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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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Abstract

Reactions of triorgano-gallium and -indium etherates with N'-(2hydroxybenzylidine)benzohydrazide and N'-(2-hydroxy-3-methoxybenzylidine)benzohydrazide in refluxing benzene afforded complexes of composition $[{RM} - O(C_6H_3R'-3)CH = N-N=C(C_6H_5)O-]$ (M = Ga, In; R = Me, Et; R' = H, OMe). These complexes have been characterized by elemental analysis, IR, UV-vis, and NMR (¹H and ${}^{13}C{}^{1}H$) 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.

Keywords: Gallium, Indium, dianionic tridentate, photoluminescence, X-ray structures

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 $[R_2M(\mu-OR')]_2$ 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 fictionalized 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]. Luminescences from group 13 metal complexes, particularly AlQ₃, 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 AlQ₃ [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 monooragno-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 to 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/ 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 ¹H and ¹³C NMR spectra, recorded in dmso-d₆, 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 ¹H NMR spectra of the complexes due to deprotonation of the ligands. The methyl-gallium and -indium complexes showed a characteristic high-field singlet due to methyl group in the ¹H and ¹³C{¹H} NMR spectra. The ¹³C{¹H} NMR resonances due to –CH=N- in the complexes are deshielded by ~9 ppm with respect to the resonance of the free ligands on enolization and coordination with metal is deshielded by 4.1-6.3 ppm. The ¹³C NMR resonances assignable to C-2 and C-1' are also deshielded with respect to the corresponding resonances for the free ligand.



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

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 form 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 Intramolecular 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 shit in the emission maximum for the complexes. Further, complexation with Ga/In, there is a slight improvement in the quantum yield (Table1). 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 depicited in Figures 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 Ga₂O₂ 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 Ga₂O₂ 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 Ga₂O₂ ring and widening of the interplanar angle of ligands may be attributed to the presence of steric hinderance 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 slight disorder/ enlarges U_{ij} parameters in the atoms of the neighboring benzene rings in 2 and 6.

The four-, six- and five-membered rings in these dimeric structures are arranged one after the other, an arrangement distincly different from those reported in $[MeGa(-O(C_6H_4)CH=N(C_6H_4)-O_-)]_2$ where four-, five- and six-membered rings are placed one after the other [2] but is similar to ONS tridentate Schiff base system, e.g. $[MeGa(-O(C_6H_4)CH=N(C_6H_4)-S_-)]_2$. This behaviour can be attributed to the fact that the phenoxy oxygen is a stronger donor as compared to alkoxy group and takes the bridging position. The five-membered rings GaNNCO are almost planar while the six-membered chelate rings GaNCCCO are puckered with Ga atoms out of plane. The two rings are not co-planar in all the three complexes. The five membered rings GaNNCO are slightly out of plane with respect to the adjacent benzene rings with inter planar angles being 7.66° (for 1), 8.91°-11.23° (for 2) and 16.45°-19.18° (for 6). The maximum angle for 6 suggests additional strain due to ethyl groups on the gallium atoms.

The coordination geometry around the gallium atom defined by CNO_3 donor atoms can be described as distorted square pyramidal on the basis of τ indices ($\tau = 0.34$ in **1**, 0.35-0.40 in **2** and 0.30-0.41 in **6**). Five coordinate geometries in metal complexes can be quantified using the τ index, as described by Addision, et al. [28]. The bridging Ga-O distances are slightly longer than non-bridging

Ga-O distances (2.100 and 1.922 Å for 1; 2.144 and 1.919 Å for 2 and 2.134 (5) and 2.117 (6) Å for 6). The M-C, M-O and M-N distances are in conformity with the values reported in the literature [2, 3, 29, 30, 31].

The analysis of molecular structure of complex **6**, shows major continuous disorder in the ethyl groups on gallium atom. These groups occupy the apical postion of the distorted square pyramidal geometry of gallium atom. The terminal methyl fragments seem to occupy favorably two of the total three possible postions in staggered conformation. The position above the six membered ring is most favored, followed by postion above four membered MOMO ring. The probability of finding the methyl in third position which may lie directly above the oxygen atoms of N=N-C-O fragment, is negligible due to repulsion from the lone pair of oxygen atoms. The positions are schematically shown in Figure 4b and 4c.

3. Experimental

3.1 Materials and Physical Measurements

All experiments involving organo-gallium and –indium compounds were carried out in anhydrous conditions under a nitrogen atmosphere using Schlenk techniques. Solvents were dried using standard methods. Triorganogallium etherates ($R_3Ga.OEt_2$; R = Me, Et) were prepared using gallium-magnesium alloy (Mg_5Ga_2) and alkyl iodide in diethyl ether. Trimethylindium etherate was prepared using MeMgI and InCl₃ in diethyl ether. Ether contents in each preparation were evaluated by ¹H NMR integration [31]. The ligands were prepared by a condensation reaction between an aldehyde (salicyldehyde or *o*-vanillin) and benzhydrazide in refluxing methanol as described in the literature [17, 32].

Elemental analysis was carried out on a Carlo-Erba EA-1110 CHNS analyzer. Infrared spectra were recorded as KBr plates on a Jasco FT-IR 6100 spectrometer. The NMR (¹H and ¹³C{¹H}) spectra were recorded on a Bruker Avance-II 300 spectrometer in 5 mm tubes as CDCl₃/dmso-d₆ solutions. Chemical shifts were referenced to internal chloroform/dimethyl sulfoxide peak. Electronic spectra were recorded in toluene on a UV-vis Jasco V-630 spectrophotometer. All luminescence measurements were carried out at room temperature on an Edinburgh Instruments FLSP 920 system, having a 450W Xe lamp. Quantum yields were measured using an integrating sphere coated with BaSO₄. All emission spectra were corrected for the detector response and excitation spectra for the lamp profile. Emission measurements were carried out with a resolution of 5 nm.

3.2 X-ray Crystallography

Intensity data for $[{MeGa}{-O(C_6H_4)CH=N-N=C(C_6H_5)O-}]_2$ (1), $[{MeGa}{-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}]_2$ (2), recrystallized from benzene and $[{EtGa}{-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}]_2$ (6), recrystallized from hexane, were collected at room temperature on a Rigaku AFC 7S diffractometer using graphite monochromated Mo-K α radiation (0.71069 Å). The structures

were solved using direct methods [33] and refined by full matrix least square method [34] on F^2 using data corrected for absorption effects using empirical procedures [35]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in their geometrically idealized positions with coordinate and thermal parameters riding on host atoms. The molecular structures are drawn using ORTEP [36]. Crystallographic and structural determination data are listed in Table 5.

3.3 Synthesis of complexes

$3.3.1 \ [{MeGa}{-O(C_6H_4)CH=N-N=C(C_6H_5)O-}] (1)$

To a benzene solution (25 mL) of trimethylgallium etherate (237 mg, containing 87 mg (0.75 mmol) Me₃Ga), was added a solution of [HO(C₆H₄)CH=N-NH-C(O)(C₆H₅)] (181 mg, 0.75 mmol) with stirring which was refluxed for 5 h. The solvent was evaporated under a reduced pressure to give a yellow crystalline solid, which was recrystallized from benzene as yellow crystals (223 mg, 92 % yield), mp 265 °C, Anal. Calcd. for C₁₅H₁₃GaN₂O₂: C, 55.77; H, 4.06; N, 8.67 %. Found: C, 55.80; H, 4.40; N, 8.59 %. IR in KBr (ν in cm⁻¹): 1615, 1598 (C=N); 592 (Ga-C); 530 (Ga-O). ¹H NMR (dmso-d₆) δ : -0.36 (s, 3H, MeGa); 6.62 (t, 1H, ³J_{HH} = 8.3 Hz, C-4); 6.67 (d, 1H, ³J_{HH} = 9.3 Hz, C-6); 7.22 (t, 1H, ³J_{HH} = 9.3 Hz, C-5); 7.32 (d, 1H, ³J_{HH} = 8.7 Hz, C-3); 7.40-7.48 (m, 3H, C-3', 4', 5'); 7.80 (d, 2H, ,³J_{HH} = 8.3 Hz, C-2', 6'); 8.74 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : -4.8 (MeGa); 115.8 (C-3), 118.1 (C-1), 121.3 (C-5), 127.6 (C-2', 6'), 128.6 (C-3', 5'), 131.1 (C-4'), 133.7 (C-4), 133.9 (C-6), 134.3 (C-1'), 157.7 (CH=N), 166.5 (C-2), 168.6 (C=N).

$3.3.2 [{MeGa}{-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}] (2)$

Prepared similar to **1** using trimethylgallium etherate (406 mg, containing 148 mg (1.29 mmol) Me₃Ga) and [HO(C₆H₃-OMe)CH=N-NH-C(O)(C₆H₅)] (349 mg, 1.29 mmol) as a yellow crystalline solid (417 mg, 91 % yield), m.p. 272 °C, Anal. Calcd. for C₁₆H₁₅GaN₂O₃: C, 54.43; H, 4.28; N, 7.34 %. Found: C, 54.68; H, 4.49; N, 7.49 %. IR in KBr (υ in cm⁻¹): 1652 (weak), 1608 (C=N); 582 (Ga-C); 564 (Ga-O). ¹H NMR (dmso-d₆) δ : -0.38 (s, 3H, MeGa); 3.72 (s, 3H, OMe); 6.54 (t, 1H, ³J_{HH} = 8.7 Hz, C-5); 6.92 (m, 2H, C-4,6); 7.41-7.47 (m, 3H, C-3',4',5'); 8.00 (d, 2H, ³J_{HH} = 7.3 Hz, C-2',6'); 8.72 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : -4.9 (MeGa); 56.0 (OMe); 115.0 (C-4,6), 117.7 (C-1), 125.2 (C-5), 127.7 (C-2',6'), 128.6 (C-3',5'), 131.1 (C-4'), 134.2 (C-1'), 151.4 (C-2), 157.1 (C-3), 157.7 (CH=N), 168.6 (C=N).

$3.3.3 [{MeIn}{-O(C_6H_4)CH=N-N=C(C_6H_5)O-}]$ (3)

Prepared similar to **1** in 85 % yield, m.p. >300 °C, Anal. Calcd. for $C_{15}H_{13}InN_2O_2$: C, 48.94; H, 3.56; N, 7.61 %. Found: C, 49.19; H, 3.35; N, 7.53 %. IR in KBr (υ in cm⁻¹): 1611 (C=N). ¹H NMR (dmso-d₆) δ : -0.19 (s, 3H, MeIn); 6.50 (t, 1H, ³J_{HH} = 8.3 Hz, C-4); 6.62 (d, 1H, ³J_{HH} = 9.3 Hz, C-6); 7.12 (t, 1H, ³J_{HH} = 9.3 Hz, C-5); 7.24 (d, 1H, ³J_{HH} = 8.7 Hz, C-3); 7.40 (br, 3H, C-3',4',5'); 8.05 (d, 2H, ³J_{HH} = 5.3 Hz, C-2',6'); 8.56 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : -4.6 (MeIn); 114.0 (C-3), 119.3 (C-1), 122.2 (C-5), 127.6 (C-2',6'), 128.3 (C-3',5'), 130.2 (C-4'), 132.3 (C-4), 134.5 (C-6), 136.8 (C-1'), 157.0 (CH=N), 167.6 (C-2), 169.6 (C=N).

$3.3.4 [{MeIn} - O(C_6H_3 - OMe)CH = N - N = C(C_6H_5)O -]]$ (4)

Prepared similar to **1** in 92 % yield, m.p. 280 °C (decompose.), Anal. Calcd. for $C_{16}H_{15}InN_2O_3$: C, 48.27; H, 3.79; N, 7.03 %. Found: C, 48.05; H, 3.98; N, 7.20 %. IR in KBr (υ in cm⁻¹): 1608 (C=N). ¹H NMR (dmso-d₆) δ : -0.17 (s, 3H, MeIn); 3.70 (s, 3H, OMe); 6.41 (t, 1H, ³J_{HH} = 8.3 Hz, C-5); 6.78 (d, 1H, ³J_{HH} = 8.0 Hz, C-4); 6.85 (d, 1H, ³J_{HH} = 8.7 Hz, C-6); 7.40 (br, 3H, C-3',4',5'); 8.05 (d, 2H, ³J_{HH} = 5.0 Hz, C-2',6'); 8.54 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : -4.3 (MeIn); 55.9 (OMe), 112.9 (C-4), 113.7 (C-6), 118.7 (C-1), 126.3 (C-5), 127.6 (C-2',6'), 128.3 (C-3',5'), 130.2 (C-4'), 136.8 (C-1'), 152.1 (C-2), 157.1 (CH=N), 160.6 (C-3), 167.4 (C=N).

$3.3.5 [{EtGa}{-O(C_6H_4)CH=N-N=C(C_6H_5)O-}] (5)$

Prepared similar to **1** in 80 % yield, m.p. 235 °C, Anal. Calcd. for $C_{16}H_{15}GaN_2O_2$: C, 57.02; H, 4.49; N, 8.31 %. Found: C, 57.08; H, 4.63; N, 8.13 %. IR in KBr (v in cm⁻¹): 1615, 1600 (C=N); 562 (Ga-C); 528 (Ga-O). ¹H NMR (dmso-d₆) δ : 0.33 (q, 2H, ³J_{HH} = 9.0 Hz, Ga**CH**₂); 0.93 (t, 3H, ³J_{HH} = 8.7 Hz, GaCH₂**CH**₃); 6.60 (t, 1H, ³J_{HH} = 8.3 Hz, C-4); 6.68 (d, 1H, ³J_{HH} = 9.0 Hz, C-6); 7.20 (t, 1H, ³J_{HH} = 8.0 Hz, C-5); 7.30 (d, 1H, ³J_{HH} = 8.7 Hz, C-3); 7.40-7.46 (m, 3H, C-3',4',5'); 8.01 (d, 2H, ³J_{HH} = 6.7 Hz, C-2',6'); 8.73 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : 5.8 (Ga**CH**₂); 10.0 (GaCH₂**CH**₃); 115.8 (C-3), 118.3 (C-1), 121.3 (C-5), 127.6 (C-2',6'), 128.6 (C-3',5'), 131.1 (C-4'), 133.7 (C-4), 133.8 (C-6), 134.3 (C-1'), 157.6 (CH=N), 166.7 (C-2), 168.9 (C=N).

$3.3.6 [{EtGa}{-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}]$ (6)

Prepared similar to **1** in 90 % yield, m.p. 248°C, Anal. Calcd. for $C_{17}H_{17}GaN_2O_3$: C, 55.63; H, 4.67; N, 7.63 %. Found: C, 55.58; H, 4.90; N, 7.33 %. IR in KBr (υ in cm⁻¹): 1613 (C=N); 566 (Ga-C); 519 (Ga-O). ¹H NMR (dmso-d₆) δ : 0.30 (q, 2H, ³J_{HH} = 9.0 Hz, Ga**CH**₂); 0.90 (t, 3H, ³J_{HH} = 8.7 Hz, Ga**CH**₂**CH**₃); 3.73 (s, 3H, OMe); 6.54 (t, 1H, ³J_{HH} = 9.0 Hz, C-5); 6.90 (t, 2H, ³J_{HH} = 9.3 Hz, C-4,6); 7.40-7.47 (m, 3H, C-3',4',5'); 7.99 (d, 2H, ³J_{HH} = 8.0 Hz, C-2',6'); 8.70 (s, 1H, CH=N). ¹³C{¹H} NMR (dmso-d₆) δ : 5.7 (Ga**CH**₂); 9.9 (GaCH₂**CH**₃); 56.1 (OMe); 115.0 (C-4), 115.2 (C-6), 117.9 (C-1), 125.2 (C-5), 127.7 (C-2',6'), 128.6 (C-3',5'), 131.1 (C-4'), 134.2 (C-1'), 151.5 (C-2), 157.5 (CH=N), 157.7 (C-3), 168.9 (C=N).

Conclusions

Monoorgano -gallium and -indium complexes have been synthesised from dianionic tridentate ONO Schiff bases. The complexes adopt a dimeric structure containing phenolate bridges.

The 4-, 6- and 5-membered rings in these dimeric complexes lie one after another. The complexes are emissive in toluene solution with quantum yield always higher than free ligands.

Supporting Information

CCDC-Nos. 1424492, 1424491 and 1424493 contain the supplementary crystallographic data for $[\{MeGa\}\{-O(C_6H_4)CH=N-N=C(C_6H_5)O-\}]_2$ (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), respectively for this paper. These data can be obtained free of charge at 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; E-mail: <u>deposit@ccdc.cam.ac.uk</u>]. Representative NMR, UV-vis and emission spectra are also included in supplementary information.

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Table 1. Uv-Vis absorption, excitation and emission data of ligands and their monoorgano-gallium

 and –indium complexes in toluene

Complexes	Uv-vis absorption,	Excitation λ	Emission λ	Stokes	Quantum
	λ in nm	in nm	in nm	shift	yield (η)
					in %
$[HO(C_6H_4)CH=N-NH-C(O)(C_6H_5)]$	297, 328	312, 408	515	107	1
$[HO(C_6H_3-OMe)CH=N-NH-C(O)(C_6H_5)]$	297, 339	370	550	210	2
$[{MeGa} - O(C_6H_4)CH = N-N = C(C_6H_5)O-] (1)$	297, 328, 355, 374	410	475	65	5
	(sh), 396 (sh)				
$[{MeGa} - O(C_6H_3 - OMe)CH = N-N = C(C_6H_5)O-] (2)$	337, 351(sh), 375,	310, 384	470	86	3
	397				
$[{MeIn} {-O(C_6H_4)CH=N-N=C(C_6H_5)O-}] (3)$	297, 328, 396	302, 340, 414	514	100	5
$[{MeIn} {-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}] (4)$	332, 375, 398(sh)	304, 370, 405	460	55	2
$[{EtGa} {-O(C_6H_4)CH=N-N=C(C_6H_5)O-}] (5)$	297, 328, 358(sh),	303, 340, 408	464	56	4
	376(sh), 399(sh)				
$[{EtGa}{-O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-}]$ (6)	338, 350(sh), 375,	307, 373, 410	465	55	3
	400				

Ga1-O1	1.922 (4)	Ga1-C15	1.934 (7)
Ga1-O1 ⁱ	2.100 (4)	Ga1-N1	2.006 (6)
Ga1-O2	1.941 (4)	N1-N2	1.390 (7)
C7-N1	1.279 (8)	C8-O2	1.314 (7)
C8-N2	1.293 (8)		
C15-Ga1-N1	116.9 (3)	O1-Ga1-N1	81.75 (19)
C15-Ga1-O1	100.7 (2)	O2-Ga1-N1	78.9 (2)
C15-Ga1-O1 ⁱ	115.8 (3)	O2-Ga1-O1 ⁱ	144.62 (19)
C15-Ga1-O2	114.4 (2)	Ol ⁱ -Gal-Nl	124.5 (2)
O1-Ga1-O1 ⁱ	72.80 (18)	Ga1-O1-Ga1 ⁱ	106.35 (18)
O1-Ga1-O2	94.45 (18)		

Table 2. Selected geometric parameters (Å/°) for $[{MeGa} - O(C_6H_4)CH = N-N = C(C_6H_5)O_2]_2$ (1)

Ga1-C31	1.921 (8)	Ga2-C32	1.932 (7)
Ga1-O1	1.950 (5)	Ga2-O2	1.921 (5)
Gal-O2	2.144 (5)	Ga2-O5	1.939 (5)
Ga1-O6	1.919 (5)	Ga2-O6	2.125 (5)
Ga1-N1	2.031 (6)	Ga2-N3	2.028 (7)
N1-N2	1.396 (8)	N3-N4	1.409 (8)
C8-N1	1.281 (9)	C22-N3	1.280 (9)
C1-N2	1.309 (10)	C15-N4	1.322 (10)
C1-O1	1.288 (9)	C15-O5	1.287 (9)
C31-Ga1-O1	114.3 (3)	C32-Ga2-O2	120.2 (3)
C31-Ga1-O2	99.6 (3)	C32-Ga2-O5	113.9 (3)
C31-Ga1-O6	120.7 (3)	C32-Ga2-O6	101.3 (3)
C31-Ga1-N1	114.1 (3)	C32-Ga2-N3	113.4 (3)
N1-Ga1-O1	78.6 (3)	N3-Ga2-O2	123.3 (2)
N1-Ga1-O2	80.9 (2)	N3-Ga2-O5	78.3 (3)
N1-Ga1-O6	121.4 (2)	N3-Ga2-O6	81.2 (2)
01-Ga1-O2	145.3 (2)	O2-Ga2- O5	95.2 (2)
O1-Ga1-O6	95.9 (2)	O2-Ga2- O6	72.05 (19)
O2-Ga1-O6	71.66 (19)	O5-Ga2- O6	144.0 (2)
Ga1-02-Ga2	107.6(2)	Ga1-06-Ga2	108.5(2)

Table 3. Selected geometric parameters (Å/°) for $[{MeGa} - O(C_6H_3 - OMe)CH = N - N = C(C_6H_5)O -]_2$ (2)

Gal-C31a	1.82 (8)	Ga2-C33a	1.93 (4)
Ga1-O1	2.117 (6)	Ga2-O1	1.922 (5)
Ga1-O2	1.951 (5)	Ga2-O4	2.134 (5)
Ga1-O4	1.908 (5)	Ga2-O5	1.923 (6)
Ga1-N2	2.032 (7)	Ga2-N4	2.022 (7)
N1-N2	1.394 (8)	N3-N4	1.411 (9)
C8-N2	1.287 (10)	C22-N4	1.269 (9)
C1-N1	1.314 (10)	C15-N3	1.315 (11)
C1-O2	1.283 (10)	C15-O5	1.271 (10)
C31a-Ga1-O1	105 (3)	C33a-Ga2-O1	117.3 (8)
C31a-Ga1-O2	110 (3)	C33a-Ga2-O4	102.6 (11)
C31a-Ga1-O4	110 (2)	C33a-Ga2-O5	110.8 (11)
C31a-Ga1-N2	126 (2)	C33a-Ga2-N4	121.5 (8)
N2-Ga1-O1	81.6 (3)	N4-Ga2-O1	118.7 (2)
N2-Ga1-O2	77.9 (3)	N4-Ga2-O4	80.3 (3)
N2-Ga1-O4	122.7 (3)	N4-Ga2-O5	78.7 (3)
O1-Ga1-O2	144.2 (2)	O1-Ga2- O4	71.6 (2)
O1-Ga1-O4	72.3 (2)	01-Ga2- 05	96.0 (3)
O2-Ga1-O4	94.8 (2)	O4-Ga2- O5	146.3 (2)
Ga1-O1-Ga2	108.0 (3)	Ga1-O4-Ga2	107.8 (2)

Table 4. Selected geometric parameters (Å/°) for $[{EtGa} - O(C_6H_3 - OMe)CH = N - N = C(C_6H_5)O -]_2$ (6)

Table !	5. Crystallography data for [{MeGa}{-O(C_6H_4)CH	H=N-N=0	$C(C_6H_5)O-\}]_2$ (1) and $[{MeGa}]$
	$O(C_6H_3-OMe)CH=N-N=C(C_6H_5)O-\}]_2$	(2)	and	$[{EtGa} - O(C_6H_3 - OMe)CH = N-$
	$N=C(C_6H_5)O-]_2(6)$			

Formula	$C_{30}H_{26}Ga_2N_4O_4$ (1)	$C_{32}H_{30}Ga_2N_4O_6. 2(C_6H_6)$ (2)	$C_{34}H_{34}Ga_2N_4O_6(6)$
М	645.99	862.26	734.11
Size (mm)	$0.10 \times 0.10 \times 0.05$	$0.20 \times 0.10 \times 0.05$	$0.15 \times 0.15 \times 0.10$
Crystal system	monoclinic	triclinic	triclinic
Space group	C 2/c	P -1	P -1
a/Å	17.000 (3)	10.578 (3)	10.747 (2)
b/Å	10.2238 (11)	13.193 (3)	12.376 (5)
c/Å	16.866 (2)	15.936 (3)	15.044 (2)
α/°	90	99.342 (18)	66.010 (16)
β/°	107.540 (11)	91.67 (2)	78.988 (13)
$\gamma/^{o}$	90	105.36 (2)	66.95 (2)
$V/Å^3$	2795.1 (7)	2110.0 (10)	1681.0 (8)
Z	4	2	2
$d_{calc}/g \text{ cm}^{-3}$	1.535	1.357	1.452
$\mu (mm^{-1})/F(000)$	1.971/1312	1.328/888	1.652/754
θ for data collection/°	2.513 to 27.523	2.598 to 27.518	2.584 to 27.515
Limiting indices	$-22 \le h \le 12$	$-7 \le h \le 13$	$-7 \le h \le 13$
	$0 \le k \le 13$	$-17 \le k \le 16$	$-14 \le k \le 16$
	$-20 \le l \le 21$	$-20 \le l \le 20$	$-19 \le l \le 19$
No. of unique reflns	3214	9687	7704
No. of obsd reflns with $I > 2\sigma(I)$	1617	2940	1932
Data/restraints/parameters	3214/0/182	9687/0/485	7704/58/441
Final R_1 , ωR_2 indices	0.0.000/0.11.00	0.0540/0.1007	0.0740/0.1600
(R_factor_gt/wR_factor_gt)	0.0633/0.1168	0.0742/0.1236	0.0748/0.1688
R_1 , ωR_2 (all data)		0.0000/0.1040	0.00000 1000
(R_factor_all/wR_Factor_ref)	0.1666/0.1509	0.3039/0.1840	0.3399/0.1097
Goodness of fit on F ²	1.050	0.925	0.918
Largest diff. peak and hole (e.Å ⁻³)	0.593 and -1.043	0.382 and -0.498	0.321 and -0.392

List Figure Captions

- Fig. 1. Emission spectra (a) $[HO(C_6H_4)CH=N-NH-C(O)(C_6H_5)]$ and (b) $[\{MeGa\}\{-O(C_6H_4)CH=N-N=C(C_6H_5)O-\}]$ (1) with their corresponding excitation spectra.
- **Fig. 2.** ORTEP diagram of $[{MeGa} \{-O(C_6H_4)CH=N-N=C(C_6H_5)O-\}]_2$ (1) (ellipsoids drawn with 25% probability; hydrogen atoms are omitted for clarity).
- **Fig. 3.** ORTEP diagram of [{MeGa}{-O(C₆H₃-OMe)CH=N-N=C(C₆H₅)O-}]₂.2C₆H₆ (**2**.2C₆H₆) (ellipsoids drawn with 20% probability; hydrogen atoms and solvent molecule are omitted for clarity).
- Fig. 4. (a) ORTEP diagram of [{EtGa}{-O(C₆H₃-OMe)CH=N-N=C(C₆H₅)O-}]₂ (6) (ellipsoids drawn with 10% probability; hydrogen atoms and solvent molecule are omitted for clarity); (b) Orientation of ethyl groups in (6); (c) Three possible confirmations of 6 (confirmation in red have least probability as observed from molecular structure).



Fig. 1. Emission spectra (a) $[HO(C_6H_4)CH=N-NH-C(O)(C_6H_5)]$ and (b) $[\{MeGa\}\{-O(C_6H_4)CH=N-N=C(C_6H_5)O-\}]$ (1) with their corresponding excitation spectra.



Fig. 2. ORTEP diagram of $[{MeGa} {-O(C_6H_4)CH=N-N=C(C_6H_5)O-}]_2$ (1) (ellipsoids drawn with 25% probability; hydrogen atoms are omitted for clarity).

17



Fig. 3. ORTEP diagram of [{MeGa}{-O(C₆H₃-OMe)CH=N-N=C(C₆H₅)O-}]₂.2C₆H₆ (2.2C₆H₆) (ellipsoids drawn with 20% probability; hydrogen atoms and solvent molecule are omitted for clarity).



(a)



Fig. 4. (a) ORTEP diagram of [{EtGa}{-O(C₆H₃-OMe)CH=N-N=C(C₆H₅)O-}]₂ (**6**) (ellipsoids drawn with 10% probability; hydrogen atoms and solvent molecule are omitted for clarity); (b) Orientation of ethyl groups in (**6**); (c) Three possible confirmations of **6** (confirmation in red have least probability as observed from molecular structure).

Graphical abstract – pictogram and synopsis

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

Manoj K. Pal, Nisha Kushwah, Amey P. Wadawale, Sandip Dey, V. Sudarsan and Vimal K. Jain



Complexes of composition [$\{RM\}$ $\{-O(C_6H_3R'-3)CH=N-N=C(C_6H_5)O-\}$] (M = Ga, In) were synthesized from reactions of triorgano-gallium and –indium etherates with benzohydrazide schiff bases. The complexes were emissive in toluene at room temperature. They adopt a dimeric structure with phenolate oxygen bridges. Gallium atom acquires a distorted square pyramidal configuration.

Highlights

- > Mono-organo Ga/In complexes with benzohydrazide schiff bases were synthesized
- > These complexes have dimeric phenolate oxygen bridged structure
- ➢ Central Ga₂O₂ ring is slightly bent
- > Variation in interplanar angles is observed with varying substituents
- > Complexes of organo- Ga/In with benzohydrazide schiff bases are emissive in toluene