

Diorgano-gallium and -indium complexes with *N*-heterocyclic carboxylic acids: Synthesis, characterization and structures of $[\text{Me}_2\text{M}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})]_2$, $\text{M} = \text{Ga}$ or In

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Abstract

The reaction of triorgano-gallium and -indium etherate with heterocyclic carboxylic acids in benzene at room temperature yields complexes of the type $[\text{R}_2\text{M}(\text{L})]_n$ ($\text{M} = \text{Ga}$ or In ; $\text{R} = \text{Me}$ or Et ; $\text{L} = 2-(\text{C}_5\text{H}_4\text{N})\text{CO}_2$, $2-(\text{C}_4\text{H}_3\text{N}_2)\text{CO}_2$ or $2-(\text{C}_9\text{H}_6\text{N})\text{CO}_2$). These complexes have been characterized by elemental analysis, IR, UV–vis, NMR (^1H and $^{13}\text{C}\{^1\text{H}\}$) and mass spectral data. Complexes with $\text{L} = (\text{C}_5\text{H}_4\text{N})\text{CO}_2^-$ and $(\text{C}_9\text{H}_6\text{N})\text{CO}_2^-$ showed photoluminescence on excitation with ~ 250 or ~ 310 nm radiation, respectively. Single crystal X-ray structural analysis of $[\text{Me}_2\text{M}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$ ($\text{M} = \text{Ga}$ or In), revealed a dimeric structure with five-coordinate metal atoms arising from the presence of two tridentate bridging picolinate ligands.

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1. Introduction

The chemistry of organo-gallium and -indium with anionic oxo ligands has been of interest for quite some time and more recently due to their relevance as molecular precursors for the preparation of metal oxide thin films [1,2]. Compounds of composition R_2ML ($\text{R} = \text{alkyl}$; $\text{M} = \text{Ga}$ or In ; $\text{L} = \text{anionic oxo ligands}$) have been isolated as mono-, bi- or tri-meric species in which the coordination number of central metal atom varies between four and six. The nature of R , M and L governs the overall stereochemistry of the molecule. Among anionic oxo ligands, both single and internally functionalized alkoxides have been extensively studied and several of them have been employed as catalysts and also as molecular precursors

for MOCVD [3,4]. Unlike alkoxides, organo-gallium and -indium carboxylates are relatively under explored [5–11] and when studied, investigations were limited to simple carboxylic acids. The complexes $[\text{R}_2\text{Ga}(\text{O}_2\text{CR}')]_2$ ($\text{R} = \text{Me}$, Et , Bu^t ; $\text{R}' = \text{Me}$, Et , Ph , $\text{C}_6\text{H}_4\text{CN}-3$, $\text{C}_6\text{H}_4\text{Br}-3$) are centrosymmetric dimers in which two “ R_2Ga ” units are bridged by two carboxylate groups [5,6]. By contrast, diorgano-indium acetates, $[\text{R}_2\text{In}(\text{OAc})]_\infty$ ($\text{R} = \text{Me}$ or Et) are polymeric in which the indium atoms are six-coordinated and are bonded to two approximately trans alkyl groups and four oxygen atoms [7,8]. A similar polymeric structure has been reported recently for $[\text{Et}_2\text{In}(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{NH}_2-2)]_n$ [9]. This molecule comprises an extended one-dimensional chain containing a diethylindium moiety chelated asymmetrically by the carboxylate group and one of the oxygen atoms bridges the next indium atom in the chain; the NH_2 group does not participate in coordination [9]. The complex $[\text{Bu}_2\text{In}(\text{O}_2\text{CEt})]_n$, on pyrolysis, yields indium oxide thin films [10].

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With the above perspective in mind, it was considered worthwhile to study organo-gallium and -indium complexes with internally functionalized carboxylic acids. The results of this work are reported herein.

2. Results and discussion

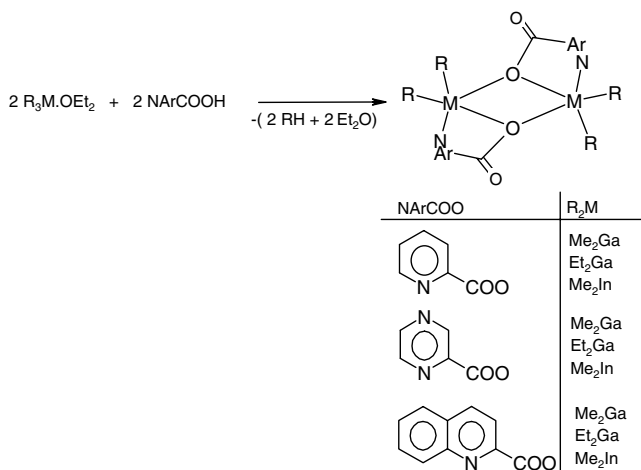
2.1. Synthesis

Diorgano-gallium and -indium complexes of the type R_2ML have been synthesized by the metathetical reaction between trialkyl metal (Ga/In) · diethyl ether adduct and the free ligands (LH) in 1:1 stoichiometry in benzene solution (Scheme 1). These complexes were isolated as either off-white to colorless crystalline solids.

2.2. Spectroscopic characterization

The IR spectra of the complexes displayed an absorption band of medium to strong intensity in the range $500\text{--}560\text{ cm}^{-1}$ for Ga–C stretching and $520\text{--}560\text{ cm}^{-1}$ for In–C stretching [12,13]. The IR spectra of picolinic, quinaldic and pyrazine carboxylic acid complexes exhibit C=O stretching at $\sim 1660\text{ cm}^{-1}$ indicating the presence of non-chelating carboxylate groups.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Table 1) displayed the expected resonances and multiplicities. The metal-bound alkyl group signals are deshielded with reference to $R_3M \cdot \text{OEt}_2$ resonances. This suggests coordination of the electron-withdrawing *N*-heterocyclic carboxylate to the metal atom. The methyl resonance in four-, five-, and six-coordinate mono-, bi-, and tri-, nuclear Me_2ML ($M = \text{Ga}$ or In) complexes appear in a narrow range thus limiting its utility in diagnosis of either metal coordination number or the nuclearity of the complexes [13,14]. The C-4 and C-6 carbon resonances in picolinates and C-4 in quinaldic acid complexes are deshielded relative to the corresponding signals for the free ligand indicating O^\ominusN chelation [15].



Scheme 1.

The mass spectra of some representative complexes have been recorded and the resulting data are given in Table 2. The mass spectra of $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})]_2$ and $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})]_2$ showed peaks higher than the formula weight, suggesting their associated nature. The spectra also showed peaks attributable to formula weight and the fragment ions of compositions R_2M^+ and RML^+ . However, the mass spectrum of $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})]_2$ showed fragments originating from tri-meric species (Table 2), although the molecular structure showed this complex as a dimer. The higher m/e peaks are suggested to have formed as a result of recombination of fragment ions.

The electronic spectra exhibited bands in the region $240\text{--}310\text{ nm}$ attributed to $\pi\text{--}\pi^*$ transitions within the ligand moiety. Photoluminescence spectra of some representative complexes have been recorded in dichloromethane solution. These complexes displayed emission bands (Fig. 1) in the region $356\text{--}371\text{ nm}$ on excitation with $240\text{--}257\text{ nm}$ (Table 3). The emission intensities in these complexes are stronger than the free ligands. Fluorescence enhancement in metal chelates is generally observed owing to enhanced rigidity of the chelating ligand which minimizes loss of energy by a non-radiative pathway, consequently increasing $\pi\text{--}\pi^*$ transition intensity. Recently, photoluminescence in organo-gallium and -indium complexes has been reported [11,16,17].

2.3. Molecular structures of $[\text{Me}_2\text{M}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$, $M = \text{Ga}$ or In

The molecular structure of the dinuclear complex $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$ is shown in Fig. 2a and selected geometric parameters are collected in Table 4. The structure is constructed about a central rectangular Ga_2O_2 core with the two $\mu_2\text{-oxo}$ atoms derived from two different 2-picolinate-carboxylate groups. Each 2-picolinate ligand chelates a gallium atom via an aforementioned bridging-oxo atom and the pyridine-nitrogen atom, forming a five-membered, effectively planar, chelate ring; the carbonyl O2 and O4 atoms do not coordinate. The remaining positions in the five-coordinate geometry about the gallium atom are occupied by the methyl groups. The C_2NO_2 donor set defines a highly distorted geometry. Using the τ values [18] calculated for five-coordinate geometries as a guide, which should equal 0.0 for an ideal square pyramid and 1.0 for an ideal trigonal bipyramid, values of 0.26 and 0.23 are computed for the Ga1 and Ga2 atoms, respectively. The molecular structure of the indium analog, Fig. 2b and Table 4, is essentially in agreement with that just described. The central In_2O_2 core is decidedly squarer owing to the near equivalence of the In–O bonds. The disparity in the Ga–O and Ga–N bond distances observed in the structure of $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$ is not as pronounced in the In–O and In–N distances in $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$. This reflects the propensity of the larger indium atom to increase its coordination number, i.e. its increased Lewis acidity. The C_2NO_2 donor set defines a

Table 1
Analytical, IR, ^1H and ^{13}C $\{^1\text{H}\}$ NMR data of diorgano-gallium and -indium carboxylates

Complexes	% Yield	M.p. ($^{\circ}\text{C}$)	% Analysis found (Calc.)				^1H NMR data, δ in ppm	$^{13}\text{C}\{^1\text{H}\}$ NMR data, δ in ppm	IR (cm^{-1})	
			C	H	N	Ga/ In			$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{C})$
$[\text{Me}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_5\text{H}_4\text{N})\}]_2$	97	172	42.9 (43.3)	4.9 (4.5)	6.4 (6.3)	30.9 (31.4)	-0.13 (s, Me_2Ga); 7.79 (t, 7.0 Hz, 1H, H-4); 8.23 (t, 8.0 Hz, 1H, H-5); 8.45-8.49 (m, 2H, H-3, H-6)	-6.5 (s, Me_2Ga); 125.7 (C-3); 127.9 (C-5); 141.9 (C-4); 144.6 (C-2); 148.3 (C-6) 164.7 (C=O)	1685	547
$[\text{Et}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_5\text{H}_4\text{N})\}]_2$	96	85				27.3 (27.9)	0.58 (q, 7.8 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 0.94 (t, 7.7 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 7.80 (dt, 0.9 Hz d, 6.4 Hz t, 1H, H-4); 8.24 (dt, 1.4 Hz d, 7.8 Hz t, 1H, H-5); 8.45-8.49 (m, 2H, H-3, H-6)	3.6 (s, $\text{CH}_3\text{CH}_2\text{Ga}$); 8.8 (s, $\text{CH}_3\text{CH}_2\text{Ga}$); 125.8 (C-3); 127.7 (C-5); 141.9 (C-4); 144.7 (C-2); 148.8 (C-6) 165.1 (C=O)	1670	537
$[\text{Me}_2\text{In}\{\text{O}_2\text{C}(\text{C}_5\text{H}_4\text{N})\}]_2$	98	240				42.5 (43.0)	0.03 (s, Me_2In); 7.60 (d, 5.8 Hz); 8.00 (t, 7.0 Hz); 8.37 (d, 7.7 Hz); 8.45 (br)	-4.5 (s, Me_2In); 125.5 (C-3); 127.3 (C-5); 139.6 (C-4); 146.0 (C-2); 148.8 (C-6); 165.5 (C=O)	1667	535
$[\text{Me}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_4\text{H}_3\text{N}_2)\}]_2$	97	220 ^a	37.1 (37.7)	4.4 (4.1)	12.4 (12.6)	32.2 (31.3)	-0.04 (s, Me_2Ga); 8.47 (s, H-5); 9.13 (s, H-6); 9.72 (s, H-3)	-5.7 (s, Me_2Ga); 138.1 (C-5); 141.7 (C-3); 148.7 (C-2); 149.2 (C-6); 163.4 (C=O)	1687	552
$[\text{Et}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_4\text{H}_3\text{N}_2)\}]_2$	96	180				27.0 (27.8)	0.64 (q, 8.1 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 0.97 (t, 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 8.46 (s, H-5); 9.12 (s, H-6); 9.71 (s, H-3)	4.8 (s, $\text{CH}_3\text{CH}_2\text{Ga}$); 8.9 (s, $\text{CH}_3\text{CH}_2\text{Ga}$) 138.8 (C-5); 141.6 (C-3); 148.1 (C-2); 149.0 (C-6); 163.8 (C=O)	1686	571
$[\text{Me}_2\text{In}\{\text{O}_2\text{C}(\text{C}_4\text{H}_3\text{N}_2)\}]_2$	97	235 ^a				42.3 (42.8)	0.05 (s, Me_2In); 8.46 (s, H-5); 8.96 (s, H-6); 9.58 (s, H-3)	-3.8 (s, Me_2In); 140.1 (C-5); 143.0 (C-3); 147.9 (C-2); 148.5 (C-6); 164.6 (C=O)	1658	544
$[\text{Me}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_9\text{H}_6\text{N})\}]_2$	98	213	52.3 (53.0)	5.0 (4.4)	7.2 (5.2)	25.4 (25.6)	0.00 (s, Me_2Ga); 7.80-7.85 (m, 1H, H-6); 7.97 (d, 3.5 Hz, 2H, H-7,8); 8.10 (d, 8.3 Hz, 1H, H-5); 8.52 (d, 8.4 Hz, 1H, H-3); 8.66 (d, 8.4 Hz, 1H, H-4)	-6.4 (s, Me_2Ga); 121.1 (C-3); 124.2, 129.0, 129.5, 130.0, 132.9 (C-7); 142.2 (C-4); 142.5, 149.6 (C-2); 165.1 (C=O)	1684	521
$[\text{Et}_2\text{Ga}\{\text{O}_2\text{C}(\text{C}_9\text{H}_6\text{N})\}]_2$	98	130				22.7 (23.2)	0.67 (q, 8.1 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 0.91 (t, 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Ga}$); 7.82 (dt, 1.4 Hz d, 6.6 Hz t, 1H, H-6); 7.92 (s, 1H, H-7); 8.10 (d, 7.7 Hz, 2H, H-5,8); 8.47 (dd, 1.5 Hz, 8.4 Hz, 1H, H-3); 8.68 (d, 8.4 Hz, 1H, H-4)	4.0 (s, $\text{CH}_3\text{CH}_2\text{Ga}$); 9.0 (s, $\text{CH}_3\text{CH}_2\text{Ga}$); 121.1 (C-3); 124.3, 128.2, 129.0, 129.6, 129.9, 132.9 (C-7); 142.4 (C-4), 149.8 (C-2); 165.6 (C=O)	1684	521
$[\text{Me}_2\text{In}\{\text{O}_2\text{C}(\text{C}_9\text{H}_6\text{N})\}]_2$	96	>300				35.9 (36.2)	0.17 (s, Me_2In); 7.76 (br, 1H, H-6); 7.91 (br, 1H, H-7); 8.06 (br, 1H, H-5); 8.13 (br, 1H, H-3); 8.49 (br, 2H, H-4,8)	-3.8 (s, Me_2In); 121.6 (C-3); 126.5, 128.4, 128.8, 129.9, 131.5 (C-7); 139.6 (C-4); 144.6, 150.0 (C-2); 165.8 (C=O)	1670	537

^a Decompose.

Table 2
Mass spectral data of diorgano-gallium and -indium carboxylates

Complex	<i>m/e</i>
[Me ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	428 ([Me ₂ Ga pic] ₂ –Me); 322 ([Me ₂ Ga pic] ₂ –pic); 222 ([Me ₂ Ga pic]); 206 ([Me ₂ Ga pic]–Me); 124 (picH ₂); 106 (C ₅ H ₄ N–CO); 99 (Me ₂ Ga)
[Et ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	369; 341; 315; 287; 267; 248 ([Et ₂ Ga pic] ⁺); 220 ([Et ₂ Ga pic]–Et); 192 ([Ga pic] ⁺); 176 (CH ₂ Gapic); 106 (C ₅ H ₄ N–CO); 98 (EtGa); 78 (C ₅ H ₄ N ⁺); 69 (Ga)
[Me ₂ In{O ₂ C(C ₅ H ₄ N)}] ₂	893; 786 ([Me ₂ In pic] ₃ –Me); 519 ([Me ₂ In pic] ₂ –Me); 412 ([Me ₂ In pic] ₃ –pic); 290; 268 ([Me ₂ In pic]); 145 (Me ₂ In ⁺)
[Me ₂ In{O ₂ C(C ₄ H ₃ N ₂)}] ₂	413 ([Me ₂ In pyz] ₂ –pyz); 268 ([Me ₂ In pyz]); 253 ([Me ₂ In pyz]–Me); 145 ([Me ₂ In] ⁺); 115 (In)

pic = 2-C₅H₄N–CO₂[–]; pyz = C₄H₃N₂–CO₂[–].

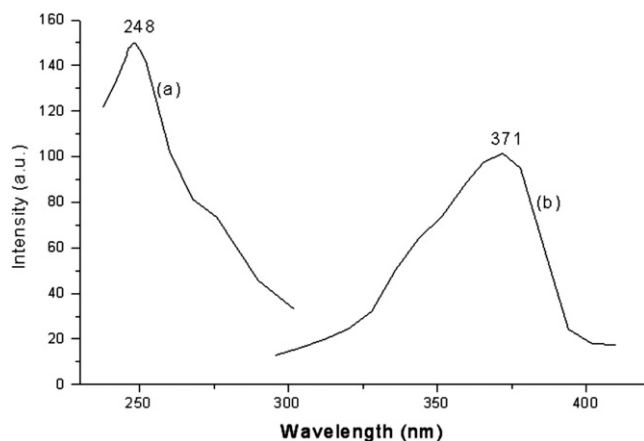


Fig. 1. Excitation (a) and emission spectra (b) of [Me₂In(O₂C–C₅H₄N)]₂ recorded in dichloromethane solution.

Table 3
Absorption and emission data of diorganometal carboxylates in CH₂Cl₂

Complex	UV–vis λ_{max} (nm)	Excitation λ_{max} (nm)	Emission λ_{max} (nm)
[Me ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	258	257	368
[Et ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	252	252	369
[Me ₂ In(O ₂ C–C ₅ H ₄ N)] ₂	–	257	371
[Me ₂ Ga(O ₂ C–C ₉ H ₆ N)] ₂	240, 308	240, 308	362, 412
[Et ₂ Ga(O ₂ C–C ₉ H ₆ N)] ₂	240, 310	240, 310	364, 412
[Me ₂ In(O ₂ C–C ₉ H ₆ N)] ₂	–	240, 308	356, 412

square pyramidal geometry as indicated by the values of τ of 0.09 and 0.13 for In1 and In2, respectively.

While comparatively rare, there are a few related structures available in the literature for comparison. A similar centrosymmetric M₂O₂ core and five-coordinate geometries, but based on C₂O₃ donor sets, as reported here for [Me₂M(O₂C–C₅H₄N-2)]₂ is found in each of the three structures of general formula [Me₂M(methyl salicylate)]₂, for M = Al, Ga and In [19]. This study correlated systematic changes in the M–O bond distances with the Lewis acidity of the central atom, which increased Al < Ga < In. The present results are consistent with this conclusion. In another related structure, motivated by the desire to provide suitable single-source precursors for Ga₂O₃ thin films [20], a similar five-coordinate geometry was reported for the monomeric compound Et₂Ga(OCH₂CH₂NMe₂) in

which the functionalized alkoxide ligands formed O-,N-chelates to the Ga atom and presumably precluded aggregation between molecules.

There are only two Me₂Ga compounds recorded in the Cambridge Crystallographic Database (CSD) [21] within a C₂NO₂ donor set in which the N-donor atom is derived from a pyridine-type molecule. Each of these, i.e. centrosymmetric [Me₂Ga(pyridine-2-methanolato)]₂ [22] and [Me₂Ga(8-quinolinolato)]₂ [23] disposed about a crystallographic site of symmetry 2/m, feature the same core as reported above for [Me₂Ga(O₂C–C₅H₄N-2)]₂. Table 5 collects geometric data for the three structures. From these data, it is apparent that similar patterns exist, e.g. disparate Ga–O(oxo) bond distances. In the structure of [Me₂Ga(O₂C–C₅H₄N-2)]₂ the respective short and long Ga–O(oxo) bond distances are longer than those of the other structures, a result clearly correlated with the presence of the electronegative carbonyl group in [Me₂Ga(O₂C–C₅H₄N-2)]₂. Concomitant with this elongation of the Ga–O bonds in [Me₂Ga(O₂C–C₅H₄N-2)]₂ is a relative shortening of the Ga–N bond compared with the other structures. Differences between the Ga–O and Ga–N bond distances for [Me₂Ga(pyridine-2-methanolato)]₂ and [Me₂Ga(8-quinolinolato)]₂ structures are also traced to electronic effects in that the stronger Ga–O(oxo) bonds in [Me₂Ga(pyridine-2-methanolato)]₂ are formed for the oxo-bridge connected to the sp³ carbon atom which reduces delocalization of π -electron density in this part of the molecule. Accordingly, the Ga–N bond distance is shorter in the structure of [Me₂Ga(8-quinolinolato)]₂ to compensate for the longer Ga–O bond so as to satisfy the valency of the Ga atom.

There are also two Me₂In structures in the literature having a C₂NO₂ donor set and carrying a pyridine-type N-donor atom according to a search of the CSD [21]. These are [Me₂In(pyridine-2-ethanolato)]₂ [24] and [Me₂In(*N*-phenyl-salicylideneaminato)]₂ [25], each of which is disposed about a crystallographic center of inversion. Again, selected geometric parameters for these are collected in Table 5 and compared to those of [Me₂In(O₂C–C₅H₄N-2)]₂. Systematic variations in the listed geometric parameters can be rationalized in terms of electronic effects. Thus, the shorter In–O(oxo) bond in the [Me₂In(pyridine-2-ethanolato)]₂ and [Me₂In(*N*-phenyl-salicylideneaminato)]₂ structures are shorter than those found

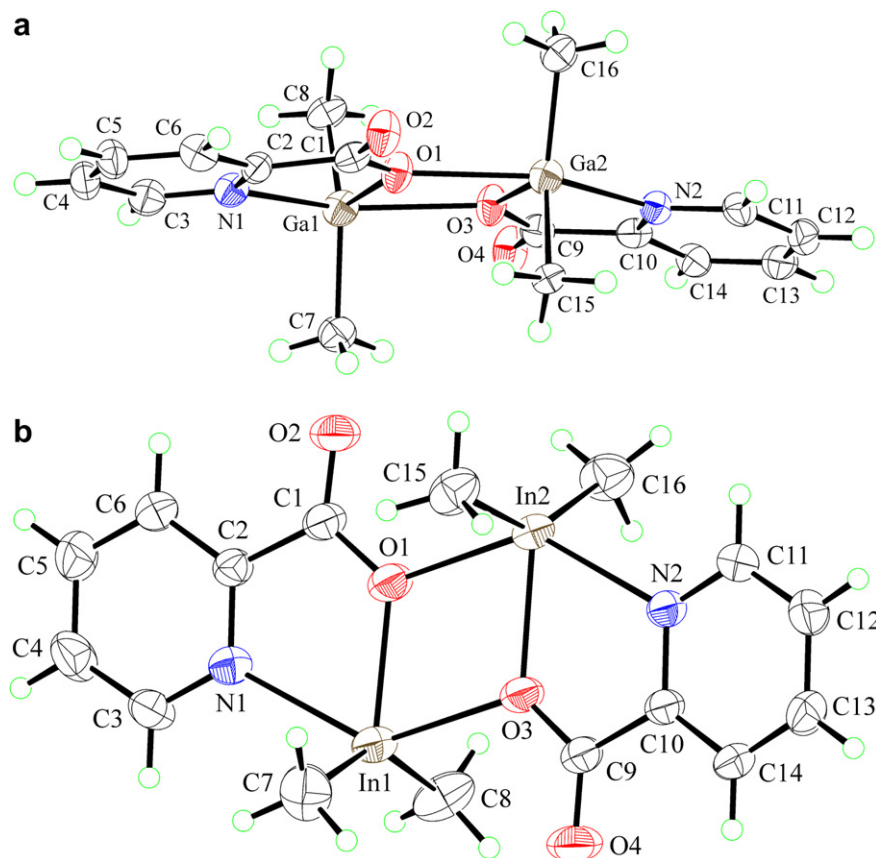


Fig. 2. Alternate views of the molecular structures showing atom numbering schemes: (a) side-on view of $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]_2$, and (b) plan view of $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]_2$.

Table 4
Selected geometric parameters (\AA , $^\circ$) for $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$ and $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$

	M = Ga	M = In
M1–O1, M2–O1	1.955(4), 2.311(4)	2.224(3), 2.362(3)
M1–O3, M2–O3	2.342(3), 1.986(4)	2.356(2), 2.237(3)
M1–N1, M2–N2	2.178(4), 2.149(4)	2.443(3), 2.402(3)
M1–C7, M2–C15	1.962(6), 1.975(5)	2.125(4), 2.138(4)
M1–C8, M2–C16	1.958(5), 1.945(6)	2.133(4), 2.130(4)
O1–M1–O3, O1–M2–O3	69.51(13), 69.70(13)	67.99(9), 67.66(9)
O1–M1–N1, O1–M2–N2	77.45(15), 147.27(15)	69.03(9), 136.86(9)
O1–M1–C7, O1–M2–C15	113.8(2), 89.67(18)	109.75(16), 93.40(15)
O1–M1–C8, O1–M2–C16	112.5(2), 93.65(19)	107.36(16), 95.83(15)
O3–M1–N1, O3–M2–N2	146.96(14), 77.83(15)	136.96(9), 69.31(9)
O3–M1–C7, O3–M2–C15	92.0(2), 110.78(19)	95.58(15), 106.00(15)
O3–M1–C8, O3–M2–C16	91.21(19), 113.8(2)	94.70(17), 109.30(14)
N1–M1–C7, N2–M2–C15	100.7(2), 98.15(18)	96.72(15), 95.47(14)
N1–M1–C8, N2–M2–C16	102.3(2), 103.3(2)	99.84(15), 100.85(15)
C7–M1–C8, C15–M2–C16	131.6(2), 133.5(2)	142.7(2), 144.42(17)
M1–O1–M2, M1–O3–M2	111.48(15), 109.09(15)	112.19(10), 111.96(10)

in $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$, a result directly correlated with the formation of a five-membered chelate ring in the latter compared with six-membered rings in the former two structures. The second In–O(oxo) bond in $[\text{Me}_2\text{In}(\text{pyr}-$

idine-2-ethanolato)]₂ is shorter than that found in $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$, for the same reason outlined above in terms of the lack of reorganization of π -electron density in the former. As a consequence, the In–N(pyridine) bond is longer in the former. Finally, additional differences between the structures of $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$ and $[\text{Me}_2\text{In}(\text{N-phenyl-salicylideneaminato})]_2$ can be related to the donor ability of the pyridine-like N-donor in the later which is in a fact an imine-N and forms a stronger bond to the In atom, thereby weakening the second In–O(oxo) bond.

The respective isomorphous crystal structures of $[\text{Me}_2\text{M}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$ are stabilized by a series of C–H...O contacts involving the non-coordinating carbonyl atoms. Symmetry related molecules associate on one side of the molecule via a pair of C3–H...O4 interactions and on the other side by a pair of C11–H...O2 contacts [26]. Each molecule is therefore connected to four other molecules. The C–H...O interactions cooperate to form a 2D array and successive layers are separated by hydrophobic interactions. A view of the unit cell contents is shown in Fig. 3 for $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$.

From the foregoing discussion it can be concluded that diorgano-gallium and -indium carboxylates can readily be obtained by the reactions of triorgano-metal etherates with carboxylic acids. The complexes are dimeric containing

Table 5
Selected geometric parameters (Å, °) for $[\text{Me}_2\text{M}(\text{N},\text{O}\text{-chelate})_2]$ compounds, M = Ga and In

<i>M = Ga</i>			
	$[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$	$[\text{Me}_2\text{Ga}(\text{pyridine}-2\text{-methanolato})_2]$ [22]	$[\text{Me}_2\text{Ga}(\text{8-quinolinolato})_2]$ [23]
Ga-(oxo)	1.955(4), 2.342(3) 1.986(4), 2.311(4)	1.925(3), 2.073(3)	1.937(2), 2.297(3)
Ga-N(pyridine)	2.178(4), 2.149(4)	2.271(4)	2.211(4)
Ga-C(methyl)	1.962(6), 1.975(5) 1.958(5), 1.945(6)	1.967(5), 1.967(5)	1.945(7), 1.948(7)
<i>M = In</i>			
	$[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$	$[\text{Me}_2\text{In}(\text{pyridine}-2\text{-ethanolato})_2]$ [24]	$[\text{Me}_2\text{In}(\text{N-phenyl-salicylideneaminato})_2]$ [25]
In-(oxo)	2.224(3), 2.356(2) 2.237(3), 2.362(3)	2.131(6), 2.239(5)	2.158(3), 2.477(3)
In-N(pyridine)	2.443(3), 2.402(3)	2.522(5)	2.366(3)
In-C(methyl)	2.125(4), 2.138(4) 2.133(4), 2.130(4)	2.140(8), 2.147(8)	2.133(5), 2.137(5)

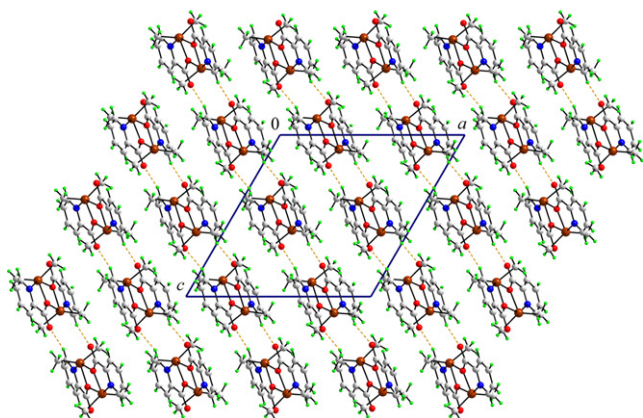


Fig. 3. Unit cell contents for $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$. Orange dashed lines indicate C–H...O interactions. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

bridging O^{N} chelated carboxylate group. The complexes show photoluminescence.

3. Experimental

All experiments employing organo-gallium and -indium compounds were performed in Schlenk flasks under anhydrous conditions in a nitrogen atmosphere. The solvents were dried using standard methods. 2-Picolinic, 2-quinaldic and pyrazine carboxylic acids were obtained from commercial sources and were used after vacuum drying. The $\text{R}_3\text{Ga} \cdot \text{OEt}_2$ (R = Me, Et) compounds were prepared from gallium–magnesium alloy and corresponding alkyl iodide in diethyl ether [27]. The $\text{Me}_3\text{In} \cdot \text{OEt}_2$ compound was prepared from MeMgI and InCl_3 in diethyl ether [14]. Diethylether contents in trialkyl metal etherate were ascertained by ^1H NMR integration. Infrared spectra were recorded between CsI plates on a Bomem MB-102 FT-IR spectrophotometer. NMR spectra (^1H and $^{13}\text{C}\{^1\text{H}\}$) were recorded on a Bruker DPX – 300 MHz instrument in 5 mm tubes in CDCl_3 solution. Chemical shift were referenced to the internal chloroform peak (δ 7.26 and δ

77.0 ppm for ^1H and $^{13}\text{C}\{^1\text{H}\}$, respectively). Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer.

3.1. Preparation of $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_4\text{H}_3\text{N}_2)]_2$

To a benzene (25 ml) solution of trimethylgallium etherate (1.85 g, 9.16 mmol), a solution of pyrazine carboxylic acid (1.14 g, 9.16 mmol) in benzene was added dropwise under a nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure to give an off-white solid (yield 1.99 g, 97%). Similarly all other compounds were prepared in 94–98% yield and were recrystallised from dichloromethane/hexane as colorless crystalline solids. One of the compounds, $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$, was sublimed under vacuum at 145 °C/1 mm Hg to give a colorless crystalline solid which showed ^1H and ^{13}C NMR spectra similar to those obtained for recrystallized product. Pertinent data are given in Table 1.

3.2. Crystallography

Intensity data for $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$ were measured on a Rigaku AFC12 κ /Saturn724 CCD fitted with Mo $\text{K}\alpha$ radiation so that $\theta_{\text{max}} = 27.5^\circ$. The structure was solved by heavy-atom methods [28] and refinement was on F^2 [29] using data that had been corrected for absorption effects with an empirical procedure [30], with non-hydrogen atoms modeled with anisotropic displacement parameters, with hydrogen atoms in their calculated positions, and using a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Intensity data for $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$ were measured on a Rigaku AFC7S diffractometer fitted with Mo $\text{K}\alpha$ radiation so that $\theta_{\text{max}} = 27.5^\circ$. The structure was solved by direct-methods [31] and refined as above. Molecular structures shown in Fig. 2 were drawn at the 50% (M = Ga) and 35% (M = In) probability levels using ORTEP [32]. The DIAMOND program [33] was used for

Table 6
Crystallographic data for $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$ and $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$

	$[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$	$[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N})_2]$
Formula	$\text{C}_{16}\text{H}_{20}\text{Ga}_2\text{N}_2\text{O}_4$	$\text{C}_{16}\text{H}_{20}\text{In}_2\text{N}_2\text{O}_4$
<i>M</i>	443.78	533.98
<i>T</i> (K)	120	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
<i>a</i> (Å)	14.6405(17)	14.898(8)
<i>b</i> (Å)	9.6104(9)	9.968(2)
<i>c</i> (Å)	14.8373(14)	14.673(10)
β (°)	120.146(5)	116.34(4)
<i>V</i> (Å ³)	1805.3(3)	1952.8(17)
<i>Z</i>	4	4
<i>d</i> _{calc} (g cm ⁻³)	1.633	1.816
Number of unique reflections	4015	4477
Number of observed reflections with $I > 2\sigma(I)$	2351	3581
<i>R</i> ($I \geq 2\sigma(I)$)	0.052	0.030
<i>a</i> , <i>b</i> for weighting scheme	0.068, 0.626	0.035, 0.788
<i>wR</i> (all data)	0.146	0.078

Fig. 3. Data manipulation and analyses were performed with TEXSAN [34] and PLATON [35]. Crystallographic data and refinement details are given in Table 6.

4. Supplementary material

CCDC-644963 and 644962 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

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References

- [1] A.J. Downs, Chemistry of Aluminium, Gallium, Indium and Thallium, Blackie Academic and Professional, Glasgow, 1993.
- [2] M.A. Paver, C.A. Russell, D.S. Wright, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), in: C.E. Housecraft (Ed.), Comprehensive Organometallic Chemistry-II, vol. 1, 1995, p. 503.
- [3] B. Neumuller, Chem. Soc. Rev. 32 (2003) 50.
- [4] C.J. Carmalt, S.J. King, Coord. Chem. Rev. 250 (2006) 682.
- [5] J. Weidlein, Z. Anorg. Allg. Chem. 378 (1970) 245.
- [6] A. Keys, S.G. Bott, A.R. Barron, Polyhedron 17 (1998) 3121.
- [7] H.D. Hausen, J. Organomet. Chem. 39 (1972) C37.
- [8] F.W.B. Einstien, M.M. Gilbert, D.G. Tuck, J. Chem. Soc., Dalton (1973) 248.
- [9] J. Lewinski, I. Justyniak, J. Lipkowski, J. Zachara, Inorg. Chem. Commun. 3 (2000) 700.
- [10] R. Nomura, S. Fujii, K. Kanaya, H. Matsuda, Polyhedron 9 (1990) 361.
- [11] S. Ghoshal, D.P. Dutta, N.P. Kushwah, V.K. Jain, Indian J. Chem. A 44 (2005) 1139.
- [12] M. Webber, T. Clarius, Phosphorus Sulfur Silicon Relat. Elem. 102 (1995) 261.
- [13] N.P. Kushwah, D.P. Dutta, V.K. Jain, Indian J. Chem. A 43 (2004) 535.
- [14] A.N. Nesmeyanov, R.A. Sokdik The Organic Compounds of B, Al, Ga, In & Tl, vol. 1, North Holland, Amsterdam, 1967.
- [15] C. Vatsa, V.K. Jain, T.K. Das, Indian J. Chem. A 30 (1991) 451.
- [16] Y. Shen, J. Han, H. Gu, Y. Zhu, Y. Pan, J. Organomet. Chem. 689 (2004) 3461; Y. Shen, H. Gu, Y. Zhu, Y. Pan, J. Organomet. Chem. 691 (2006) 1817.
- [17] N.W. Mitzel, C. Lustig, R.J.F. Berger, N. Runeberg, Angew. Chem., Int. Ed. 41 (2002) 2519.
- [18] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [19] J. Lewiński, J. Zachara, K.B. Starowieyski, J. Chem. Soc., Dalton Trans. (1997) 4217.
- [20] S. Basharat, C.J. Carmalt, S.J. King, E.S. Peters, D.A. Tocher, Dalton Trans. (2004) 3475.
- [21] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
- [22] S.J. Rettig, A. Storr, J. Trotter, K. Urich, Can. J. Chem. 62 (1984) 2783.
- [23] E.C. Onyiriuka, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 65 (1987) 782.
- [24] Y. Shen, Y. Pan, X. Jin, X. Xu, X. Sun, X. Huang, Polyhedron 18 (1999) 2423.
- [25] J. Lewiński, J. Zachara, K.B. Starowieyski, Z. Ochal, I. Justyniak, T. Kopeć, P. Stolarzewicz, M. Dranka, Organometallics 22 (2003) 3773.
- [26] Hydrogen-bonding interactions operating in the structure of $[\text{Me}_2\text{Ga}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$: C3–H3...O4ⁱ = 2.42 Å, C3...O4ⁱ = 3.297 (7) Å, and angle at H3 = 153° for i: $-x, 1/2 + y, -1/2 - z$; and C11–H11...O2ⁱⁱ = 2.32 Å, C11...O2ⁱⁱ = 3.222(7) Å, and angle at H3 = 159° for ii: $1 - x, -1/2 + y, 1/2 - z$. Hydrogen-bonding interactions operating in the structure of $[\text{Me}_2\text{In}(\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-2)]_2$: C3–H3...O4ⁱ = 2.47 Å, C3...O4ⁱ = 3.342(6) Å, and angle at H3 = 156° for i: $1/2 - x, -1/2 + y, 1/2 - z$; and C11–H11...O2ⁱⁱ = 2.37 Å, C11...O2ⁱⁱ = 3.262(5) Å, and angle at H3 = 160° for ii: $1/2 - x, 1/2 + y, -1/2 - z$.
- [27] V.I. Bregadze, L.M. Golubinskaya, L.G. Tonoyan, B.I. Kozyskin, B.G. Girbor, Dokl. Akad. Nauk. SSSR 212 (1973) 880.
- [28] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, J.M.M. Smits, C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography, Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1992.
- [29] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [30] T. Higashi, ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation. Rigaku Corporation, 3-9-12 Matsubara, Akishima, Japan, 1995.
- [31] G.M. Sheldrick, SHELXS97. Program for the solution of crystal structure, University of Göttingen, Germany, 1997.
- [32] C.K. Johnson, ORTEP II, Report ORNL-5136, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- [33] Crystal Impact. DIAMOND. Version 3.1. Crystal Impact GbR, Postfach 1251, D-53002 Bonn, Germany, 2006.
- [34] TEXSAN, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.
- [35] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2006.