



## 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  $[\text{GaCl}_2(4\text{-Mepy})_2(\text{O}_2\text{CPh})]\cdot 4\text{-Mepy}$  (**1**) and  $[\text{InCl}(4\text{-Mepy})_2(\text{O}_2\text{CPh})_2]\cdot 4\text{-Mepy}$  (**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.

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### 1. 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 [1–4]. 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 [5,6]. In our ongoing 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 [6–9]. For example, oxidative addition of lower-valent Ga and In chlorides (or metal) via addition of carboxylate ( $\text{RCO}_2^-$ ) or dithiocarbamate ( $\text{S}_2\text{C-NR}_2^-$ ) 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 [1–10]. Use

of 4-methylpyridine or  $\gamma$ -picoline solvent (ligands) has yielded complexes that most readily provide single crystals suitable for X-ray diffraction studies. Previously, reaction of sodium benzoate with  $\text{Ga}_2\text{Cl}_4$  in 4-methylpyridine resulted in isolation and structural characterization of the first oxo-centered main group trinuclear carboxylate,  $[\text{Ga}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CC}_6\text{H}_5)_6(4\text{-MeC}_5\text{H}_5\text{N})_3](\text{GaCl}_4)$  [9]. Similarly, oxidation of indium powder with benzoyl peroxide produced the first example of a mononuclear eight-coordinate indium (III) benzoate,  $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-MeC}_5\text{H}_5\text{N})_2$  [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. 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

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ACROS and heated under vacuum for 24 h 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%) and indium (I) chloride (99.995%) (both from Alfa Aesar) were purchased in argon-filled ampoules and transferred in an inert atmosphere glove box. Benzoyl peroxide ((C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>2</sub> – Aldrich) was deaerated under vacuum at room temperature prior to use.

## 2.2. Preparation of [GaCl<sub>2</sub>(4-Mepy)<sub>2</sub>(O<sub>2</sub>CPh)]·4-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 h. 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 h at room temperature.

## 2.3. Preparation of [InCl(4-Mepy)<sub>2</sub>(O<sub>2</sub>CPh)]·4-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 lay-

ered 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 CCD-based X-ray diffractometer system using Mo K $\alpha$  ( $\lambda$  = 0.71073 Å). Crystals used for data collection were cemented to a quartz fiber with epoxy glue. Data were measured using  $\omega$  scans of 0.3° per frame for 10 s 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<sup>®</sup> software package [11] using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS [12,13] supplied by Sheldrick [14]. Structures were solved and refined using the Bruker SHELXTL<sup>®</sup> (version 5.1) software package [14,15] in space groups of  $P\bar{1}$  (**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 [14]. Crystallographic data are given in Table 1, selected bond lengths and angles are given in Table 2.

## 3. Results and discussion

### 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,

**Table 1**  
Summary of X-ray diffraction data.

Compound	1	2
Empirical formula	C <sub>25</sub> H <sub>26</sub> Cl <sub>2</sub> GaN <sub>3</sub> O <sub>2</sub>	C <sub>32</sub> H <sub>31</sub> ClInN <sub>3</sub> O <sub>4</sub>
Molecular weight	541.11	671.87
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
<i>a</i> (Å)	10.5987 (13)	13.1565 (13)
<i>b</i> (Å)	11.3705 (15)	8.2116 (8)
<i>c</i> (Å)	12.6660 (17)	28.796 (3)
$\alpha$ (°)	104.525 (2)	90
$\beta$ (°)	101.976 (3)	94.460 (2)
$\gamma$ (°)	111.981 (2)	90
<i>V</i> (Å <sup>3</sup> )	1290.7 (3)	3101.6 (5)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.392	1.439
$\mu$ (mm <sup>-1</sup> )	1.30	0.89
<i>F</i>	556	1368
Crystal size (mm)	0.38 × 0.23 × 0.09	0.31 × 0.14 × 0.08
$\theta$ range for collection (°)	2.2–22.3	2.5–22.2
No. collected	6882	15 267
No. ind. ( <i>R</i> <sub>int</sub> )	4505 (0.029)	5462 (0.054)
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	1.000, 0.537	1.000, 0.580
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.044	0.053
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.084 <sup>a</sup>	0.119 <sup>b</sup>
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.48, -0.41	1.17, -0.47
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.000	0.999
CCDC deposit no.	753 437	753 438

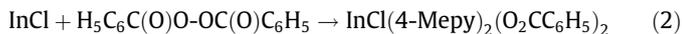
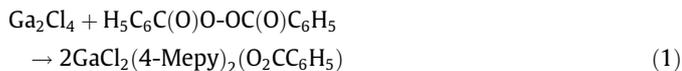
<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$ , 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)

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.

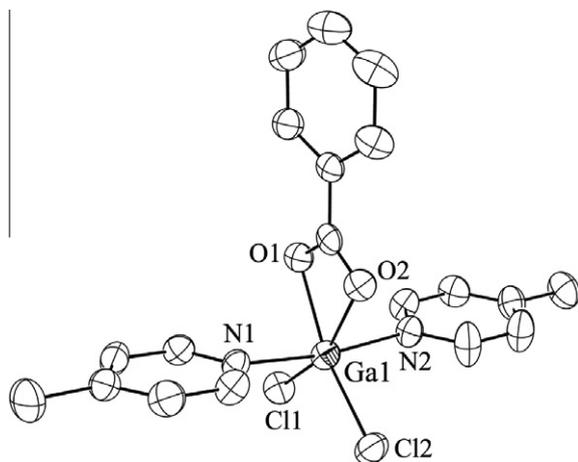


The starting material for reaction (1) is actually more accurately described as a Ga(I)Ga(III) species:  $\text{Ga}^+[\text{GaCl}_4]^-$ . The reaction most likely proceeds through an intermediate ethane-like formally Ga(II) complex,  $\text{Ga}_2\text{Cl}_4(\gamma\text{-pic})_2$  (3). An unsuccessful attempt to produce a gallium basic carboxylate [9], resulted in the isolation and structural characterization of the Ga(II) dimer [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,  $[\text{GaCl}_2(\gamma\text{-pic})_4]^+[\text{GaCl}_4]^-$  (4) [7]. The isolation and structural characterization of 1 brings to five the number of related structures from the reaction of benzoate-containing reagents and  $\text{Ga}_2\text{Cl}_4$  in  $\gamma$ -picoline, reinforcing the utility of  $\text{Ga}_2\text{Cl}_4$  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,  $\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ , by oxidation of indium metal powder with a 3:2 excess of benzoyl peroxide in  $\gamma$ -picoline [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 [5,6].

### 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 [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 [17]. A very thorough discussion of

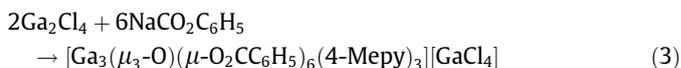


**Fig. 1.** ORTEP diagram and atomic labeling scheme of first coordination sphere of  $[\text{GaCl}_2(\text{O}_2\text{CPh})(4\text{-Mepy})_2]\cdot 4\text{-Mepy}$  (1) (hydrogen atoms and the co-crystallized picoline not shown for clarity).

coordination of metal carboxylates can be found in a classic monograph [18].

The angle formed by the chelating benzoate in 1, O1–Ga–O2, is  $62.83(10)^\circ$ , and is significantly larger than the average angle for compound 2 of  $56.28(13)^\circ$  but is comparable to an average angle of  $62.6(1)^\circ$  for three structurally-characterized chelating carboxylates previously reported [19–21]; 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 [19] and two compounds stabilized by chelating heterocyclic ligands, one with (pyrazolyl)borate [20] and the other with benzoxazole [21].

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



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 [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 [19–21] that range from 2.042(2) to 2.127(3) Å, with the four-coordinate organometallic dimeric compound having the shortest average bond length (2.049(2) Å) [19]. Of the four structurally-characterized chelating gallium carboxylates, only the (pyrazolyl)borate compound had asymmetrical coordination of the carboxylate moiety ( $\Delta\text{Ga-O} = 0.079(3)$  Å) [20].

This can be contrasted to the surprisingly complex structure of methylgallium diacetate,  $\text{H}_3\text{C-Ga}(\text{O}_2\text{CCH}_3)_2$  [22]. This structure includes dative, bridging, and mono-dentate acetate coordination resulting in Ga–O bond distances ranging from 1.873(3) to 2.219(3) Å. As noted previously [17], several reports of related organometallic indium compounds, dimethyl [23] and diethyl [24] acetate include simultaneously bridging and chelating acetate coordination. A much more straightforward Ga acetate mono-dentate interaction is found in a neutral acetato tetraphenylporphyrin complex ( $\text{Ga}(\text{OAc})(\text{tpp})$ ) with Ga–O bond length of 1.874(4) Å [25], very similar to the mono-dentate Ga–O bond length of 1.873(3) Å [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 ( $\text{AgO}_2\text{CR})_2$  where a dimer ( $\text{R} = \text{C}(\text{Me})=\text{C}(\text{Me})\text{H}$ ) with bridging carboxylates is stabilized as a monomer by the addition of triphenylphosphine ligands:  $[\text{AgO}_2\text{CR}(\text{PPh}_3)_2]$  ( $\text{R} = \text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{CH}_2=\text{C}(\text{H})\text{CH}_2$ , and  $\text{C}(\text{Me})=\text{C}(\text{Me})\text{H}$ ) with a subsequent average increase of 0.235(3) Å for a chelated versus bridging Ag–O bond length [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 carboxylates of methylgalliumdiacetate [22], 1.25(2) Å for the bridging benzoates of compound 5 [9], 1.255(2) Å for the chelating acetate of the benzoxazole [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)–1.301(2) Å for dimeric substituted benzoates with multiple coordination modes [27].

The 2.105(3) Å average Ga–N bond length for the ligated picolines is comparable to 2.105(5) Å for 4 [7] and 2.085(9) Å for 5 [9]. This is slightly longer than Ga–N bond length of 2.058(4) Å for the (pyrazolyl)borate [20] and 2.034(2) Å for the benzoxazole [21] compounds. It is longer than the Ga–N (picoline) bond length

of 2.005(6) Å of the Ga(II) complex, **3** [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) [7], **5** (anion – 2.126(12) Å) [9], and 2.2827(16) Å averaged for  $[\text{GaCl}_2(\gamma\text{-pic})_2(\text{S}_2\text{CNR}_2)]$  (R = Me [8], Et [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 [9,28]. 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  $\text{sp}^2$  hybridized  $\text{RCO}_2^-$  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  $\text{CO}_2^-$  angle ranged from 123° to 128° [9]. In  $\text{CH}_3\text{Ga}(\text{OAc})_2$ , the average bridging  $\text{CO}_2^-$  bonding angle was 120.3(3)°; the mono-dentate acetate had a 122.0(5)°  $\text{CO}_2^-$  bonding angle [19]; and the mono-dentate acetate of  $(\text{Ga}(\text{OAc})(\text{tpp}))$  had a 122.9(5)°  $\text{CO}_2^-$  bonding angle [22]. The other chelating carboxylates [19,21] 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 [17,18]. 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  $\Delta$ In–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 [4,10,29–36]. 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 [10]. Asymmetrical bonding of chelating-carboxylate groups to an In(III) center has been observed for other eight-coordinate carboxylates:  $\text{In}(\text{O}_2\text{C-Me})_3\text{L}$  (L = phen,  $\Delta$ In–O = 0.157(7) Å and 0.198(7) Å; L = bipy,  $\Delta$ In–O = 0.172(6) Å) [37]. A related but simpler, *cis*-dichloro chelating-benzoate 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 [32]. Another octahedral benzoate compound with a tetradentate  $\text{N}_2\text{S}_2$  bis(aminoethanethiol) chelate had a significantly more asymmetric benzoate coordination with In–O bond

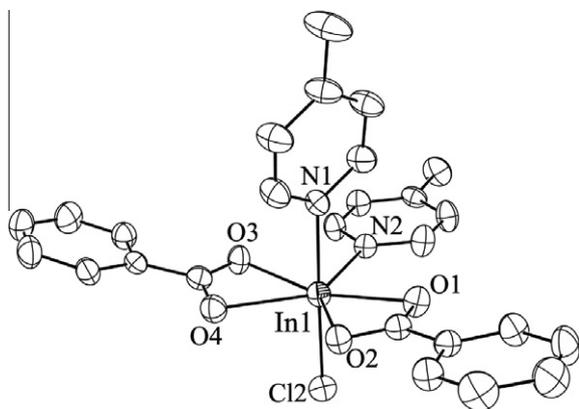


Fig. 2. ORTEP diagram and atomic labeling scheme of first coordination sphere of  $[\text{InCl}(\text{O}_2\text{CPh})_2(4\text{-Mepy})_2](4\text{-Mepy})$  (**2**) (hydrogen atoms and the co-crystallized picoline not shown for clarity).

lengths of 2.247(3) Å and 2.390(3) Å [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 [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 [31].

An unsymmetrical acetate is found in a  $(\text{TPP})\text{In}(\text{O}_2\text{CCH}_3)$  (TPP = tetraphenylporphinate) complex with In–O bond lengths of 2.215(4) Å and 2.322(4) Å [33]. A pair of related tetra-arylporphyrinato indium carboxylates  $(\text{TRP})\text{In}(\text{O}_2\text{CCH}_3)$  (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) carboxylates [34]. An asymmetrically-bound acetate is also found in an  $(\text{OEP})\text{In}(\text{O}_2\text{CCH}_3)$  (OEP = octaethylporphyrinato) complex with In–O bond lengths of 2.60(2) Å and 2.14(1) Å [35]. Two related ylido-containing halide compounds had In–O coordination that varied from slightly (<0.1 Å) to moderately asymmetric (>0.25 Å) [29]. Finally, the most asymmetric bidentate chelate is found in a dimeric  $\mu$ -oxo bridged neutral seven-coordinate complex  $[\text{L}_2\text{In}_2(\text{CH}_3\text{CO}_2)_4(\mu\text{-O})]\cdot 2\text{NaClO}_4$  (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 [36] are present.

The In–Cl bond length in **2** is 2.4132(15) Å and similar to the related octahedral chloro-benzoate compound, 2.391(2) Å [32]. It is also comparable to the *cis*-In–Cl bond length in  $\text{mer-InCl}_3(4\text{-Etpy})_3$  of 2.41 Å but shorter than the *trans*-In–Cl bond length of 2.46 Å [38]. The *cis*-(2.471(1) Å) and *trans*-(2.476(2) Å) In–Cl bond lengths in  $\text{mer-InCl}_3(\text{py})_3\cdot\text{py}$  [39] are practically equal within experimental error. The ylido compound with chloride ligands has an In–Cl bond length that ranges from 2.26(1) to 2.49(1) Å [29].

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 [32]. This is typically not observed in the family of  $\text{mer-InX}_3(\text{Rpy})_3$  (R = H, X = I, Br; R = Et; X = Cl; R = Me, and X = I) complexes where the average In–N bond length is 2.31 Å [38–41]. There is some asymmetry in  $\text{mer-InCl}_3(\text{py})_3\cdot\text{py}$  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 [4] and the triazacyclononane chelate (2.271(5)–2.324(5) Å) [36]. The tetradentate bis(aminoethanethiol) octahedral compound (2.298(3) and 2.367(3) Å) was also similar [30]. The In–N bond lengths for the porphyrin compounds were shorter and ranged from 2.16 to 2.18 Å [33–35].

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  $\text{InO}_4\text{N}$  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 [19–21]. The individual nearest-neighbor atoms in the  $\text{InO}_4\text{N}$  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  $\text{RCO}_2^-$  average bond angle of  $119.9(5)^\circ$ . The closely-related eight-coordinate *tris*-benzoato *bis*-picoline indium (III) complex had quite similar O–In–O angles of  $56.5(3)^\circ$  and  $55.9(2)^\circ$  [10]. The eight-coordinate complex also had a nearly symmetrical  $\text{RCO}_2^-$  average bond angle of  $119.5(8)^\circ$ . The octahedral benzoato complex, isostructural with compound **1**, had a similar  $\text{RCO}_2^-$  angle ( $118.9(6)^\circ$ ), with a wider O–In–O angle of  $57.5(1)^\circ$  [32], similar to the larger of the two angles of compound **2**, but significantly less than the O–Ga–O angle of  $62.83(10)^\circ$  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 ( $54.6(3)^\circ$ ) and  $\text{RCO}_2^-$  ( $118.5(4)^\circ$ ) angles [33,34]. The dimeric  $\mu$ -oxo bridged neutral seven-coordinate complex  $[\text{L}_2\text{In}_2(\text{CH}_3\text{CO}_2)_4(\mu\text{-O})]\cdot 2\text{NaClO}_4$  ( $\text{L} = 1,4,7$ -triazacyclononane) with asymmetric chelating acetate groups had a significantly constrained O–In–O bond angle of  $48.9(2)^\circ$ . The smaller O–In–O angle with the porphyrin-containing structures is expected as the macrocycles impose steric strain. The ylido compounds [29] and the multi-nuclear cluster compounds [31] had larger bond angles ranging from around  $57^\circ$  to  $59^\circ$ .

As noted above and compiled in Table 3, there are nearly 15 chelated In(III) carboxylate or related molecular structures that are five [29] six [29–36], seven (**2** and [4,31,36]), and eight [10,37] coordinate. Many of these chelating-carboxylate structures consist of a macrocyclic or large heterocyclic chelating ligand [4,30,33–36] or multi-nuclear cluster structure [31]. It is reasonable to assert that the aromatic benzoato chelate and pyridine-like ligands [10,32], electron-withdrawing halide ligands (**2**, [29,32]) and solvent of crystallization (**2**, [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,  $[\text{InCl}_3(\text{L}')(\text{MeOH})]$  and  $[\text{InCl}(\eta^2\text{-C}_2\text{O}_4)(\text{L}')(\text{OH}_2)]$  ( $\text{L}' = 2,6$ -bis(acetyloxime)-pyridine) [42,43]. A final observation to make is that compounds **1** and **2** adopt a roughly pentagonal bipyramidal structure. Compound **1**, and the isostructural In complex [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.

### 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 [4,10,19–21,26,30,33–37], carboxylates with unsaturated bonds or pendant groups for structural or electronic stabilization [4,26,27,29,44,45], or electronic-withdrawing ligands such as halides and  $\text{CF}_3\text{CO}_2^-$  (**1**, **2**, [29,32,37,38,46]). Interestingly, several structures contained multiple modes of coordination to identical carboxylate groups [27,31].

**Table 3**  
Selected bond distances (Å) and angles ( $^\circ$ ) for molecular complexes with chelating carboxylates of Ga, In and other metals with similar ionic radii.

Compound	CN	$d_{\text{M-O}}$ (Å)	O–M–O ( $^\circ$ )	O–C–O ( $^\circ$ )	Reference
$[\text{Ag}(\text{O}_2\text{CR})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ R = $\text{CH}_2\text{CN}$ , $(\text{CH}_2)_2\text{CH}=\text{CH}_2$ , or $\text{C}(\text{Me})=\text{C}(\text{H})\text{Me}$	4	2.401(3)–2.495(2)	52.61(7)–53.86(6)	122.6(2)–126.4(3)	[26]
$\{[\text{Ga}(\text{Me}_3\text{Si})_2\text{CH}_2]_2(\text{ndc})\}\cdot 2\text{MeC}_5\text{H}_9$ H <sub>2</sub> ndc = 1,6-naphthalenedicarboxylic acid	4	2.042(2), 2.056(2)	64.53(8)	118.0(3)	[19]
$[\text{InCl}_3(\eta^2\text{-O}_2\text{CC}(\text{P}(\text{C}_6\text{H}_5)_3)_2)]$	5	2.181(6), 2.304(6)	58.7(2)	118.6(8)	[29]
$[\text{InI}_2(\eta^2\text{-O}_2\text{CC}(\text{P}(\text{C}_6\text{H}_5)_3)_2)][\text{I}^-]$	6	2.168(5)–2.437(5)	57.0(2), 58.6(2)	117.9(7), 120.1(7)	[29]
$[\text{H}_2\text{B}(\text{pz})_2]_2\text{Ga}(\text{O}_2\text{CCH}_3)$ pz = $\{\text{N}_2(\text{CH}_3)\}$	6	2.048(3), 2.127(3)	62.3(1)		[20]
$[\text{Ga}(\text{hbo})_2(\text{O}_2\text{CCH}_3)]$ Hhbo = 2-(2'-hydroxyphenyl)-2-benzoxazole	6	2.117(2)	61.1(1)	118.2(4)	[21]
$[\text{GaCl}_2(\text{O}_2\text{CPh})(4\text{-Mepy})_2]\cdot 4\text{-Mepy}$	6	2.099(2), 2.102(3)	62.83(10)	117.6(4)	This work
$[\text{In}(\text{BAT-TM})(\text{O}_2\text{CC}_6\text{H}_5)]$ BAT-TM = $\text{N}_2\text{S}_2$ tetradentate ligand	6	2.247(3), 2.390(3)	56.3(1)	120.7(4)	[30]
$[\text{In}_2\text{M}_2(\text{OH})_2(\text{O}_2\text{C}^t\text{Bu})_8\text{L}_2]^a$ (M,L = Co, MeCN; M,L = Ni, MeCN/ $\text{HO}_2\text{C}^t\text{Bu}$ )	6	2.2091(13)–2.275(8)	56.9(3)–59.1(3)	117.1(10)–120.6(10)	[31]
$[\text{InCl}_2(\text{O}_2\text{CPh})(\text{py})_2]$	6	2.246(4), 2.280(4)	57.5(1)	118.9(6)	[32]
$[\text{In}(\text{TPP})(\text{O}_2\text{CCH}_3)]$ TPP = tetraphenylporphyrin	6	2.215(4), 2.322(4)	54.4(2)	118.5(4)	[33]
$[\text{In}(\text{TRP})(\text{O}_2\text{CCH}_3)]$ R = 4-pyridyl or 4-methoxyphenyl	6	2.185(6)–2.412(6)	54.4(4), 55.0(2)	115(2)–121.1(7)	[34]
$[\text{InCl}(\text{O}_2\text{CPh})_2(4\text{-Mepy})_2]\cdot 4\text{-Mepy}$	7	2.212(3)–2.417(4)	55.57(13), 56.99(12)	119.6(5), 120.2(5)	This work
$[\text{L}_2\text{In}_2(\text{O}_2\text{CCH}_3)_4(\mu\text{-O})]\cdot 2\text{NaClO}_4$ L = 1,4,7-triazacyclononane	7	2.142(5)–2.875(8)	48.9(2)		[36]
$[\text{In}_2\text{Ni}(\text{OH})_2(\text{O}_2\text{C}^t\text{Bu})_7(\text{HO}_2\text{C}^t\text{Bu})_x]^a$ (x = 1,2)	7	2.208(6)–2.249(6)	58.4(2), 58.5(2)	118.6(8), 119.0(8)	[31]
$[(\text{terpy})\text{In}(\text{N}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}_2\text{OH})]$ terpy = terpyridine	7	2.274(2), 2.354(2)	56.31(7)	120.2(2)	[4]
$[\text{SbCl}(\text{C}_6\text{H}_5)_2(\text{O}_2\text{C}(2\text{-Me})\text{C}_6\text{H}_4)_2]$	7	2.213(3)–2.296(3)	57.46(11), 57.58(11)	118.8(6), 120.5(7)	[44]
$[\text{Cd}(\text{O}_2\text{C}(3,4\text{-OH})\text{C}_6\text{H}_3)_2(\text{H}_2\text{O})_3]$	7	2.304(4)–2.513(4)	54.0(1), 54.3(1)	117.3(4), 117.6(4),	[45]
$[\text{MoBr}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]$	7	2.304(9), 2.320(9)	56.5(3)	126.0(1)	[46]
$[\text{Bi}(\text{O}_2\text{C}(2\text{-EtO})\text{C}_6\text{H}_4)_3]_2$	8	2.207(1), 2.532(1)	55.06(4)	120.2(2)	[27]
$[\text{In}(\text{O}_2\text{CPh})_3(4\text{-Mepy})_2]\cdot 4\text{H}_2\text{O}$	8	2.225(6)–2.413(5)	55.9(2), 56.5(3)	119(1), 120.0(7)	[10]
$[\text{In}(\text{O}_2\text{CCH}_3)_3\text{L}]$ L = 2,2'-bipy or 1,10-phen	8	2.221(3)–2.422(6)	54.4(2)–56.5(3)		[37]

<sup>a</sup> Data for In coordination environment only.

The structure most similar to compound **1** is the analogous six-coordinate In benzoate complex [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** [44]. The other structurally-characterized seven-coordinate In(III) carboxylate environments are sterically constrained by tri-dentate chelating ligands [4,36] or a multi-nuclear cluster environment [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 [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 [47–61], 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 Ref. [10], respectively. Table 4 includes five basic types of In polymer constructs: seven-coordinate In polymers from di- [47–49], tri- [50–53] and tetracarboxylates [54,55] and eight-coordinate In polymers from di- [56–59] and tricarboxylates [60,61], several of which are chiral [51,58,59].

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 2D and 3D 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. 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  $\gamma$ -picoline ligands, is the first example of a structurally-characterized chelating gallium benzoate. It is isostructural with a previously characterized

**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 <sub>2</sub> CPh) <sub>2</sub> (4-Mepy) <sub>2</sub> ](4-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) <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> H <sub>2</sub> ndc = 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)	[47]
[In <sub>2</sub> (OH) <sub>2</sub> (pdc) <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> H <sub>2</sub> pdc = 3,5-pyridinedicarboxylic acid	7	2.255(2), 2.311(2)	57.53(5)	121.36(18)	[48]
[In(OH)(tca)(H <sub>2</sub> O)] <sub>n</sub> H <sub>2</sub> tca = thiophene-2,5-dicarboxylic acid	7	2.209(2)–2.391(2)	56.86(7), 57.53(7)	119.8(2), 120.2(2)	[49]
{[Hbipy <sup>+</sup> ][In(Hbtc) <sub>2</sub> (bipy) <sup>-</sup> ]}·0.5H <sub>2</sub> O] <sub>n</sub> H <sub>3</sub> btc = 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)	[50]
{[Hpy <sup>+</sup> ] <sub>2</sub> [In <sub>2</sub> (btc) <sub>2</sub> (μ-OH) <sub>2</sub> <sup>2-</sup> ]} <sub>n</sub> H <sub>3</sub> btc = benzenetricarboxylic acid py = pyridine	7	2.140(11)–2.569(10)	54.8(3)–57.1(4)	119.5(13)–124.1(14)	[51]
{[In <sub>2</sub> (btc) <sub>2</sub> (bipy) <sub>2</sub> ]}·4H <sub>2</sub> O] <sub>n</sub> H <sub>3</sub> btc = 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)	[52]
{[In <sub>2</sub> (btc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]}·2H <sub>2</sub> O] <sub>n</sub> H <sub>3</sub> btc = benzenetricarboxylic acid	7	2.575(2), 2.580(2)	56.75(11), 58.10(11)	119.4(4), 119.8(4)	[53]
[In <sub>2</sub> (btcc)(bipy) <sub>2</sub> Cl <sub>2</sub> ] <sub>n</sub> H <sub>4</sub> btcc = 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)	[54,55]
[In(O <sub>2</sub> CPh) <sub>3</sub> (4-Mepy) <sub>2</sub> ]}·4H <sub>2</sub> O	8	2.225(6)–2.413(5)	55.9(2), 56.5(3)	119(1), 120.0(7)	[10]
{[H <sup>+</sup> ][In(bdc) <sub>2</sub> <sup>-</sup> ]} <sub>n</sub> H <sub>2</sub> bdc = benzenedicarboxylic acid	8	2.267(7), 2.283(7)	57.7(3)	120.8(9)	[56]
{[M(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup> ][In <sub>3</sub> (μ <sub>2</sub> -pdc) <sub>6</sub> <sup>3-</sup> ]}·15H <sub>2</sub> O] <sub>n</sub> H <sub>2</sub> pdc = 2,3-pyrazinedicarboxylic acid M = In, Cr <sub>0.7</sub> In <sub>0.3</sub> , or Fe <sub>0.3</sub> In <sub>0.7</sub>	8	2.236(4)–2.446(6)	54.9(2)–55.4(3)	120.3(5)–123.4(8)	[57]
{[Htmdp <sup>+</sup> ][In(pdc) <sub>2</sub> <sup>-</sup> ]}·(EtOH)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> tmdp = 4,4'-trimethylenedipiperidine H <sub>2</sub> pdc = 2,5-pyridinedicarboxylic acid	8	2.205(5), 2.588(5)	54.29(17)	122.5(7)	[58]
{[NR <sub>4</sub> <sup>+</sup> ][In(DL-cam) <sub>2</sub> <sup>-</sup> ]}·(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> R = CH <sub>3</sub> ; D- and L-camphorate NR <sub>4</sub> <sup>+</sup> = choline; D-camphorate	8	2.188(7)–2.407(8)	55.4(3)–57.3(3)	119.0(10)–120.7(9)	[59]
{[NR <sub>4</sub> <sup>+</sup> ][In(DL-cam) <sub>2</sub> <sup>-</sup> ]}·(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> R = n-propyl; D- or DL-camphorate NR <sub>4</sub> <sup>+</sup> = imidazolium; D-camphorate <sup>a</sup>	8	2.163(3)–2.481(3)	54.7(4)–58.2(4)	117(2)–124.8(16)	[60]
[In(btc) <sub>1.5</sub> (bipy)] <sub>n</sub> H <sub>3</sub> btc = 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)	[61]
{[H <sub>2</sub> tmdp <sup>2+</sup> ] <sub>3</sub> [In <sub>6</sub> (btc) <sub>8</sub> <sup>6-</sup> ]}·40H <sub>2</sub> O] <sub>n</sub> tmdp = 4,4'-trimethylene dipiperidine H <sub>3</sub> btc = benzenetricarboxylic acid	8	2.155(5)–2.409(5)	56.36(18)	120.3(6)	[62]

<sup>a</sup> Table entry also includes three more related structures (total of six) from same publication.

analogous In(III) benzoate complex. The seven-coordinate In(III) *bis*-benzoate also includes one chloride and two  $\gamma$ -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. Supplementary material

CCDC 753437 and 753438 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2010.08.026](https://doi.org/10.1016/j.ica.2010.08.026).

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