Ga-O angle of 62.83(10)° of **1**. With a few exceptions, the O-In-O benzoate angle ranged from a low of 55.57(13) to 56.99(12) for many of the six, seven, or eight-coordinate carboxylates. The six-coordinate porphyrin acetate compounds had slightly smaller average O-In-O (54.6(3)°) and RCO_2^- (118.5(4)°) angles (Refs. 33 and 34). The dimeric μ-oxo bridged neutral seven-coordinate complex $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]$•2NaClO4 (L = 1,4,7-triazacyclononane) with asymmetric chelating acetate groups had a significantly constrained O-In-O bond angle of 48.9(2)°. The smaller O-In-O angle with the porphyrin-containing structures is expected as the macrocycles impose steric strain. The ylide compounds (Ref. 29) and the multi-nuclear cluster compounds (Ref. 31) had larger bond angles ranging from around 57° to 59°.

As noted above and compiled in Table 3, there are nearly 15 chelated In(III) carboxylate or related molecular structures that are five (Ref. 29) six (Refs. 29 to 36), seven (**2** and (Refs. 4, 31, and 36)), and eight (Refs. 10 and 37) coordinate. Many of these chelating carboxylate structures consist of a macrocyclic or large heterocyclic chelating ligand (Refs. 4, 30, 33 to 36) or multi-nuclear cluster structure (Ref. 31). It is reasonable to assert that the aromatic benzoato chelate and pyridine-like ligands (Refs. 10 and 32), electron-withdrawing halide ligands (**2**, (Refs. 29 and 32)) and solvent of crystallization (**2**, (Ref. 10) stabilize the structures in a similar fashion without undue steric hindrance. Two other macrocycle-stabilized structures of seven-coordinate In(III) to note are two related pentagonal bipyramid complexes, $[InCl_3(L')(MeOH)]$ and $[InCl(\eta^2\text{-}C_2O_4)(L')(OH_2)]$ (L' = 2,6-bis(acetyloxime)-pyridine) (Refs. 42 and 43). A final observation to make is that compounds **1** and **2** adopt a roughly pentagonal bipyramidal structure. Compound **1**, and the isostructural In complex (Ref. 32), can be described as semi-paddlewheel with three roughly parallel aromatic rings. The semi-paddlewheel motif of compound **2** has a more propeller-like appearance with a bowl-shaped triple aromatic-ring coordination plane.

TABLE 3.—SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR MOLECULAR COMPLEXES WITH CHELATING CARBOXYLATES OF Ga, In AND OTHER METALS WITH SIMILAR IONIC RADII

Compound	CN	d_{M-O} (Å)	O-M-O (°)	O-C-O (°)	Reference
$[Ag(O_2CR)(P(C_6H_5)_3)_2]$ R = CH_2CN, $(CH_2)_2CH{=}CH_2$, or C(Me)=C(H)Me	4	2.401(3) – 2.495(2)	52.61(7) – 53.86(6)	122.6(2) – 126.4(3)	Ref. 26
$[(Ga((Me_3Si)_2CH)_2)_2(ndc)]\bullet 2MeC_5H_9$ H_2ndc = 1,6-naphthalenedicarboxylic acid	4	2.042(2), 2.056(2)	64.53(8)	118.0(3)	Ref. 19
$[InCl_3(\eta 2\text{-}O_2CC\{P(C_6H_5)_3\}_2]$	5	2.181(6), 2.304(6)	58.7(2)	118.6(8)	Ref. 29
$[InI_2(\eta 2\text{-}O_2CC\{P(C_6H_5)_3\}_2^+][I^-]$	6	2.168(5) – 2.437(5)	57.0(2), 58.6(2)	117.9(7), 120.1(7)	Ref. 29
$[H_2B(pz)_2]_2Ga(O_2CCH_3)$ pz = $\{N_2(CH)_3\}$	6	2.048(3), 2.127(3)	62.3(1)		Ref. 20
$[Ga(hbo)_2(O_2CCH_3)]$ Hhbo = 2-(2'-hydroxyphenyl)-2-benzoxazole	6	2.117(2)	61.1(1)	118.2(4)	Ref. 21
$[GaCl_2(O_2CPh)(4\text{-}Mepy)_2]\bullet 4\text{-}Mepy$	6	2.099(2), 2.102(3)	62.83(10)	117.6(4)	This work
[In (BAT-TM)$(O_2CC_6H_5)$] BAT-TM = N_2S_2 tetradentate ligand	6	2.247(3), 2.390(3)	56.3(1)	120.7(4)	Ref. 30
$[In_2M_2(OH)_2(O_2C^tBu)_8L_2]$[a] (M,L = Co, MeCN; M,L = Ni, MeCN/HO_2C^tBu)	6	2.2091(13) –2.275(8)	56.9(3) –59.1(3)	117.1(10) –120.6(10)	Ref. 31
$[InCl_2(O_2CPh)(py)_2]$	6	2.246(4), 2.280(4)	57.5(1)	118.9(6)	Ref. 32
$[In(TPP)(O_2CCH_3)]$ TPP = tetraphenylporphyrin	6	2.215(4), 2.322(4)	54.4(2)	118.5(4)	Ref. 33
$[In(TRP)(O_2CCH_3)]$ R = 4-pyridyl or 4-methoxyphenyl	6	2.185(6) – 2.412(6)	54.4(4), 55.0(2)	115(2) –121.1(7)	Ref. 34
$[InCl(O_2CPh)_2(4\text{-}Mepy)_2]\bullet(4\text{-}Mepy)$	7	2.212(3) – 2.417(4)	55.57(13), 56.99(12)	119.6(5), 120.2(5)	This work
$[L_2In_2(O_2CCH_3)_4(\mu\text{-}O)]\bullet 2NaClO_4$ L = 1,4,7-triazacyclononane	7	2.142(5) – 2.875(8)	48.9(2)		Ref. 36
$[In_2Ni(OH)(O_2C^tBu)_7(HO_2C^tBu)_x]$[a] ($x$ = 1,2)	7	2.208(6) – 2.249(6)	58.4(2), 58.5(2)	118.6(8), 119.0(8)	Ref. 31
$[(terpy)In(N_3)_2(O_2C(CH_2)_2CH_2OH)]$ terpy = terpyridine	7	2.274(2), 2.354(2)	56.31(7)	120.2(2)	Ref. 4
$[SbCl(C_6H_5)_2(O_2C(2\text{-}Me)C_6H_4)_2]$	7	2.213(3) – 2.296(3)	57.46(11), 57.58(11)	118.8(6), 120.5(7)	Ref. 44
$[Cd(O_2C(3,4\text{-}OH)C_6H_3)_2(H_2O)_3]$	7	2.304(4) – 2.513(4)	54.0(1), 54.3(1)	117.3(4), 117.6(4),	Ref. 45
$[MoBr(O_2CCF_3)(CO)_2(P(C_6H_5)_3)_2]$	7	2.304(9), 2.320(9)	56.5(3)	126.0(1)	Ref. 46
$[Bi(O_2C(2\text{-}EtO)C_6H_4)_3]_2$	8	2.207(1), 2.532(1)	55.06(4)	120.2(2)	Ref. 27
$[In(O_2CPh)_3(4\text{-}Mepy)_2]\bullet 4H_2O$	8	2.225(6) – 2.413(5)	55.9(2), 56.5(3)	119(1), 120.0(7)	Ref. 10
$[In(O_2CCH_3)_3L]$ L = 2,2'-bipy or 1,10-phen	8	2.221(3) – 2.422(6)	54.4(2) – 56.5(3)		Ref. 37

[a]Data for In coordination environment only.

3.4 Comparison of Compounds 1 and 2 with Similar Molecular Complexes of Other Metals

It is interesting to include a survey of other related chelating-carboxylate complexes of other metals similar in size to In(III) ions. Table 3 includes compounds **1** and **2**, other related indium and gallium structures, and other related structures of mostly main group complexes with higher coordination numbers and similar ionic radii (0.8 ~ 0.92 Å) to In(III) complexes. A key feature of nearly every compound in Table 3 is complexation with aromatic rings for electronic and steric stability. These chelating compounds rely on a variety of motifs for supporting the chelating structure: macrocyclic and/or multi-dentate ligands (Refs. 4, 10, 19 to 21, 26, 30, 33 to 37), carboxylates with unsaturated bonds or pendant groups for structural or electronic stabilization (Refs. 4, 26, 27, 29, 44, and 45), or electronic-withdrawing ligands such as halides and $CF_3CO_2^-$ (**1**, **2**, (Refs. 29, 32, 37, 38, and 46)). Interestingly, several structures contained multiple modes of coordination to identical carboxylate groups (Refs. 27 and 31).

The structure most similar to compound **1** is the analogous six-coordinate In benzoate complex (Ref. 32). However, due to the larger size of the In(III) ion, this structure does not contain as much strain around the chelating benzoate. The seven-coordinate Sb(V) organometallic compound is most similar in structure to **2** (Ref. 44). The other structurally-characterized seven-coordinate In(III) carboxylate environments are sterically constrained by tri-dentate chelating ligands (Refs. 4 and 36) or a multi-nuclear cluster environment (Ref. 31). Apparently, electron-withdrawing chloride ligand(s) and the inherent stability of the semi-paddlewheel

structure of the aromatic rings enables the use of simpler ligands via a straightforward synthesis used to produce compounds **1** and **2** and the related octahedral indium complex (Ref. 27).

3.5 Comparison of Molecular Indium Benzoates with Indium Coordination Polymers

While a slight departure from the major thrust of this paper, it is useful to include a brief survey of recently reported chelating-carboxylate indium coordination polymers (Refs. 47 to 61), part of a recent wave of a literature describing intriguing new hybrid organic-inorganic materials with many potential applications. Table 4 includes numerous examples of indium carboxylate polymer framework materials and seven- and eight-coordinate indium benzoates from this study (compound **2**) and Reference 10, respectively. Table 4 includes five basic types of In polymers constructs: seven-coordinate In polymers from di- (Refs. 47 to 49), tri- (Refs. 50 to 53) and tetracarboxylates (Ref. 54 and 55) and eight-coordinate In polymers from di- (Refs. 56 to 59) and tricarboxylates (Refs. 60 and 61), several of which are chiral (Refs. 51, 58, and 59).

TABLE 4.—SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR INDIUM COORDINATION POLYMERS AND MOLECULAR BENZOATES

Compound	CN	d_{M-O} (Å)	O-M-O (°)	O-C-O (°)	Reference
$[InCl(O_2CPh)_2(4\text{-Mepy})_2]\bullet(4\text{-Mepy})$	7	2.212(3) – 2.417(4)	55.57 (13), 56.99(12)	119.6(5), 120.2(5)	This work
$[In(OH)(ndc)_2(H_2O)]_n$ H_2ndc = 2,6- or 2,7-naphthalenedicarboxylic acid	7	2.247(2) – 2.3458(18)	56.39(12), 58.00(8)	119.1(2), 119.5(3)	Ref. 47
$[In_2OH)_2(pdc)_2(H_2O)]_n$ H_2pdc = 3,5-pyridinedicarboxylic acid	7	2.255(2), 2.311(2)	57.53(5)	121.36(18)	Ref. 48
$[In(OH)(tca)(H_2O)]_n$ H_2tca = thiophene-2,5-dicarboxylic acid	7	2.209(2) – 2.391(2)	56.86(7), 57.53(7)	119.8(2),120.2(2)	Ref. 49
$\{[Hbipy^+][In(Hbtc)_2(bipy)^-]\bullet 0.5H_2O\}_n$ H_3btc = benzenetricarboxylic acid bipy = 4,4'-bipyridine	7	2.208(4) – 2.360(5)	54.4(4), 55.0(2)	120.1(6), 120.3(6)	Ref. 50
$\{[Hpy^+]_2[In_2(btc)_2(\mu\text{-}OH)_2^{2-}]\}_n$ H_3btc = benzenetricarboxylic acid py = pyridine	7	2.140(11) – 2.569(10)	54.8(3) – 57.1(4)	119.5(13) –124.1(14)	Ref. 51
$\{[In_2(btc)_2(bipy)_2]\bullet 4H_2O\}_n$ H_3btc = benzenetricarboxylic acid bipy = 2,2'-bipyridine	7	2.170(4) – 2.434(4)	56.06(13), 56.38(12)	119.4(5),120.4(5)	Ref. 52
$\{[In_2(btc)_2(H_2O)_2]\bullet 2H_2O\}_n$ H_3btc = benzenetricarboxylic acid	7	2.575(2), 2.580(2)	56.75(11), 58.10(11)	119.4(4),119.8(4)	Ref. 53
$[In_2(btec)(bipy)_2Cl_2]_n$ H_4btec = benzenetetracarboxylic acid bipy = 2,2'-bipyridine	7	2.176(8) – 2.551(9)	54.7(2) –57.5(2)	118.8(7) –122.3(11)	Refs. 54 and 55
$[In(O_2CPh)_3(4\text{-Mepy})_2]\bullet 4H_2O$	8	2.225(6) – 2.413(5)	55.9(2), 56.5(3)	119(1), 120.0(7)	Ref. 10
$\{[H^+][In(bdc)_2^-]\}_n$ H_2bdc = benzenedicarboxylic acid	8	2.267(7), 2.283(7)	57.7(3)	120.8(9)	Ref. 56
$\{[M(H_2O)_6^{3+}][In_3(\mu_2\text{-}pdc)_6^{3-}]\bullet 15H_2O\}_n$ H_2pdc = 2,3-pyrazinedicarboxylic acid M = In, $Cr_{0.7}In_{0.3}$, or $Fe_{0.3}In_{0.7}$	8	2.236(4) – 2.446(6)	54.9(2) – 55.4(3)	120.3(5) – 123.4(8)	Ref. 57
$\{[(Htmdp)^+][In(pdc)_2^-]\bullet(EtOH)(H_2O)_2\}_n$ tmdp = 4,4'-trimethylenedipiperidine H_2pdc = 2,5-pyridinedicarboxylic acid	8	2.205(5), 2.588(5)	54.29(17)	122.5(7)	Ref. 58
$\{[NR_4^+][In(DL\text{-}cam)_2^-]\bullet(H_2O)_2\}_n$ R = CH_3; D- and L-camphorate NR_4^+ = choline; D-camphorate	8	2.188(7) – 2.407(8)	55.4(3) – 57.3(3)	119.0(10) –120.7(9)	Ref. 59
[a] $\{[NR_4^+][In(DL\text{-}cam)_2^-]\bullet(H_2O)_2\}_n$ R = *n*-propyl; D- or DL-camphorate NR_4^+ = imidizolium; D-camphorate*	8	2.163(3) – 2.481(3)	54.7(4) – 58.2(4)	117(2) –124.8(16)	Ref. 60
$[In(btc)_{1.5}(bipy)]_n$ H_3btc = 1,4-benzenetricarboxylic acid bipy = 2,2'-bipyridine	8	2.204(3) – 2.551(4)	53.50(11) – 57.22(10)	120.1(4), 120.5(4)	Ref. 61
$\{[H_2tmdp^{2+}]_3[In_6(btc)_8^{6-}]\bullet 40H_2O\}_n$ tmdp = 4,4'-trimethylene dipiperidine H_3btc = benzenetricarboxylic acid	8	2.155(5) –2.409(5)	56.36(18)	120.3(6)	Ref. 62

[a]Table entry also includes three more related structures (total of six) from same publication.

The most notable observation to make when viewing the relevant bond distances and angles of the polymer materials as compared to the respective molecular species is the striking similarity of the In coordination environments; this is expected due to a lack of steric strain around In atoms from the flexible polymer coordination environment, it is this flexibility that gives rise to a variety of intriguing 2–D and 3–D structural features. The In-O bond distances and O-In-O and O-C-O carboxylate angles of the polymer materials are quite similar to the molecular benzoates.

4.0 Conclusion

In summary, we have prepared two new simple chelating benzoate complexes of gallium and indium by straightforward oxidation of the Ga(II) and In(I) chlorides by benzoyl peroxide in 4-methylpyridine at room temperature. The six-coordinate gallium complex, which also includes two chloride and two g-picoline ligands, is the first example of a structurally-characterized chelating gallium benzoate. It is isostructural with a previously characterized analagous In(III) benzoate complex. The seven-coordinate In(III) *bis*-benzoate also includes one chloride and two g-picoline ligands and is the first example of its type with a simple ligand set; it is a structural analogue to a seven-coordinate Sb(V) organometallic compound. The most striking feature of these surprisingly simple compounds is a semi-paddlewheel geometry of roughly parallel aromatic rings of the benzoate and picoline ligands, which seems to lend an enhanced stability to the solid-state structures. This stability is further demonstrated by the similarity of the metal coordination environment for a number of seven or eight-coordinate indium carboxylate coordination polymer materials.

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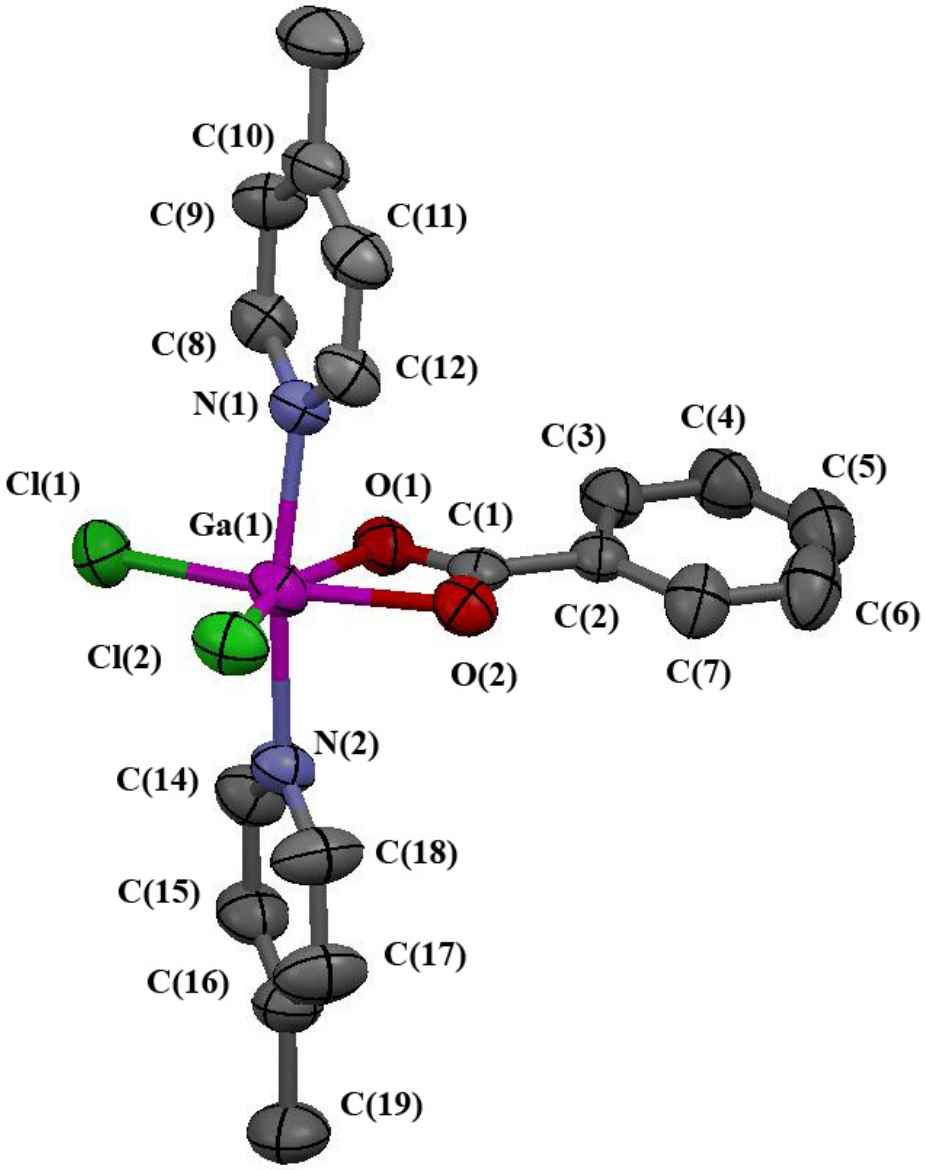
Appendix A.—Alternate Diagram of and Extensive Structural Information for Compound (1) - $[GaCl_2(4\text{-Mepy})_2(O_2CPh)]\bullet 4\text{-Mepy}$



Crystal data

$C_{25}H_{26}Cl_2GaN_3O_2$	$Z = 2$
$M_r = 541.11$	$F_{000} = 556$
Triclinic, $P\overline{1}$	$D_x = 1.392$ Mg m^{-3}
$a = 10.5987$ (13) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.3705$ (15) Å	Cell parameters from 1731 reflections
$c = 12.6660$ (17) Å	$\theta = 2.2$–22.3^o
$\alpha = 104.525$ (2)º	$\mu = 1.30$ mm^{-1}
$\beta = 101.976$ (3)º	$T = 300$ K
$\gamma = 111.981$ (2)º	Block, colorless
$V = 1290.7$ (3) Å^3	0.38 × 0.23 × 0.09 mm

Data collection

CCD area detector diffractometer	4505 independent reflections
Radiation source: fine-focus sealed tube	2485 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.029$
$T = 300$ K	$\theta_{max} = 25.0^o$
phi and ω scans	$\theta_{min} = 1.8^o$
Absorption correction: empirical (using intensity measurements) SADABS, Absorption corrections using Bruker CCD based on the method of Bob Blessing. Acta Cryst. 1995, A51, 33	$h = -12 \rightarrow 7$
$T_{min} = 0.537$, $T_{max} = 1.000$	$k = -13 \rightarrow 13$
6882 measured reflections	$l = -13 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
4505 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
298 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ga1	−0.23970 (5)	−0.44062 (5)	−0.25452 (4)	0.05802 (17)
Cl1	−0.30851 (12)	−0.62951 (11)	−0.40717 (9)	0.0740 (3)
Cl2	−0.18058 (11)	−0.49430 (12)	−0.09941 (9)	0.0765 (4)
O1	−0.2756 (3)	−0.3260 (3)	−0.3534 (2)	0.0600 (7)
O2	−0.1910 (3)	−0.2382 (3)	−0.1639 (2)	0.0622 (7)
N1	−0.4524 (3)	−0.4933 (3)	−0.2561 (3)	0.0539 (8)
N2	−0.0254 (3)	−0.3593 (3)	−0.2553 (3)	0.0610 (9)
N3	0.4579 (7)	0.1857 (6)	−0.0564 (5)	0.141 (2)
C1	−0.2320 (4)	−0.2236 (4)	−0.2594 (4)	0.0545 (11)
C2	−0.2309 (4)	−0.0946 (4)	−0.2627 (4)	0.0531 (10)
C3	−0.2995 (4)	−0.0896 (4)	−0.3650 (4)	0.0700 (12)
H3A	−0.3453	−0.1671	−0.4320	0.084*
C4	−0.3006 (5)	0.0313 (6)	−0.3685 (5)	0.0837 (15)
H4A	−0.3482	0.0345	−0.4374	0.100*
C5	−0.2326 (6)	0.1433 (6)	−0.2721 (6)	0.0909 (16)
H5A	−0.2335	0.2239	−0.2750	0.109*
C6	−0.1627 (6)	0.1412 (5)	−0.1704 (5)	0.0909 (15)
H6A	−0.1150	0.2199	−0.1045	0.109*
C7	−0.1630 (5)	0.0199 (5)	−0.1659 (4)	0.0749 (13)
H7A	−0.1166	0.0172	−0.0963	0.090*
C8	−0.5613 (5)	−0.5552 (4)	−0.3551 (4)	0.0635 (12)
H8A	−0.5413	−0.5699	−0.4240	0.076*
C9	−0.7031 (5)	−0.5987 (4)	−0.3602 (4)	0.0733 (13)
H9A	−0.7767	−0.6426	−0.4316	0.088*
C10	−0.7365 (5)	−0.5772 (5)	−0.2593 (5)	0.0735 (13)
C11	−0.6231 (6)	−0.5084 (5)	−0.1579 (4)	0.0761 (14)
H11A	−0.6399	−0.4884	−0.0879	0.091*
C12	−0.4836 (5)	−0.4684 (4)	−0.1588 (4)	0.0665 (12)
H12A	−0.4080	−0.4220	−0.0885	0.080*
C13	−0.8909 (5)	−0.6276 (5)	−0.2597 (5)	0.1088 (18)

H13A	−0.9561	−0.6736	−0.3381	0.163*
H13B	−0.9058	−0.5517	−0.2223	0.163*
H13C	−0.9086	−0.6895	−0.2189	0.163*
C14	0.0025 (5)	−0.3683 (4)	−0.3549 (4)	0.0702 (13)
H14A	−0.0741	−0.4104	−0.4244	0.084*
C15	0.1426 (5)	−0.3163 (4)	−0.3564 (4)	0.0767 (14)
H15A	0.1582	−0.3249	−0.4270	0.092*
C16	0.2574 (5)	−0.2532 (5)	−0.2573 (5)	0.0754 (14)
C17	0.2266 (5)	−0.2450 (5)	−0.1556 (4)	0.0980 (17)
H17A	0.3011	−0.2038	−0.0848	0.118*
C18	0.0855 (5)	−0.2982 (5)	−0.1596 (4)	0.0925 (16)
H18A	0.0675	−0.2903	−0.0900	0.111*
C19	0.4104 (5)	−0.1978 (5)	−0.2558 (4)	0.1003 (17)
H19A	0.4113	−0.2131	−0.3336	0.150*
H19B	0.4580	−0.2429	−0.2213	0.150*
H19C	0.4600	−0.1019	−0.2115	0.150*
C20	0.4810 (7)	0.1905 (6)	−0.1547 (8)	0.114 (2)
H20A	0.5763	0.2367	−0.1505	0.137*
C21	0.3806 (9)	0.1355 (6)	−0.2581 (6)	0.1060 (19)
H21A	0.4063	0.1405	−0.3233	0.127*
C22	0.2386 (8)	0.0712 (6)	−0.2676 (6)	0.0974 (17)
C23	0.2116 (7)	0.0679 (7)	−0.1695 (8)	0.125 (2)
H23A	0.1167	0.0253	−0.1716	0.150*
C24	0.3193 (10)	0.1250 (8)	−0.0688 (7)	0.165 (3)
H24A	0.2953	0.1219	−0.0026	0.197*
C25	0.1231 (7)	0.0103 (7)	−0.3808 (6)	0.175 (3)
H25A	0.0310	−0.0304	−0.3712	0.263*
H25B	0.1364	−0.0581	−0.4328	0.263*
H25C	0.1268	0.0797	−0.4121	0.263*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.0590 (3)	0.0678 (3)	0.0582 (3)	0.0344 (3)	0.0263 (2)	0.0255 (3)
Cl1	0.0780 (9)	0.0679 (8)	0.0761 (8)	0.0371 (7)	0.0308 (6)	0.0155 (7)
Cl2	0.0733 (9)	0.0976 (9)	0.0767 (8)	0.0449 (7)	0.0270 (6)	0.0488 (7)
O1	0.059 (2)	0.0633 (19)	0.0668 (19)	0.0302 (15)	0.0304 (15)	0.0254 (17)
O2	0.065 (2)	0.073 (2)	0.0607 (19)	0.0340 (15)	0.0322 (15)	0.0284 (17)
N1	0.051 (2)	0.064 (2)	0.053 (2)	0.0303 (19)	0.0190 (19)	0.0224 (19)
N2	0.053 (2)	0.077 (3)	0.059 (2)	0.034 (2)	0.024 (2)	0.021 (2)
N3	0.121 (5)	0.151 (5)	0.094 (4)	0.028 (4)	0.022 (4)	0.021 (4)
C1	0.037 (3)	0.060 (3)	0.069 (3)	0.019 (2)	0.029 (2)	0.023 (3)
C2	0.046 (3)	0.056 (3)	0.063 (3)	0.022 (2)	0.029 (2)	0.023 (3)
C3	0.064 (3)	0.070 (3)	0.084 (4)	0.033 (3)	0.031 (3)	0.031 (3)
C4	0.088 (4)	0.089 (4)	0.098 (4)	0.050 (3)	0.038 (3)	0.048 (4)
C5	0.110 (5)	0.083 (4)	0.118 (5)	0.055 (4)	0.071 (4)	0.052 (4)
C6	0.121 (5)	0.068 (4)	0.090 (4)	0.038 (3)	0.062 (4)	0.023 (3)
C7	0.092 (4)	0.070 (3)	0.068 (3)	0.033 (3)	0.041 (3)	0.027 (3)

C8	0.069 (3)	0.075 (3)	0.059 (3)	0.037 (3)	0.028 (3)	0.030 (3)
C9	0.057 (3)	0.090 (4)	0.074 (3)	0.034 (3)	0.015 (3)	0.034 (3)
C10	0.059 (4)	0.079 (3)	0.103 (4)	0.038 (3)	0.034 (3)	0.047 (3)
C11	0.077 (4)	0.095 (4)	0.085 (4)	0.050 (3)	0.047 (3)	0.044 (3)
C12	0.071 (4)	0.086 (3)	0.055 (3)	0.046 (3)	0.027 (3)	0.026 (3)
C13	0.071 (4)	0.120 (4)	0.162 (5)	0.047 (3)	0.060 (4)	0.069 (4)
C14	0.069 (4)	0.091 (3)	0.061 (3)	0.043 (3)	0.027 (3)	0.029 (3)
C15	0.073 (4)	0.090 (4)	0.082 (4)	0.039 (3)	0.047 (3)	0.036 (3)
C16	0.054 (3)	0.083 (4)	0.083 (4)	0.028 (3)	0.027 (3)	0.021 (3)
C17	0.062 (4)	0.135 (5)	0.066 (4)	0.026 (3)	0.012 (3)	0.025 (3)
C18	0.053 (4)	0.131 (5)	0.058 (3)	0.019 (3)	0.017 (3)	0.015 (3)
C19	0.066 (4)	0.107 (4)	0.125 (5)	0.030 (3)	0.046 (3)	0.040 (4)
C20	0.076 (5)	0.110 (5)	0.134 (6)	0.029 (4)	0.043 (5)	0.023 (5)
C21	0.098 (6)	0.112 (5)	0.125 (6)	0.046 (4)	0.061 (5)	0.053 (5)
C22	0.106 (6)	0.088 (4)	0.103 (5)	0.049 (4)	0.027 (5)	0.039 (4)
C23	0.083 (5)	0.141 (6)	0.134 (6)	0.032 (4)	0.050 (5)	0.042 (5)
C24	0.112 (7)	0.192 (8)	0.116 (7)	0.010 (6)	0.056 (6)	0.016 (6)
C25	0.156 (7)	0.187 (7)	0.147 (6)	0.068 (5)	−0.009 (5)	0.068 (6)

Geometric parameters (Å, °)

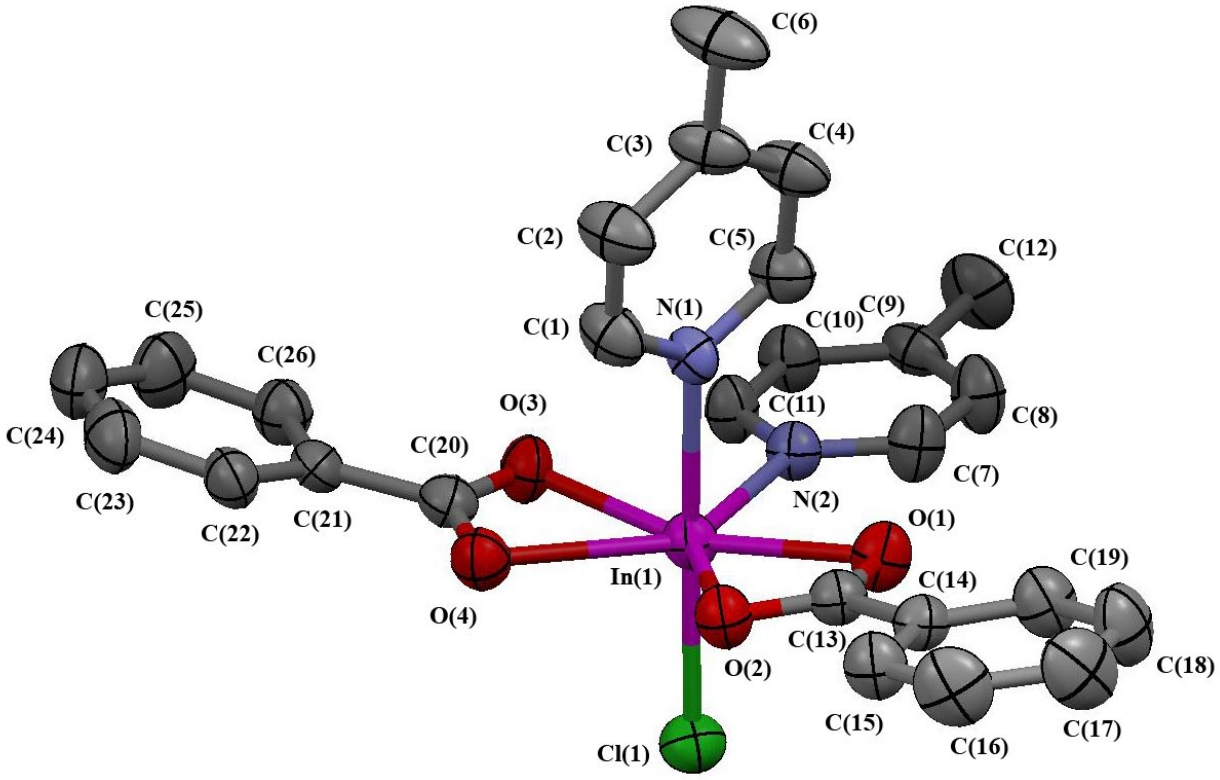
Ga1—O1	2.099 (2)	C4—C5	1.342 (6)
Ga1—N1	2.099 (3)	C5—C6	1.357 (6)
Ga1—O2	2.102 (3)	C6—C7	1.394 (6)
Ga1—N2	2.111 (3)	C8—C9	1.377 (5)
Ga1—Cl2	2.2365 (11)	C9—C10	1.383 (6)
Ga1—Cl1	2.2455 (11)	C10—C11	1.364 (6)
Ga1—C1	2.455 (4)	C10—C13	1.516 (5)
O1—C1	1.288 (4)	C11—C12	1.378 (5)
O2—C1	1.271 (4)	C14—C15	1.384 (5)
N1—C8	1.322 (4)	C15—C16	1.354 (5)
N1—C12	1.331 (4)	C16—C17	1.383 (6)
N2—C18	1.307 (5)	C16—C19	1.498 (5)
N2—C14	1.342 (5)	C17—C18	1.372 (6)
N3—C24	1.323 (7)	C20—C21	1.323 (7)
N3—C20	1.329 (7)	C21—C22	1.368 (7)
C1—C2	1.474 (5)	C22—C23	1.338 (7)
C2—C7	1.359 (5)	C22—C25	1.474 (7)
C2—C3	1.374 (5)	C23—C24	1.333 (8)
C3—C4	1.391 (5)		
O1—Ga1—N1	85.47 (10)	O2—C1—Ga1	58.9 (2)
O1—Ga1—O2	62.83 (10)	O1—C1—Ga1	58.7 (2)
N1—Ga1—O2	87.21 (11)	C2—C1—Ga1	178.7 (2)
O1—Ga1—N2	86.64 (11)	C7—C2—C3	119.3 (4)
N1—Ga1—N2	171.04 (12)	C7—C2—C1	121.0 (4)
O2—Ga1—N2	85.43 (11)	C3—C2—C1	119.7 (4)
O1—Ga1—Cl2	159.73 (8)	C2—C3—C4	120.0 (4)
N1—Ga1—Cl2	93.01 (9)	C5—C4—C3	119.7 (5)
O2—Ga1—Cl2	96.92 (8)	C4—C5—C6	121.3 (5)

N2—Ga1—Cl2	92.92 (10)	C5—C6—C7	119.3 (5)
O1—Ga1—Cl1	95.30 (8)	C2—C7—C6	120.4 (5)
N1—Ga1—Cl1	92.62 (10)	N1—C8—C9	122.6 (4)
O2—Ga1—Cl1	158.09 (8)	C8—C9—C10	120.2 (4)
N2—Ga1—Cl1	92.32 (10)	C11—C10—C9	116.7 (4)
Cl2—Ga1—Cl1	104.96 (4)	C11—C10—C13	120.9 (5)
O1—Ga1—C1	31.65 (11)	C9—C10—C13	122.4 (5)
N1—Ga1—C1	85.39 (11)	C10—C11—C12	120.2 (5)
O2—Ga1—C1	31.18 (11)	N1—C12—C11	122.8 (4)
N2—Ga1—C1	85.67 (12)	N2—C14—C15	121.5 (4)
Cl2—Ga1—C1	128.08 (11)	C16—C15—C14	121.3 (5)
Cl1—Ga1—C1	126.95 (11)	C15—C16—C17	116.4 (5)
C1—O1—Ga1	89.6 (2)	C15—C16—C19	122.7 (5)
C1—O2—Ga1	89.9 (2)	C17—C16—C19	120.9 (5)
C8—N1—C12	117.5 (4)	C18—C17—C16	119.6 (4)
C8—N1—Ga1	120.6 (3)	N2—C18—C17	124.0 (5)
C12—N1—Ga1	121.9 (3)	C21—C20—N3	125.9 (6)
C18—N2—C14	117.2 (4)	C20—C21—C22	119.1 (7)
C18—N2—Ga1	121.8 (3)	C23—C22—C21	116.5 (6)
C14—N2—Ga1	121.1 (3)	C23—C22—C25	122.6 (8)
C24—N3—C20	113.2 (6)	C21—C22—C25	120.9 (8)
O2—C1—O1	117.6 (4)	C24—C23—C22	120.7 (7)
O2—C1—C2	121.3 (4)	N3—C24—C23	124.6 (7)
O1—C1—C2	121.0 (4)		

N1—Ga1—O1—C1	88.6 (2)	O1—Ga1—C1—C2	81 (15)
O2—Ga1—O1—C1	−0.62 (19)	N1—Ga1—C1—C2	−8(15)
N2—Ga1—O1—C1	−87.2 (2)	O2—Ga1—C1—C2	−100 (15)
Cl2—Ga1—O1—C1	2.1 (3)	N2—Ga1—C1—C2	171 (15)
Cl1—Ga1—O1—C1	−179.22 (18)	Cl2—Ga1—C1—C2	−98 (15)
O1—Ga1—O2—C1	0.63 (19)	Cl1—Ga1—C1—C2	82 (15)
N1—Ga1—O2—C1	−85.7 (2)	O2—C1—C2—C7	11.6 (5)
N2—Ga1—O2—C1	89.2 (2)	O1—C1—C2—C7	−168.9 (3)
Cl2—Ga1—O2—C1	−178.42 (19)	Ga1—C1—C2—C7	111 (15)
Cl1—Ga1—O2—C1	4.4 (3)	O2—C1—C2—C3	−168.3 (4)
O1—Ga1—N1—C8	58.8 (3)	O1—C1—C2—C3	11.2 (5)
O2—Ga1—N1—C8	121.7 (3)	Ga1—C1—C2—C3	−69 (15)
N2—Ga1—N1—C8	87.1 (10)	C7—C2—C3—C4	−0.8 (6)
Cl2—Ga1—N1—C8	−141.5 (3)	C1—C2—C3—C4	179.2 (3)
Cl1—Ga1—N1—C8	−36.3 (3)	C2—C3—C4—C5	1.0 (7)
C1—Ga1—N1—C8	90.6 (3)	C3—C4—C5—C6	−0.2 (7)
O1—Ga1—N1—C12	−122.4 (3)	C4—C5—C6—C7	−0.8 (8)
O2—Ga1—N1—C12	−59.4 (3)	C3—C2—C7—C6	−0.2 (6)
N2—Ga1—N1—C12	−94.1 (9)	C1—C2—C7—C6	179.9 (4)
Cl2—Ga1—N1—C12	37.4 (3)	C5—C6—C7—C2	1.0 (7)
Cl1—Ga1—N1—C12	142.5 (3)	C12—N1—C8—C9	−2.8 (6)
C1—Ga1—N1—C12	−90.6 (3)	Ga1—N1—C8—C9	176.1 (3)
O1—Ga1—N2—C18	126.9 (4)	N1—C8—C9—C10	0.6 (6)
N1—Ga1—N2—C18	98.6 (9)	C8—C9—C10—C11	2.0 (6)
O2—Ga1—N2—C18	63.9 (4)	C8—C9—C10—C13	−177.6 (4)

Cl2—Ga1—N2—C18	−32.8 (4)	C9—C10—C11—C12	−2.4 (6)
Cl1—Ga1—N2—C18	−138.0 (3)	C13—C10—C11—C12	177.2 (4)
C1—Ga1—N2—C18	95.2 (4)	C8—N1—C12—C11	2.3 (6)
O1—Ga1—N2—C14	−53.1 (3)	Ga1—N1—C12—C11	−176.6 (3)
N1—Ga1—N2—C14	−81.3 (10)	C10—C11—C12—N1	0.4 (6)
O2—Ga1—N2—C14	−116.1 (3)	C18—N2—C14—C15	0.6 (6)
Cl2—Ga1—N2—C14	147.2 (3)	Ga1—N2—C14—C15	−179.5 (3)
Cl1—Ga1—N2—C14	42.1 (3)	N2—C14—C15—C16	−0.5 (7)
C1—Ga1—N2—C14	−84.8 (3)	C14—C15—C16—C17	0.6 (7)
Ga1—O2—C1—O1	−1.0 (3)	C14—C15—C16—C19	178.9 (4)
Ga1—O2—C1—C2	178.5 (3)	C15—C16—C17—C18	−0.8 (7)
Ga1—O1—C1—O2	1.0 (3)	C19—C16—C17—C18	−179.1 (4)
Ga1—O1—C1—C2	−178.5 (3)	C14—N2—C18—C17	−0.8 (7)
O1—Ga1—C1—O2	−178.9 (3)	Ga1—N2—C18—C17	179.3 (4)
N1—Ga1—C1—O2	92.2 (2)	C16—C17—C18—N2	0.9 (8)
N2—Ga1—C1—O2	−88.3 (2)	C24—N3—C20—C21	−3.6 (11)
Cl2—Ga1—C1—O2	2.0 (2)	N3—C20—C21—C22	2.6 (10)
Cl1—Ga1—C1—O2	−177.97 (16)	C20—C21—C22—C23	−0.6 (9)
N1—Ga1—C1—O1	−88.8 (2)	C20—C21—C22—C25	179.1 (5)
O2—Ga1—C1—O1	178.9 (3)	C21—C22—C23—C24	0.0 (10)
N2—Ga1—C1—O1	90.6 (2)	C25—C22—C23—C24	−179.6 (7)
Cl2—Ga1—C1—O1	−179.06 (15)	C20—N3—C24—C23	3.0 (12)
Cl1—Ga1—C1—O1	1.0 (2)	C22—C23—C24—N3	−1.4 (13)

Appendix B.—Alternate Diagram of and Extensive Structural Information for Compound (2) - $[InCl(4\text{-}Mepy)_2(O_2CPh)_2]\bullet 4\text{-}Mepy$



Crystal data

$C_{32}H_{31}ClInN_3O_4$	F_{000} = 1368
M_r = 671.87	D_x = 1.439 Mg m^{-3}
Monoclinic, *P*2(1)/*n*	Mo *K*α radiation, λ = 0.71073 Å
a = 13.1565 (13) Å	Cell parameters from 3347 reflections
b = 8.2116 (8) Å	θ = 2.5–22.2º
c = 28.796 (3) Å	μ = 0.89 mm^{-1}
β = 94.460 (2)º	*T* = 300 K
V = 3101.6 (5) Å^3	Block, colorless
Z = 4	0.31 × 0.14 × 0.08 mm

Data collection

CCD area detector diffractometer	5462 independent reflections
Radiation source: fine-focus sealed tube	3611 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.054
T = 300 K	θ_{max} = 25.0º
phi and ω scans	θ_{min} = 1.7º
Absorption correction: empirical (using intensity measurements) SADABS, Absorption corrections using Bruker CCD based on the method of Bob Blessing. Acta Cryst. 1995, A51, 33	*h* = −15→8
T_{min} = 0.580, T_{max} = 1.000	*k* = −9→9
15267 measured reflections	*l* = −34→34

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.053	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.119	$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.001
5462 reflections	$\Delta\rho_{max}$ = 1.17 e Å^{-3}
370 parameters	$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
In1	0.68251 (3)	1.41205 (5)	0.578113 (12)	0.04688 (15)
Cl2	0.58777 (11)	1.65800 (18)	0.59029 (5)	0.0592 (4)
O1	0.6919 (3)	1.3314 (5)	0.65388 (11)	0.0561 (10)
O2	0.8143 (3)	1.4832 (5)	0.63096 (12)	0.0553 (10)
O3	0.6614 (3)	1.4110 (5)	0.50116 (12)	0.0588 (10)
O4	0.7972 (3)	1.5404 (5)	0.52763 (13)	0.0602 (10)
N1	0.7836 (3)	1.1841 (5)	0.57169 (13)	0.0432 (10)
N2	0.5396 (3)	1.2527 (5)	0.57165 (14)	0.0460 (10)
N3	0.2568 (6)	0.9454 (9)	0.6921 (3)	0.104 (2)
C1	0.8773 (5)	1.1979 (7)	0.5588 (2)	0.0637 (16)
H1A	0.8982	1.2993	0.5488	0.076*
C2	0.9459 (5)	1.0715 (8)	0.5593 (2)	0.0733 (18)
H2A	1.0108	1.0881	0.5495	0.088*
C3	0.9176 (4)	0.9204 (7)	0.5743 (2)	0.0644 (16)
C4	0.8211 (4)	0.9051 (7)	0.5877 (2)	0.0659 (16)
H4A	0.7982	0.8048	0.5977	0.079*
C5	0.7576 (5)	1.0375 (7)	0.5865 (2)	0.0608 (16)
H5A	0.6926	1.0242	0.5965	0.073*
C6	0.9907 (5)	0.7800 (8)	0.5769 (3)	0.099 (2)
H6A	0.9574	0.6851	0.5879	0.148*
H6B	1.0486	0.8062	0.5979	0.148*
H6C	1.0129	0.7588	0.5465	0.148*
C7	0.5004 (4)	1.1811 (8)	0.60763 (19)	0.0615 (16)
H7A	0.5347	1.1927	0.6369	0.074*
C8	0.4124 (4)	1.0911 (8)	0.60400 (19)	0.0647 (16)
H8A	0.3888	1.0433	0.6304	0.078*
C9	0.3591 (4)	1.0713 (6)	0.5617 (2)	0.0517 (14)
C10	0.3977 (4)	1.1470 (7)	0.52470 (19)	0.0576 (15)
H10A	0.3636	1.1387	0.4953	0.069*
C11	0.4869 (4)	1.2357 (7)	0.53060 (18)	0.0557 (14)
H11A	0.5113	1.2858	0.5047	0.067*

C12	0.2637 (5)	0.9711 (8)	0.5554 (2)	0.079 (2)
H12A	0.2482	0.9270	0.5849	0.119*
H12B	0.2735	0.8838	0.5341	0.119*
H12C	0.2082	1.0385	0.5433	0.119*
C13	0.7765 (4)	1.4016 (7)	0.66243 (17)	0.0480 (12)
C14	0.8311 (4)	1.3872 (6)	0.70934 (17)	0.0482 (13)
C15	0.7898 (5)	1.2986 (7)	0.74325 (19)	0.0642 (16)
H15A	0.7272	1.2473	0.7369	0.077*
C16	0.8406 (6)	1.2846 (8)	0.7870 (2)	0.082 (2)
H16A	0.8118	1.2235	0.8098	0.099*
C17	0.9311 (6)	1.3583 (9)	0.7970 (2)	0.091 (2)
H17A	0.9640	1.3514	0.8267	0.109*
C18	0.9740 (5)	1.4444 (9)	0.7622 (2)	0.082 (2)
H18A	1.0379	1.4918	0.7682	0.098*
C19	0.9243 (4)	1.4608 (7)	0.7192 (2)	0.0620 (16)
H19A	0.9533	1.5218	0.6964	0.074*
C20	0.7404 (5)	1.4884 (7)	0.49409 (19)	0.0530 (14)
C21	0.7661 (4)	1.5138 (6)	0.44540 (17)	0.0477 (13)
C22	0.8611 (5)	1.5703 (7)	0.43560 (19)	0.0577 (15)
H22A	0.9080	1.6017	0.4598	0.069*
C23	0.8863 (5)	1.5804 (8)	0.3902 (2)	0.0751 (18)
H23A	0.9501	1.6197	0.3838	0.090*
C24	0.8195 (6)	1.5338 (9)	0.3548 (2)	0.082 (2)
H24A	0.8377	1.5391	0.3243	0.098*
C25	0.7243 (6)	1.4783 (9)	0.3638 (2)	0.079 (2)
H25A	0.6780	1.4476	0.3393	0.095*
C26	0.6978 (5)	1.4681 (7)	0.40905 (19)	0.0616 (16)
H26A	0.6335	1.4303	0.4151	0.074*
C27	0.2399 (7)	0.8450 (10)	0.7259 (3)	0.096 (2)
H27A	0.2923	0.7764	0.7373	0.115*
C28	0.1511 (8)	0.8373 (10)	0.7445 (3)	0.099 (3)
H28A	0.1444	0.7643	0.7687	0.119*
C29	0.0706 (7)	0.9290 (12)	0.7302 (4)	0.116 (3)
C30	0.0847 (8)	1.0329 (11)	0.6939 (4)	0.116 (3)
H30A	0.0319	1.0986	0.6814	0.140*
C31	0.1787 (10)	1.0366 (11)	0.6770 (3)	0.117 (3)
H31A	0.1883	1.1092	0.6529	0.141*
C32	−0.0293 (9)	0.9161 (14)	0.7502 (6)	0.264 (10)
H32A	−0.0248	0.8383	0.7751	0.396*
H32B	−0.0799	0.8811	0.7264	0.396*
H32C	−0.0481	1.0204	0.7619	0.396*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.0420 (2)	0.0519 (2)	0.0459 (2)	−0.0073 (2)	−0.00168 (15)	0.00058 (19)
Cl2	0.0544 (9)	0.0605 (9)	0.0617 (8)	0.0047 (7)	−0.0014 (7)	−0.0033 (7)
O1	0.039 (2)	0.079 (3)	0.049 (2)	−0.011 (2)	−0.0055 (17)	−0.0019 (19)

O2	0.053 (2)	0.062 (2)	0.050 (2)	−0.010 (2)	−0.0013 (18)	0.0047 (18)
O3	0.053 (2)	0.072 (3)	0.052 (2)	−0.010 (2)	0.0122 (18)	0.004 (2)
O4	0.065 (3)	0.060 (3)	0.055 (2)	−0.010 (2)	0.002 (2)	0.0003 (18)
N1	0.029 (2)	0.047 (3)	0.054 (3)	−0.008 (2)	0.002 (2)	0.003 (2)
N2	0.038 (2)	0.053 (3)	0.047 (2)	−0.004 (2)	0.000 (2)	0.001 (2)
N3	0.101 (5)	0.100 (5)	0.111 (5)	0.008 (4)	0.015 (4)	0.016 (4)
C1	0.049 (4)	0.056 (4)	0.086 (4)	−0.009 (3)	0.004 (3)	0.006 (3)
C2	0.044 (4)	0.055 (4)	0.122 (6)	−0.006 (3)	0.012 (4)	−0.001 (4)
C3	0.048 (4)	0.045 (3)	0.098 (5)	−0.004 (3)	−0.011 (3)	−0.012 (3)
C4	0.052 (4)	0.044 (3)	0.101 (5)	−0.008 (3)	0.000 (3)	−0.002 (3)
C5	0.043 (4)	0.057 (4)	0.084 (4)	−0.010 (3)	0.013 (3)	−0.005 (3)
C6	0.067 (5)	0.051 (4)	0.177 (8)	0.011 (4)	−0.003 (5)	0.002 (4)
C7	0.044 (4)	0.092 (5)	0.046 (3)	−0.013 (3)	−0.008 (3)	0.005 (3)
C8	0.048 (4)	0.085 (5)	0.061 (4)	−0.016 (4)	0.002 (3)	0.018 (3)
C9	0.040 (3)	0.040 (3)	0.074 (4)	−0.003 (3)	0.001 (3)	0.001 (3)
C10	0.044 (3)	0.068 (4)	0.059 (3)	−0.014 (3)	−0.004 (3)	0.001 (3)
C11	0.054 (4)	0.067 (4)	0.045 (3)	−0.014 (3)	−0.004 (3)	0.007 (3)
C12	0.058 (4)	0.080 (5)	0.100 (5)	−0.031 (4)	−0.001 (4)	0.000 (4)
C13	0.045 (3)	0.050 (3)	0.048 (3)	0.000 (3)	−0.001 (2)	−0.002 (3)
C14	0.047 (3)	0.050 (3)	0.046 (3)	0.001 (3)	−0.003 (2)	−0.001 (2)
C15	0.061 (4)	0.071 (4)	0.059 (4)	−0.011 (3)	−0.012 (3)	0.007 (3)
C16	0.098 (6)	0.091 (5)	0.055 (4)	−0.020 (5)	−0.009 (4)	0.019 (4)
C17	0.111 (6)	0.096 (6)	0.059 (4)	−0.012 (5)	−0.038 (4)	0.007 (4)
C18	0.061 (4)	0.094 (6)	0.086 (5)	−0.023 (4)	−0.024 (4)	−0.003 (4)
C19	0.054 (4)	0.071 (4)	0.059 (4)	−0.012 (3)	−0.005 (3)	0.001 (3)
C20	0.057 (4)	0.045 (3)	0.057 (4)	0.006 (3)	0.005 (3)	0.003 (3)
C21	0.056 (4)	0.039 (3)	0.049 (3)	0.003 (3)	0.005 (3)	0.006 (2)
C22	0.062 (4)	0.053 (4)	0.059 (3)	−0.007 (3)	0.009 (3)	0.008 (3)
C23	0.068 (4)	0.080 (5)	0.080 (5)	−0.002 (4)	0.025 (4)	0.016 (4)
C24	0.102 (6)	0.088 (5)	0.058 (4)	0.003 (4)	0.021 (4)	0.012 (4)
C25	0.091 (6)	0.094 (5)	0.049 (4)	−0.006 (4)	−0.006 (4)	0.003 (3)
C26	0.059 (4)	0.066 (4)	0.060 (4)	−0.009 (3)	0.005 (3)	0.002 (3)
C27	0.101 (7)	0.087 (6)	0.100 (6)	0.003 (5)	0.003 (5)	0.008 (5)
C28	0.114 (7)	0.083 (6)	0.105 (6)	−0.018 (6)	0.038 (6)	0.004 (5)
C29	0.073 (6)	0.077 (6)	0.204 (11)	0.000 (5)	0.044 (7)	−0.013 (7)
C30	0.096 (7)	0.082 (6)	0.167 (10)	0.020 (6)	−0.020 (7)	−0.005 (6)
C31	0.168 (11)	0.094 (7)	0.088 (6)	0.007 (7)	0.001 (7)	0.011 (5)
C32	0.149 (11)	0.122 (10)	0.55 (3)	−0.019 (8)	0.191 (15)	−0.032 (13)

Geometric parameters (Å, °)

In1—O3	2.212 (3)	C7—C8	1.371 (7)
In1—O1	2.274 (3)	C8—C9	1.366 (7)
In1—N2	2.286 (4)	C9—C10	1.365 (7)
In1—O2	2.292 (4)	C9—C12	1.501 (7)
In1—N1	2.312 (4)	C10—C11	1.381 (7)
In1—Cl2	2.4132 (15)	C13—C14	1.484 (7)
In1—O4	2.417 (4)	C14—C15	1.364 (7)
In1—C13	2.639 (5)	C14—C19	1.376 (8)

In1—C20	2.667 (6)	C15—C16	1.384 (8)
O1—C13	1.261 (6)	C16—C17	1.347 (9)
O2—C13	1.259 (6)	C17—C18	1.382 (9)
O3—C20	1.248 (6)	C18—C19	1.362 (8)
O4—C20	1.249 (6)	C20—C21	1.482 (7)
N1—C1	1.319 (7)	C21—C22	1.382 (7)
N1—C5	1.331 (7)	C21—C26	1.378 (7)
N2—C7	1.330 (6)	C22—C23	1.377 (8)
N2—C11	1.330 (6)	C23—C24	1.348 (9)
N3—C27	1.308 (9)	C24—C25	1.375 (9)
N3—C31	1.318 (11)	C25—C26	1.378 (8)
C1—C2	1.374 (8)	C27—C28	1.324 (10)
C2—C3	1.375 (8)	C28—C29	1.338 (12)
C3—C4	1.362 (8)	C29—C30	1.372 (12)
C3—C6	1.500 (8)	C29—C32	1.479 (12)
C4—C5	1.370 (8)	C30—C31	1.364 (12)
O3—In1—O1	162.40 (15)	C3—C2—C1	119.4 (6)
O3—In1—N2	82.98 (14)	C4—C3—C2	117.0 (6)
O1—In1—N2	83.94 (14)	C4—C3—C6	121.6 (6)
O3—In1—O2	134.10 (14)	C2—C3—C6	121.4 (6)
O1—In1—O2	56.99 (12)	C3—C4—C5	120.0 (6)
N2—In1—O2	140.78 (14)	N1—C5—C4	123.7 (5)
O3—In1—N1	86.83 (14)	N2—C7—C8	123.8 (5)
O1—In1—N1	81.50 (14)	C7—C8—C9	120.2 (5)
N2—In1—N1	90.28 (15)	C8—C9—C10	116.5 (5)
O2—In1—N1	81.33 (14)	C8—C9—C12	122.6 (5)
O3—In1—Cl2	97.07 (11)	C10—C9—C12	120.9 (5)
O1—In1—Cl2	95.43 (11)	C9—C10—C11	120.5 (5)
N2—In1—Cl2	93.44 (11)	N2—C11—C10	123.0 (5)
O2—In1—Cl2	93.60 (10)	O2—C13—O1	119.6 (5)
N1—In1—Cl2	174.91 (10)	O2—C13—C14	120.5 (5)
O3—In1—O4	55.57 (13)	O1—C13—C14	119.9 (5)
O1—In1—O4	135.57 (13)	O2—C13—In1	60.2 (3)
N2—In1—O4	138.45 (14)	O1—C13—In1	59.5 (3)
O2—In1—O4	79.23 (13)	C14—C13—In1	177.1 (4)
N1—In1—O4	85.11 (14)	C15—C14—C19	119.0 (5)
Cl2—In1—O4	94.37 (10)	C15—C14—C13	120.2 (5)
O3—In1—C13	159.22 (15)	C19—C14—C13	120.8 (5)
O1—In1—C13	28.52 (14)	C14—C15—C16	120.3 (6)
N2—In1—C13	112.33 (16)	C17—C16—C15	120.9 (6)
O2—In1—C13	28.50 (14)	C16—C17—C18	118.7 (6)
N1—In1—C13	79.40 (15)	C19—C18—C17	121.0 (6)
Cl2—In1—C13	95.96 (12)	C18—C19—C14	120.0 (6)
O4—In1—C13	107.33 (16)	O4—C20—O3	120.2 (5)
O3—In1—C20	27.68 (15)	O4—C20—C21	121.1 (5)
O1—In1—C20	160.17 (16)	O3—C20—C21	118.7 (5)
N2—In1—C20	110.58 (17)	O4—C20—In1	64.8 (3)
O2—In1—C20	106.74 (17)	O3—C20—In1	55.4 (3)
N1—In1—C20	84.89 (15)	C21—C20—In1	173.4 (4)

Cl2—In1—C20	97.02 (12)	C22—C21—C26	118.9 (5)
O4—In1—C20	27.90 (14)	C22—C21—C20	121.1 (5)
C13—In1—C20	134.10 (19)	C26—C21—C20	119.8 (5)
C13—O1—In1	92.0 (3)	C21—C22—C23	120.2 (6)
C13—O2—In1	91.3 (3)	C24—C23—C22	120.6 (6)
C20—O3—In1	96.9 (3)	C23—C24—C25	120.1 (6)
C20—O4—In1	87.3 (3)	C24—C25—C26	119.9 (6)
C1—N1—C5	115.9 (5)	C25—C26—C21	120.2 (6)
C1—N1—In1	120.6 (4)	N3—C27—C28	122.5 (9)
C5—N1—In1	122.9 (4)	C27—C28—C29	123.5 (9)
C7—N2—C11	116.0 (5)	C28—C29—C30	115.7 (9)
C7—N2—In1	123.8 (4)	C28—C29—C32	123.1 (12)
C11—N2—In1	120.1 (3)	C30—C29—C32	121.1 (12)
C27—N3—C31	115.5 (8)	C31—C30—C29	117.8 (9)
N1—C1—C2	124.0 (5)	N3—C31—C30	125.1 (9)
O3—In1—O1—C13	132.4 (4)	O3—In1—C13—O2	42.0 (6)
N2—In1—O1—C13	174.6 (3)	O1—In1—C13—O2	−177.0 (5)
O2—In1—O1—C13	−1.7 (3)	N2—In1—C13—O2	177.2 (3)
N1—In1—O1—C13	83.4 (3)	N1—In1—C13—O2	91.3 (3)
Cl2—In1—O1—C13	−92.5 (3)	Cl2—In1—C13—O2	−86.6 (3)
O4—In1—O1—C13	9.4 (4)	O4—In1—C13—O2	9.9 (3)
C20—In1—O1—C13	36.2 (6)	C20—In1—C13—O2	19.2 (4)
O3—In1—O2—C13	−160.7 (3)	O3—In1—C13—O1	−141.0 (4)
O1—In1—O2—C13	1.7 (3)	N2—In1—C13—O1	−5.8 (4)
N2—In1—O2—C13	−4.1 (4)	O2—In1—C13—O1	177.0 (5)
N1—In1—O2—C13	−83.7 (3)	N1—In1—C13—O1	−91.7 (3)
Cl2—In1—O2—C13	95.9 (3)	Cl2—In1—C13—O1	90.4 (3)
O4—In1—O2—C13	−170.4 (3)	O4—In1—C13—O1	−173.1 (3)
C20—In1—O2—C13	−165.7 (3)	C20—In1—C13—O1	−163.8 (3)
O1—In1—O3—C20	−133.4 (5)	O3—In1—C13—C14	−63 (8)
N2—In1—O3—C20	−175.7 (3)	O1—In1—C13—C14	78 (8)
O2—In1—O3—C20	−10.4 (4)	N2—In1—C13—C14	72 (8)
N1—In1—O3—C20	−85.1 (3)	O2—In1—C13—C14	−105 (8)
Cl2—In1—O3—C20	91.7 (3)	N1—In1—C13—C14	−14 (8)
O4—In1—O3—C20	1.2 (3)	Cl2—In1—C13—C14	168 (8)
C13—In1—O3—C20	−36.8 (6)	O4—In1—C13—C14	−95 (8)
O3—In1—O4—C20	−1.2 (3)	C20—In1—C13—C14	−86 (8)
O1—In1—O4—C20	160.9 (3)	O2—C13—C14—C15	−180.0 (5)
N2—In1—O4—C20	3.4 (4)	O1—C13—C14—C15	−0.2 (8)
O2—In1—O4—C20	170.4 (3)	In1—C13—C14—C15	−77 (8)
N1—In1—O4—C20	88.3 (3)	O2—C13—C14—C19	−0.7 (8)
Cl2—In1—O4—C20	−96.8 (3)	O1—C13—C14—C19	179.0 (5)
C13—In1—O4—C20	165.6 (3)	In1—C13—C14—C19	103 (8)
O3—In1—N1—C1	76.1 (4)	C19—C14—C15—C16	0.7 (9)
O1—In1—N1—C1	−117.1 (4)	C13—C14—C15—C16	179.9 (6)
N2—In1—N1—C1	159.1 (4)	C14—C15—C16—C17	0.3 (11)
O2—In1—N1—C1	−59.4 (4)	C15—C16—C17—C18	−2.0 (12)
Cl2—In1—N1—C1	−63.9 (13)	C16—C17—C18—C19	2.8 (12)
O4—In1—N1—C1	20.4 (4)	C17—C18—C19—C14	−1.9 (11)

C13—In1—N1—C1	−88.2 (4)	C15—C14—C19—C18	0.2 (9)
C20—In1—N1—C1	48.4 (4)	C13—C14—C19—C18	−179.1 (5)
O3—In1—N1—C5	−113.3 (4)	In1—O4—C20—O3	2.0 (5)
O1—In1—N1—C5	53.5 (4)	In1—O4—C20—C21	−176.6 (5)
N2—In1—N1—C5	−30.3 (4)	In1—O3—C20—O4	−2.2 (6)
O2—In1—N1—C5	111.2 (4)	In1—O3—C20—C21	176.5 (4)
Cl2—In1—N1—C5	106.7 (12)	O3—In1—C20—O4	177.9 (5)
O4—In1—N1—C5	−169.0 (4)	O1—In1—C20—O4	−42.4 (6)
C13—In1—N1—C5	82.4 (4)	N2—In1—C20—O4	−177.6 (3)
C20—In1—N1—C5	−140.9 (4)	O2—In1—C20—O4	−9.8 (3)
O3—In1—N2—C7	174.2 (5)	N1—In1—C20—O4	−89.2 (3)
O1—In1—N2—C7	6.0 (4)	Cl2—In1—C20—O4	86.1 (3)
O2—In1—N2—C7	10.8 (6)	C13—In1—C20—O4	−19.3 (4)
N1—In1—N2—C7	87.4 (5)	O1—In1—C20—O3	139.7 (4)
Cl2—In1—N2—C7	−89.1 (4)	N2—In1—C20—O3	4.5 (4)
O4—In1—N2—C7	170.3 (4)	O2—In1—C20—O3	172.2 (3)
C13—In1—N2—C7	8.7 (5)	N1—In1—C20—O3	92.9 (3)
C20—In1—N2—C7	172.0 (4)	Cl2—In1—C20—O3	−91.8 (3)
O3—In1—N2—C11	−10.2 (4)	O4—In1—C20—O3	−177.9 (5)
O1—In1—N2—C11	−178.4 (4)	C13—In1—C20—O3	162.8 (3)
O2—In1—N2—C11	−173.5 (4)	O3—In1—C20—C21	−28 (3)
N1—In1—N2—C11	−96.9 (4)	O1—In1—C20—C21	112 (3)
Cl2—In1—N2—C11	86.5 (4)	N2—In1—C20—C21	−23 (4)
O4—In1—N2—C11	−14.0 (5)	O2—In1—C20—C21	144 (3)
C13—In1—N2—C11	−175.6 (4)	N1—In1—C20—C21	65 (4)
C20—In1—N2—C11	−12.3 (4)	Cl2—In1—C20—C21	−120 (4)
C5—N1—C1—C2	1.0 (9)	O4—In1—C20—C21	154 (4)
In1—N1—C1—C2	172.3 (5)	C13—In1—C20—C21	135 (3)
N1—C1—C2—C3	−0.6 (10)	O4—C20—C21—C22	11.2 (8)
C1—C2—C3—C4	0.5 (10)	O3—C20—C21—C22	−167.5 (5)
C1—C2—C3—C6	−178.1 (6)	In1—C20—C21—C22	−141 (3)
C2—C3—C4—C5	−0.9 (9)	O4—C20—C21—C26	−174.2 (5)
C6—C3—C4—C5	177.7 (6)	O3—C20—C21—C26	7.1 (8)
C1—N1—C5—C4	−1.4 (8)	In1—C20—C21—C26	33 (4)
In1—N1—C5—C4	−172.5 (4)	C26—C21—C22—C23	0.0 (8)
C3—C4—C5—N1	1.4 (9)	C20—C21—C22—C23	174.6 (5)
C11—N2—C7—C8	1.4 (9)	C21—C22—C23—C24	−0.7 (10)
In1—N2—C7—C8	177.2 (5)	C22—C23—C24—C25	1.2 (11)
N2—C7—C8—C9	−0.3 (10)	C23—C24—C25—C26	−0.9 (11)
C7—C8—C9—C10	−0.9 (9)	C24—C25—C26—C21	0.2 (10)
C7—C8—C9—C12	178.6 (6)	C22—C21—C26—C25	0.3 (9)
C8—C9—C10—C11	1.1 (9)	C20—C21—C26—C25	−174.5 (5)
C12—C9—C10—C11	−178.4 (6)	C31—N3—C27—C28	−1.3 (13)
C7—N2—C11—C10	−1.2 (8)	N3—C27—C28—C29	0.9 (14)
In1—N2—C11—C10	−177.2 (4)	C27—C28—C29—C30	0.8 (14)
C9—C10—C11—N2	0.0 (9)	C27—C28—C29—C32	178.0 (10)
In1—O2—C13—O1	−3.0 (5)	C28—C29—C30—C31	−1.9 (14)
In1—O2—C13—C14	176.7 (4)	C32—C29—C30—C31	−179.2 (10)
In1—O1—C13—O2	3.0 (5)	C27—N3—C31—C30	0.0 (14)
In1—O1—C13—C14	−176.7 (4)	C29—C30—C31—N3	1.5 (15)

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13. SUPPLEMENTARY NOTES

14. ABSTRACT
Two new heteroleptic chelated-benzoato gallium (III) and indium (III) complexes have been prepared and structurally characterized. The molecular structures of $[GaCl_2(4\text{-Mepy})_2(O_2CPh)]$4-Mepy (1) and $[InCl(4\text{-Mepy})_2(O_2CPh)_2]$4-Mepy (2) have been determined by single-crystal x-ray diffraction. The gallium compound (1) is a distorted octahedron with *cis*-chloride ligands co-planar with the chelating benzoate and the 4-methylpyridines *trans* to each other. This is the first example of a Ga(III) structure with a chelating benzoate. The indium compound (2) is a distorted pentagonal bipyramid with two chelating benzoates, one 4-methylpyridine in the plane and a chloride *trans* to the other 4-methylpyridine. The indium *bis*-benzoate is an unusual example of a seven-coordinate structure with classical ligands. Both complexes, which due to the chelates, could also be described as pseudo-trigonal bipyramidal, include a three-bladed motif with three roughly parallel aromatic rings that along with a solvent of crystallization and electron-withdrawing chloride ligand(s) stabilize the solid-state structures.

15. SUBJECT TERMS
Indium compounds; Gallium compounds; Chlorides; Vapor deposition; Solar cells; Crystal structure

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