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Diorgano-gallium and -indium complexes with salen ligands: Synthesis, characterization, crystal structure and C–C coupling reactions

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ABSTRACT

The reactions of triorgano-gallium and -indium etherate with salen ligands in benzene afforded complexes of the type $[R_2MOC_6H_4CR'{=}NCH_2-]_2$, (R/M/R′ = Me/Ga/H (**1**), Et/Ga/H (**2**), Me/In/H (**3**), Et/Ga/Me (**4**)) in nearly quantitative yields. These complexes have been characterized by elemental analysis, IR, UV–Vis, NMR (^1H and $^{13}C\{^1H\}$) and mass spectral data. The organogallium complexes showed photoluminescence in blue-green region. The complex, $[(Me_2Ga)_2(O-(C_6H_4)CH{=}N-CH_2-)_2]$ on recrystallization from benzene–hexane and dichloromethane gave orthorhombic and monoclinic forms, respectively. Both the forms are dimeric with gallium atoms acquiring a distorted tetrahedral configuration defined by two methyl groups, phenolate oxygen and azomethene nitrogen. The complexes $[(Me_2Ga)_2(O-(C_6H_4)CH{=}N-CH_2-)_2]$ and $[(Me_2In)_2(O-(C_6H_4)CH{=}N-CH_2-)_2]$ have been employed as alkylating agent for C–C coupling reaction of 1-bromonaphthalene in presence of $PdCl_2(PPh_3)_2$.

1. Introduction

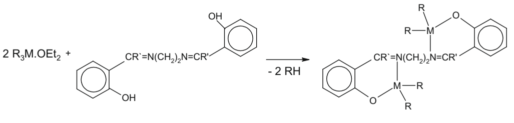
The chemistry of organo-gallium/-indium compounds with oxo ligands has been actively pursued for quite some time [1–3]. Interest in these compounds, particularly with internally functionalized ligands, appears to be due to their wide structural diversity [1], potential applications as catalyst [4,5] as well as molecular precursors for the preparation of metal oxide thin films [6–8] and photophysical properties [9–12].

The compounds of the type R_2ML (R = alkyl, M = Ga or In; LH = anionic oxo ligand) have been isolated as mono-, bi- and tri-nuclear derivatives with metal acquiring coordination number between four and six. The structural preferences in these complexes are governed by the nature of R, M and L [13–25]. Recently we have described the synthesis of diorgano-gallium/-indium complexes containing internally functionalized anionic oxo ligands [9,10,26,27]. These complexes have a centrosymmetric "$M_2(\mu\text{-}O)_2$" core and show photoluminescence.

In view to assess photophysical and catalytic properties of bi- and high-nuclearity organo-gallium and -indium complexes lacking oxo-bridges, we have chosen salen ligands, although a few organo-gallium and -indium complexes with these ligands have been reported earlier [28–32]. In this report we describe the preparation of organo-gallium and -indium complexes with $salenH_2$ and $acenH_2$, their photophysical and catalytic properties and distortion isomerism in $[Me_2GaOC_6H_4CH{=}NCH_2-]_2$.

2. Results and discussion

Reactions of *N*,*N*′-ethylenebis(salicylideneimine) ($salenH_2$) and *N*,*N*′-ethylenebis(2-hydroxy-α-benzyledeneimine) ($acenH_2$) with trialkylgallium etherate or trimethylindium etherate in 1:2 stoichiometry in benzene readily afforded bimetallic complexes, $[R_2MOC_6H_4CR'{=}NCH_2-]_2$, in nearly quantitative yield (Eq. (1)).



(1)

M	R	R′	
Ga	Me	H	**1**
Ga	Et	H	**2**
In	Me	H	**3**
Ga	Et	Me	**4**

The electronic spectra displayed a number of bands attributable to transitions in the benzenoid ring (>300 nm) and in azomethine linkage (<300 nm). The $n \rightarrow \pi^*$ transition of the ligand (~370 nm) is red shifted (~10 nm) in organogallium complexes suggesting coordination of azomethine nitrogen to the metal atom. The $\nu C{=}N$ absorption in the IR spectra of the complexes appear at lower wave numbers relative to the free ligand. A strong band in the region 570–587 cm^{-1} has been attributed to νGa–C stretching absorptions [27].

The ^1H and $^{13}C\{^1H\}$ NMR spectra of ligands and complexes showed expected signals and peak multiplicities. The methyl resonances of gallium complexes appear at higher field than that of the corresponding indium derivatives. The NCH_2 resonances both in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes are shielded with respect to the signal for the corresponding ligands. This

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suggests coordination of azomethine nitrogen to the metal atom. As the consequence of the shift in electron density towards metal through nitrogen coordination, the CR′═N (R′ = H or Me) resonance in the $^{13}C\{^1H\}$ NMR spectra of the organogallium complexes is deshielded (~5 ppm) as compared to the free ligand.

The mass spectrum of **1** exhibited multiplets at *m*/*e* 466 and 451 assignable to molecular ion and the parent ion minus one methyl group, respectively. These multiplets are consistent with the isotopic patterns for two gallium atoms in a molecule (^{69}Ga (60.4%), ^{71}Ga (39.6%)).

2.1. Photophysical properties

Although 8-hydroxyquinolinate (Ox) and azomethine coordinated complexes (e.g., Al(Ox)$_3$) have been employed as organic light-emitting diodes (OLEDs) [33–38], organometallic complexes derived from chelating ligands are emerging as potential molecules for OLED applications [9–12,39,40].

The emission bands for the free ligands and complexes are summarized in Table 1. These bands both for ligand and complexes appeared in blue-green region (Fig. 1). On complexation there is a slight increase in quantum yield. The observed absorptions and emissions in diorganogallium complexes can be attributed to transitions localized on the salen ligands while enhanced quantum yields in the complexes could be due to the rigidity of the chelating ligand. The latter minimizes the loss of energy by a non-radiative pathway and consequently increases π–π^* transition intensity.

*2.2. Structure of [Me$_2$GaOC$_6$H$_4$CH═NCH$_2$–]$_2$ (**1**)*

The complex crystallizes in orthorhombic (from benzene–hexane mixture) and monoclinic (from dichloromethane) forms representing an example of distortion isomerism in organogallium chemistry. This is the first example, to the best of our knowledge, of distortion isomerism in organogallium chemistry, although distortion isomerism for transition metal complexes is not uncommon [41]. The molecular structures of both the forms are similar except some variations in geometric parameters which are collected in Table 2. In orthorhombic form the molecule is distorted from *Ci* symmetry whereas monoclinic form, which crystallizes with a molecule of dichloromethane, retains this symmetry as illustrated in Fig. 2. The geometric parameters for the orthorhombic form are in conformity with the one reported earlier by Trotter and co-workers [28].

The molecule (Fig. 3) essentially comprises of two four-coordinated dimethylgallium fragments containing five membered chelating ligands and these two fragments are linked through a –CH$_2$–CH$_2$– spacer. Each gallium atom has a distorted tetrahedral configuration defined by two methyl groups and phenolic oxygen and azomethine nitrogen atoms. The Ga–C, Ga–O and Ga–N distances are well in agreement with the reported values [3,10,28].

3. Cross alkylation reactions

Organoindium compounds have been employed for cross-coupling of arylhalides in the presence of palladium chloride catalysts [4,5,42]. In general mononuclear organoindium complexes are better alkylating agents than the binuclear complexes containing "In$_2$(μ-O)$_2$" core [42]. The bimetallic salen complexes described here are akin to mononuclear compounds, they may be useful in cross-coupling reactions. Thus in a preliminary experiment, 1-bromonaphthalene is readily methylated to 1-methylnaphthalene (^{1}H NMR (in CDCl$_3$) δ: 2.75 (s, Me–)) by **3** in the presence of PdCl$_2$(PPh$_3$)$_2$ as a catalyst. The reaction of [PdCl$_2$(PPh$_3$)$_2$] with **3** in a separate experiment (Eq. (2)), has shown the formation of *trans*-[PdClMe(PPh$_3$)$_2$] (^{1}H NMR (in CDCl$_3$) δ: −0.01 (t, 6.5 Hz, Pd-Me); $^{31}P\{^1H\}$ 30.2 ppm). Similarly other palladium complexes,

Table 1
Excitation and emission data of salen ligands and their diorganogallium complexes in dichloromethane.

Compounds	Excitation λ in nm	Emission λ in nm	Quantum yield (η) in %
[HO(C$_6$H$_4$)CH═NCH$_2$–]$_2$	365	470	0.4
[HO(C$_6$H$_4$)CMe═NCH$_2$–]$_2$	435	473	3.0
[Me$_2$GaO(C$_6$H$_4$)CH═NCH$_2$–]$_2$	412	462	1.2
[Et$_2$GaO(C$_6$H$_4$)CH═NCH$_2$–]$_2$	335	485	0.1
[Et$_2$GaO(C$_6$H$_4$)CMe═NCH$_2$–]$_2$	355	475	1.0

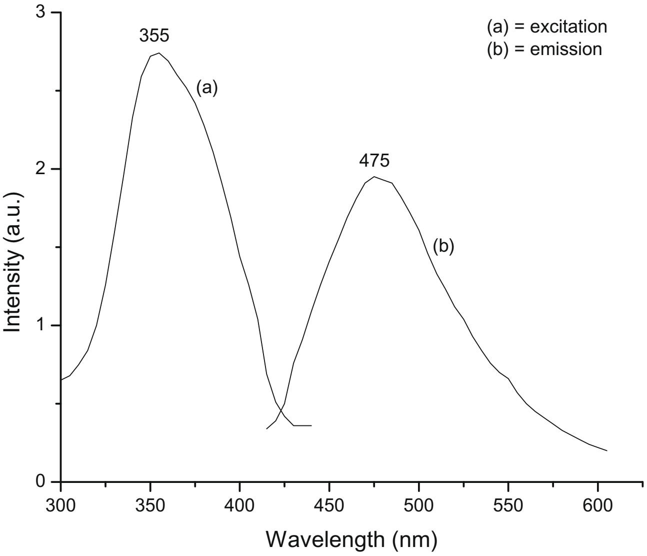

Fig. 1. Excitation spectra (a) and emission spectra (b) of [{Et$_2$GaO–(C$_6$H$_4$)C(CH$_3$)═N–CH$_2$–}$_2$] recorded in dichloromethane solution.

Table 2
Selected geometric parameters (Å, °) for [(Me$_2$Ga)$_2$(O–(C$_6$H$_4$)CH═N–CH$_2$–)$_2$] recrystallized in benzene–hexane mixture and CH$_2$Cl$_2$ solvents.

	Orthorhombic		Monoclinic
	Literature[a]	This work	This work
Ga1–O1	1.869 (2)	1.867 (4)	1.895 (3)
Ga2–O2	1.874 (2)	1.873 (4)	–
Ga1–N1	2.026 (3)	2.022 (5)	2.048 (3)
Ga2–N2	2.035 (3)	2.029 (5)	–
Ga1–C10	1.950 (5)	1.921 (7)	1.955 (4)
Ga1–C9	1.948 (6)	1.942 (7)	1.951 (4)
Ga2–C19	1.959 (5)	1.929 (6)	–
Ga2–C20	1.938 (5)	1.931 (6)	–
O1–Ga1–C10	106.5 (3)	111.5 (3)	108.90 (18)
O1–Ga1–C9	105.7 (3)	105.7 (3)	108.51 (19)
O2–Ga2–C19	112.6 (2)	111.4 (3)	–
O2–Ga2–C20	107.3 (2)	107.0 (3)	–
O1–Ga1–N1	94.0 (1)	94.04 (18)	91.99(11)
O2–Ga2–N2	92.7 (1)	92.41 (18)	–
C10–Ga1–C9	124.6 (4)	124.6 (4)	127.6 (2)
C19–Ga2–C20	123.8 (3)	125.5 (3)	–
C10–Ga1–N1	110.2 (3)	106.2 (2)	105.65 (18)
C9–Ga1–N1	106.3 (2)	110.5 (3)	108.37 (16)
C19–Ga2–N2	104.4 (2)	103.8 (3)	–
C20–Ga2–N2	111.8 (2)	111.7 (3)	–
C11–O2–Ga2	126.6 (2)	127.2 (4)	–
C1–O1–Ga1	128.1 (2)	128.4 (4)	126.6 (2)
C7–N1–Ga1	122.2 (2)	122.7 (4)	122.0 (2)
C8–N1–Ga1	119.6 (3)	119.3 (4)	119.5 (3)
C17–N2–Ga2	121.6 (2)	121.8 (4)	–
C18–N2–Ga2	118.8 (3)	118.1 (4)	–

[a] Ref. [28].