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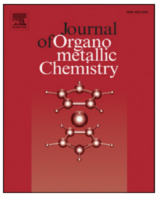

Monoorgano-gallium and –indium complexes derived from dianionic tridentate ONO Schiff bases: Synthesis, crystal structures and photoluminescence

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Reactions of triorgano-gallium and –indium etherates with N′-(2-hydroxybenzylidine)benzohydrazide and N′-(2-hydroxy-3-methoxybenzylidine)benzohydrazide in refluxing benzene afforded complexes of composition $[\{RM\}\{-O(C_6H_3R'\text{-}3)CH{=}N{-}N{=}C(C_6H_5)O-\}]$ (M=Ga, In; R=Me, Et; R′=H, OMe). These complexes have been characterized by elemental analysis, IR, UV-vis, and NMR (^1H and $^{13}C\{^1H\}$) spectroscopy. The molecular structures of $[\{MeGa\}\{-O(C_6H_4)CH{=}N{-}N{=}C(C_6H_5)O-\}]_2$ (**1**), $[\{MeGa\}\{-O(C_6H_3{-}OMe)CH{=}N{-}N{=}C(C_6H_5)O-\}]_2$ (**2**) and $[\{EtGa\}\{-O(C_6H_3{-}OMe)CH{=}N{-}N{=}C(C_6H_5)O-\}]_2$ (**6**) were established by X-ray crystallography. These complexes adopt a dimeric structure with phenolate oxygen bridges with the gallium atom acquiring a distorted square pyramidal configuration. These complexes are emissive in toluene solution at room temperature.

1. Introduction

The chemistry of organo-gallium and –indium compounds with oxo ligands has been actively pursued for quite some time [1]. The sustained interest in these complexes may be attributed to their rich structural diversity [1–3], polymorphism [4,5] and remarkable photophysical properties [2–4,6]. They have potential applications in catalysis [4,7], as anti tumour agents [8] as well as single source molecular precursors for deposition of metal oxide thin films [9,10]. In general, dimeric complexes of composition $[R_2M(\mu\text{-}OR')]_2$ with four coordinated metal atom are formed with simple alkoxy ligands [11]. However, with internally functionalized ligands both mono- and bi-nuclear complexes have been isolated [12–14]. Dianionic tridentate ligands yield monoorganometal complexes in which metal atom can acquire four- or five-coordinate geometry; the latter being preferentially adopted by indium complexes [2].

Schiff bases represent an important family of internally functionalized ligands which played a pivotal role in the development of coordination chemistry. These ligands, both anionic and dianionic have been used for the synthesis of group 13 metal complexes [15]. N-Salicylidene benzoylhydrazones offer not only several bonding possibilities [16] but also exhibit interesting luminescent properties. Numerous transition metals complexes from these ligands have been synthesized [16–18] with scant attention to main group elements [19]. The metal chelates derived from tridentate dianionic Schiff bases have been shown to be highly luminescent [20,21]. Luminescence from group 13 metal complexes, particularly AlQ_3, have been exploited for organic light emitting diodes (OLEDs) [22–24]. Gallium complexes have been projected as promising candidates to replace aluminium derivatives, as they exhibit better efficiency than AlQ_3 [25,26]. The photophysical properties of monoorgano-gallium complexes are little explored [2]. With this perspective and in pursuance of our interest on organo-gallium and –indium complexes, we have synthesized mono-organo-gallium and –indium complexes with dianonic tridentate benzhydrazide ligands. Results of this work are reported herein.

2. Results and discussion

2.1. Synthesis and characterization of complexes

Reactions of N′-(2-hydroxybenzylidine)benzohydrazide and N′-(2-hydroxy-3-methoxybenzylidine)benzohydrazide with trialkyl metal etherate in refluxing benzene afforded monoalkyl metal complexes as yellow solids in 80–92% yield (Scheme 1). The absorption due to imine linkage (–CH=N–) in the IR spectra are shifted to lower wave numbers (45–60 cm^{-1}) with respect to the free ligand indicating coordination of nitrogen atom to gallium/

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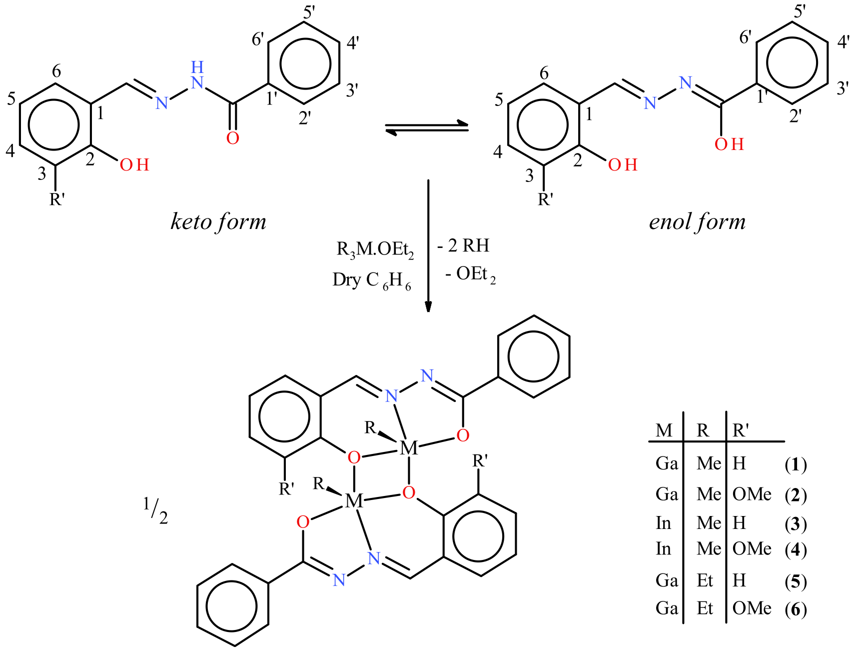

M	R	R′	
Ga	Me	H	(**1**)
Ga	Me	OMe	(**2**)
In	Me	H	(**3**)
In	Me	OMe	(**4**)
Ga	Et	H	(**5**)
Ga	Et	OMe	(**6**)

Scheme 1. Synthesis of monoorgano-gallium and -indium complexes.

indium metal. The absorptions in the regions 580–606 and 519–530 cm^{-1}, which were absent in the corresponding free ligands, have been assigned to M–C and M–O stretching, respectively [2,10,27].

The ^{1}H and ^{13}C NMR spectra, recorded in DMSO-d_6, displayed characteristic peaks with expected multiplicities for metal alkyl and ligand fragment. The OH (12.15 ppm) and NH proton resonances (~11.0 ppm) of the ligands are absent in the ^{1}H NMR spectra of the complexes due to deprotonation of the ligands. The methylgallium and -indium complexes showed a characteristic high-field singlet due to methyl group in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{13}C{^{1}H} NMR resonances due to –CH=N– in the complexes are deshielded by ~9 ppm with respect to the resonances for free ligands indicating nitrogen coordination to the metal. The carbonyl carbon resonance of the free ligands on enolization and coordination with metal is deshielded by 4.1–6.3 ppm. The ^{13}C NMR resonances assignable to C-2 and C-1′ are also deshielded with respect to the corresponding resonances for the free ligand.

2.2. Photo physical studies

The absorption spectra corresponding to ligands with R′=H and R′=OMe showed two peaks due to π to π* and n to π* transitions corresponding to keto and enol forms of the ligand (Table 1). Due to low value of HOMO-LUMO gap in keto form corresponding peak is red shifted with respect to that of enol form [3,3a]. These ligands on excitation gave broad emission in the visible region; however their emission quantum yields are relatively poor (1–2%) as can be seen from Table 1. Substitution of electron donating groups in the benzene ring of the ligands generally leads to blue shift in the emission maximum. This is due to increased electron density in the benzene ring. As expected the OMe substituted ligand showed a blue shift in the emission maximum compared to the unsubstituted ligand. Excitation spectra corresponding to these ligands (Fig. 1) also showed a trend similar to that of absorption spectra. Significant Stoke shift has been observed for these ligands as can be seen from the difference in the wavelength corresponding to excitation and emission peak maximum (Fig. 1, Table 1). Such large Stoke shift confirms existence of the Excited State Intra-molecular Proton Transfer (ESIPT) which takes place with the enol form of the ligand resulting in its keto form. Upon complex formation with Ga and In, conversion to keto form is prevented consequently leads to blue shift in the emission maximum for the complexes. Further, complexation with Ga/In, there is a slight improvement in the quantum yield (Table 1). This is due to increase in electron density with the molecules and associated increase in the transition probabilities on complexation. Due to heavy metal ion effect, In complexes are expected to have lower quantum yield values as compared to that of Ga derivatives.

2.3. Crystal structures of [{MeGa}{–O(C_6H_4)CH=N–N=C(C_6H_5)O–}]$_2$ (1), [{MeGa}{–O(C_6H_3–OMe)CH=N–N=C(C_6H_5)O–}]$_2$ (2) and [{EtGa}{–O(C_6H_3–OMe)CH=N–N=C(C_6H_5)O–}]$_2$ (6)

The molecular structures of [{MeGa}{–O(C_6H_4)CH=N–N=C(C_6H_5)O–}]$_2$ (**1**), [{MeGa}{–O(C_6H_3–OMe)CH=N–N=C(C_6H_5)O–}]$_2$ (**2**) and [{EtGa}{–O(C_6H_3–OMe)CH=N–N=C(C_6H_5)O–}]$_2$ (**6**) were established by single crystal X-ray diffraction analyses. The ORTEP plots are depicted in Figs. 2–4 and selected interatomic parameters are given in Tables 2–4. All the three complexes adopt a dimeric structure with five coordinated gallium atom bridged through phenolate oxygen atoms resulting in a four-membered rhombohedral Ga_2O_2 ring. The latter is slightly bent with an angle of 12.02, 3.89 and 4.73° for **1**, **2** and **6**, respectively. The ligands adopt a *syn-trans* configuration with respect to the central Ga_2O_2 ring. The inter planar angles between the mean planes of ligands are 85.07, 88.63 and 88.87° for **1**, **2** and **6**, respectively. Increased planarity of Ga_2O_2 ring and widening of the interplanar angle of ligands may be attributed to the presence of steric hindrance of -OMe group present in **2** and **6** with the oxygen atom of neighbouring/opposite ligand. The distances between oxygen atoms of methoxy group and enolic oxygen are 2.8665 (av.) and 2.916 (av.) Å in **2** and **6**, respectively, which is less than the sum of van der Waal radii of two oxygen atoms (3.04 Å). The result of this short interaction is also evident from the slightly disordered/enlarged U_{ij} parameters of atoms in the neighboring benzene rings in **2** and **6**.