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Synthesis, Characterization, Photoluminescence, and Computational Studies of Monoorgano-Gallium and -Indium Complexes Containing Dianionic Tridentate ONE (E = O or S) Schiff Bases

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Supporting Information

ABSTRACT: The reactions of triorgano-gallium and -indium etherate with dianionic tridentate Schiff bases (2-hydroxy-*N*-salicylideneaniline (1a), 2-hydroxy-*N*-(2-hydroxy-3-methoxybenzylidene)aniline (1b), and 2-mercapto-*N*-salicylideneaniline (1c)) in benzene yielded complexes of the type $[RM\{O(2-C_6H_3R'-3)-CH=N(2-C_6H_4)E\}]$ (where R = Me, Et; M = Ga, In; R' = H, OMe; E = O, S) in nearly quantitative



yields. These complexes have been characterized by elemental analysis, IR, UV–vis, and NMR (¹H and ¹³C{¹H}) spectroscopy. The molecular structures of $[MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)]$ (2a) and $[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)]$ (2b) were established by X-ray crystallography. Photoluminescence data of these complexes showed that the quantum yield was mainly affected by the substituent/groups attached to the phenyl moiety of the ligands rather than the metal atom. Density functional theory calculations have been used to assess all the possible structures and to evaluate the complexation energies corresponding to $[MeM{O(2-C_6H_4)-CH=N(2-C_6H_4)E}]$ (M = Ga, In; E = O, S) complexes.

INTRODUCTION

The chemistry of organo-gallium/-indium complexes derived from an internally functionalized anionic oxo-ligand has been an active area of extensive current research due to several obvious reasons.¹ These complexes exhibit rich structural diversity¹⁻³ and show interesting photophysical⁴⁻⁶ and antitumor⁷ properties. They find applications in catalysis^{8,9} and as single-source molecular precursors for deposition of metal oxide thin films.¹⁰

Schiff bases are an important family of internally functionalized ionic ligands. These ligands have played a pivotal role in the development of coordination chemistry. Both anionic (e.g., *N*-phenylsalicylidineimine¹¹) and dianionic ligands (such as Salen¹²) have been employed for the synthesis of complexes of group 13 metals. Organo-gallium and -indium complexes containing these ligands have been isolated in the form of monomers, dimers, and trimers.^{2,4,6,9,12}

Luminescence from complexes of group 13 metals, in particular AlQ_3 ,¹³ has been exploited for organic light emitting diodes (OLEDs).¹⁴ The essential requirements for a complex that can be used for OLED applications include high fluorescence in the solid state, high electron mobility, thermal stability (glass transition temperature above 200 °C and decomposition temperature above 400 °C), and low vapor pressure to aid preparation of good-quality thin films at relatively low temperatures. A number of studies are reported regarding the light-emitting aluminum and gallium complexes. Gallium complexes have been projected as promising candidates¹⁵ to replace aluminum derivatives, as they exhibit better efficiency than AlQ_3 .¹⁶ Gallium complexes, both classical^{17,18} and organometallic derivatives, ^{4–6} have been reported to exhibit bright

luminescence. Metal chelates derived from tridentate dianionic Schiff bases have been shown to be highly luminescent.¹⁸ The photophysical properties of monoorgano-gallium complexes are little explored. With this perspective and in pursuance of our interest on organo-gallium and -indium complexes, we have synthesized monoorgano-gallium and -indium complexes with dianionic tridentate Schiff bases. To understand the structural aspects and to assess the luminescence properties, complexes with ligands containing ring substitution by an electron-withdrawing group (OMe) and one of the phenolates by a thiolate group have also been investigated. Results of this work are presented herein.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. Treatment of trialkyl-gallium/-indium etherate with dianionic tridentate ligands, 2-hydroxy-N-salicylideneaniline, 2-hydroxy-N-(2-hydroxy-3-methoxybenzylidene)aniline, and 2-mercapto-N-salicylideneaniline, in benzene at room temperature afforded complexes of composition [RM{O(2-C₆H₃OR'-3)-CH=N(2-C₆H₄)E}] (R = Me, Et; M = Ga, In; R' = H, Me; E = O, S) as pale yellow crystalline solids (Scheme 1). These complexes are stable in air, as there was no change in the ¹H NMR spectrum of **2a** after keeping it in open air for 4 days.

The C==N absorption in the IR spectra of the complexes containing a O^NN^O donor set is shifted to lower wave numbers (15– 30 cm⁻¹) than the absorption for the corresponding free ligands.

Received: October 25, 2011 Published: May 3, 2012

Scheme 1. Synthesis of Monoorgano-Gallium and -Indium Complexes



The shift was rather small for complexes derived from the O^NN^S donor set. The shifting was more pronounced in the case of indium complexes with reference to the analogous gallium derivatives, indicating stronger coordination of nitrogen to the indium atom. The IR spectra of the complexes displayed an absorption in the region 560–605 cm⁻¹, which was absent in the spectra of free ligands. This absorption has been assigned to metal–carbon stretching based on the M–C stretching reported in the literature for organogallium/indium complexes.^{19–21}

The ¹H and ¹³C{¹H} NMR spectra, recorded in DMSO- d_{6i} showed characteristic peaks due to alkyl metal and ligand protons/carbons. The methyl metal singlets appeared in the region δ –0.65 to –0.27 ppm. The ¹H NMR spectra exhibited a singlet in the region 8.51-8.89 ppm, characteristic of coordination of the imino nitrogen atom of the -CH=Ngroup to the metal center. The alkylmetal carbon resonances in the ¹³C NMR spectra appeared in the expected region. The benzothiazoline carbon resonance of 1c at δ 63.5 ppm appeared in the region 166.4-172.0 ppm in its complexes, which is characteristic for the C=N group. Similarly 1a and 1b and their complexes showed a C=N signal in their ¹³C NMR spectra in the region 159.4-171.4 ppm. The C-1 resonances for the salicyladehyde and o-valine fragments are shielded (0.3-3.4 ppm), while the C-1 signal for the o-aminophenol fragment is deshielded (5.4-8.8 ppm). In contrast a reverse trend was noticed for the complexes containing a O^AN^AS ligand; that is, C-1 for the salicyladehyde fragment is deshielded (7.2-11.1 ppm), and the o-aminothiophenol fragment is shielded (5.1-7.2 ppm). In the former complexes, the o-aminophenol fragment acts as a bridge, as confirmed by X-ray structural analyses of 2a and 2b. It can be inferred that in the O[^]N[^]S complexes the o-aminothiophenol fragment may be at a terminal position. This may be due to the preference of a hard metal center for the hard ligand (oxygen) in a bridging position. The oaminothiophenol fragment of O^N^S is known to act as both a bridging ligand as in $[{O(MeC_6H_3)CH=N(C_6H_4)S)}_2$ {Ti- $(OPr^{j})_{2}^{2}_{2}^{2^{2^{2}}}$ and a terminal ligand as in $[{O(C_{6}H_{4})CH=N(C_{6}H_{4})-$ S)₂{ $Ti(OPr^{i})_{2}$ ₂].²²

Interestingly the ¹H NMR spectra of gallium complexes (**2a** and **2b**) in CD_2Cl_2 showed two set of resonances of nearly equal integration at room temperature, whereas under similar conditions only one set of resonances are observed in DMSO- d_6 as described above. In contrast the ¹H NMR spectra of the indium (**2f**) complex exhibited only one set of resonances in both CD_2Cl_2 and DMSO- d_6 . This suggests that gallium complexes exist in a mixture of monomeric–dimeric forms in dichloromethane solution (Scheme 2), whereas indium complexes retained their dimeric structure in solution.





Crystal Structures of 2a and 2b. The molecular structures of **2a** and **2b** were established by single-crystal X-ray diffraction analysis. ORTEP drawings are shown in Figures 1 and 2, and the



Figure 1. Crystal structure of $[MeGa(-O-(2-C_6H_4)-CH=N(2-C_6H_4)-O-)]\cdot CH_2Cl_2$ (2a) grown in dichloromethane solvent.

selected interatomic parameters are given in Tables 1 and 2. Both complexes crystallize with two molecules of dichloromethane. There are two independent molecules of **2a** in the crystal unit cell, which differ very slightly in bond lengths, angles, and torsion angles; only one of them is shown in the figure. The coordination geometry defined by " μ_2 -O^NN^OC" donor atoms around the gallium atom can be described as square pyramidal on the basis of τ indices (0.016 for **2a** and 0.01 for **2b**). Five-coordinate geometries in metal complexes can be quantified using the τ index, as described by Addision.²³

Both the complexes are dimeric with no unusual short intermolecular contacts. The Schiff base ligand is coordinated through one nitrogen atom and two phenolate oxygen atoms; one of them (*o*-aminophenol fragment) is μ_2 -bridging. All these atoms lie in the equatorial positions. The two bridging phenolate oxygens form a planar four-membered Ga₂O₂ ring. The five- and six-membered



Figure 2. (a) Crystal structure of $[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)]$ (2b) grown in dichloromethane solvent. (b) Packing diagram.

chelate rings formed by O^NO ligands are puckered. The two six-membered rings lie (on either side) one above and other below the Ga₂O₂ ring at an angle of 57.24° and 56.39° in **2a** and 65.66° in **2b**. The Ga–C, ^{3,9,24,25} Ga–N, ^{3,9} and Ga–O^{3,5,9,25} distances are well in agreement with those reported in the literature for organo-gallium compounds. The bridging Ga–O distance is slightly longer than nonbridging Ga–O distances.

Photophysical Properties. Figure 3 shows the emission spectra of **1a**, **1b**, and **1c** obtained after excitation at wavelengths corresponding to their respective excitation peak maximum. The emission spectra of **1a** and **1b** are identical and consist of two significantly overlapping peaks with peak maxima around 518 and 553 nm. Unlike this, a broad peak around 453 nm was observed for **1c**. On the basis of earlier studies on similar ligands,^{15,26} the observed emission peak has been attributed to significantly overlapping $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ electronic transitions. Incorporation of a methoxy group in one of the phenyl rings (**1b**) did not have any effect on the emission and excitation maxima. However, replacement of phenolic OH (**1a**) by a SH group (**1c**) resulted in a blue shift of the emission maximum (453 nm). The electron density created within the ligand moiety could be lower when an OH group is replaced by a SH group. Lower electron

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molecule	a	molecule	b
Ga1–O1	1.891(5)	Ga2–O3	1.887(5)
Ga1–O2	2.018(4)	Ga2–O4	2.013(5)
Ga1–N1	2.059(6)	Ga2-N2	2.050(5)
Ga1-C14	1.930(9)	Ga2-C28	1.937(8)
Ga1–O2′	1.984(5)	Ga2–O4′	1.995(4)
Ga1′–O2	1.984(5)	Ga2'04	1.995(4)
O1-C1	1.329(8)	O3-C15	1.312(8)
O2-C8	1.360(8)	O4-C23	1.357(7)
N1-C7	1.286(8)	N2-C21	1.284(9)
N1-C13	1.408(8)	N2-C22	1.418(9)
O1-Ga1-N1	89.1(2)	O3-Ga2-N2	89.2(12)
O1-Ga1-O2	137.7(3)	O3-Ga2-O4	136.4(2)
O1-Ga1-O2'	90.1(2)	O3-Ga2-O4'	90.6(2)
O1-Ga1-C14	113.0(3)	O3-Ga2-C28	112.9(3)
N1-Ga1-O2	77.7(2)	N2-Ga2-O4	78.0(2)
N1-Ga1-O2'	134.3(2)	N2-Ga2-O4'	136.6(2)
N1-Ga1-C14	111.7(3)	N2-Ga2-C28	110.9(3)
O2-Ga1-O2'	72.6(2)	O4-Ga2-O4'	72.6(2)
O2-Ga1-C14	109.2(3)	O4-Ga2-C28	110.5(3)
O2'-Ga1-C14	110.5(3)	O4'-Ga2-C28	109.0(3)
Ga1–O2–Ga1′	107.4(2)	Ga2–O4–Ga2'	107.4(2)

Table 1. Selected Geometric Parameters (Å/deg) for $[MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)]$ (2a)

Table 2. Selected Geometric Parameters (Å/deg) for $[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)]$ (2b)

Ga1–O1	1.870(3)	Ga1′-O2	1.932(3)
Ga1–O2	2.126(3)	O1-C1	1.287(4)
Ga1–O2′	1.932(3)	O2-C8	1.341(4)
Ga1-N1	1.992(3)	N1-C7	1.282(5)
Ga1-C14	1.924(4)	N1-C13	1.402(5)
01-Ga1-N1	92.64(13)	N1-Ga1-C14	125.58(17)
O1-Ga1-O2	157.84(12)	O2-Ga1-O2'	74.70(11)
O1-Ga1-O2'	93.55(12)	O2-Ga1-C14	98.33(15)
O1-Ga1-C14	103.73(16)	O2'-Ga1-C14	115.89(17)
N1-Ga1-O2	75.94(11)	Ga1–O2–Ga1′	105.30(11)
N1-Ga1-O2'	114.35(12)		

densities stabilize the ligand moiety as well as decrease the extent of electron–electron repulsion, and hence higher energy is required to excite the electron from lower levels to higher energy levels. This leads to a blue shift in the emission and excitation peak maxima. Among the three ligands, the maximum quantum yield of emission has been observed for 1a (7%). This is because the radiative recombination of electrons and holes are severely affected by the nonradiative processes like C–H and O–H vibrations as well as the presence of heavier elements (like S). The ligand 1ahas relatively fewer C–H linkages as compared to 1b and also does not have heavier elements like S as in 1c and hence shows the highest quantum yield of luminescence.

Figure 4 shows the emission spectra of gallium complexes (2a, 2b, and 3a). The emission spectra of the complexes are broader and red-shifted compared to that of free ligands. Red shift in the emission maxima has been attributed to an increase in the electron density in the ligand moiety brought about by the combined effect of removal of protons from OH/SH groups as well as its coordination to metal atom. The broadening may be due to lack of flexibility with the ligand moiety caused by the formation of coordination polyhedra with the Ga atom. Even though ligands 1a and 1b have comparable emission maxima and intensities, their

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Figure 3. Emission spectra from ligands (a) 1a, (b) 1b, and (c) 1c in dichloromethane. The excitation wavelengths are 468 nm for 1a and 1b ligands and 388 nm for the 1c ligand.

complexes (2a and 2b) exhibited different emission maxima. This can be attributed to the presence of OCH_3 groups, leading to increased electron density in the ligand moiety after deprotonation of OH groups. For 3a, the effects are much more significant due to the greater electron-donating nature of sulfur compared to oxygen after deprotonation, consequently resulting in higher electron density in the ligand moiety and associated increase in the extent of electron–electron repulsion. This facilitates excitation of electrons from the ground state to the excited state. This is responsible for the red shift of the emission maximum for the complex as compared to the free ligand. Similar results were also observed for indium complexes (Table 3).

Emission spectra were also recorded by replacing the methyl group attached to the metal atom with an ethyl group. The emission spectra from representative indium complexes (2f and 2h) are shown in Figure 5. The emission maximum, line shape, and quantum yields are unaffected by replacement of the methyl group by an ethyl group (Table 3). This is because the emission and excitation peaks are characteristic of the transitions taking place between the energy levels of the ligand moiety and the groups attached with the metal atom. The measured quantum yields for the complexes are lower than that reported for other gallium complexes.



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Figure 4. Emission spectra from complexes (a) 2a (b) 2b, and (c) 3b in dichloromethane. The excitation wavelength is 490 nm.

Computational Studies. It has not been possible for us to determine the X-ray structures of all the complexes. Therefore, we have adopted density functional theory to determine the structures of all the complexes in a systematic way. For this purpose we have optimized structures of the free ligands and all the complexes resulting from these ligands with Ga(III) and In(III) ions. For the free ligand two conformations are possible, viz., anti and syn, and the corresponding optimized structures are given in the Supporting Information. The anti conformation is more stable irrespective of the donor atoms involved; that is, except for nitrogen the other two donor centers are oxygen or one is oxygen and another is sulfur. We have used two different initial structures for each of the complexes considered in this work, and the corresponding optimized structures are given in Figure 6. In the case of form A, bridging bonds are associated with five-membered rings, whereas for form B bridging bonds are associated with six-membered rings. The minimum energy structure involving form A (bearing only O and N atoms) consists of a bridged structure with four-membered, five-membered, and six-membered rings lying one after another (Figure 6a). It is true for both Ga and In complexes. On the other hand, the minimum energy structure for form \mathbf{B} (bearing O, S, and N atoms) corresponds to a structure where four-membered, sixmembered, and five-membered rings are placed one after another

Table 3. UV–Vis Absorption, Excitation, and Emission Data of Ligands and Their Monoorgano-Gallium and -Indium Complexes in Dichloromethane

compound	UV–vis absorption, λ in nm	excitation λ in nm	emission λ in nm	quantum yield (η) in %
$HO(2-C_6H_4)-CH=N(2-C_6H_4)-OH$ (1a)	270, 353	468	518, 553	7
HO(2-C ₆ H ₃ OMe-3)-CH=N(2-C ₆ H ₄)-OH (1b)	278, 345	468	517, 554	2
$HO(2-C_6H_4)-CH=N(2-C_6H_4)-SH(1c)$	259,286, 310, 333, 350	390	465	1
$[MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)] (2a)$	243, 305, 346, 414	488	580	2
$[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)] (2b)$	251, 317, 360, 427	275, 490	580	3
$[MeGa(-O(2-C_{6}H_{4})-CH=N(2-C_{6}H_{4})-S-)] (3a)$	251, 281, 308, 426	350, 490	680	2
$[EtGa(-O-(C_6H_4)-CH=N-(C_6H_4)-O-)]$ (2c)	245, 303, 349, 416	488	576	5
$[EtGa(O-(C_{6}H_{3}OMe-3)-CH=N-(C_{6}H_{4})-O-)] (2d)$	251, 315, 333, 361, 429	490	560	3
$[EtGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-S-)]$ (3b)	251, 285, 308, 428	350, 490	680	1
$[MeIn(-O-(C_6H_4)-CH=N-(C_6H_4)-O-)] (2e)$	292, 315, 370, 430	275, 355, 473	555	1
$[MeIn(-O-(C_6H_3OMe-3)-CH=N-(C_6H_4)-O-)] (2f)$	317, 370, 431	275, 355, 490	580	1
$[MeIn(-O(2-C_{6}H_{4})-CH=N(2-C_{6}H_{4})-S-)] (3c)$	254, 282, 338, 428	350	560	1
$[EtIn(-O-(C_6H_4)-CH=N-(C_6H_4)-O-)] (2g)$	250, 295, 358, 415	501	552	1
$[EtIn(-O-(C_6H_3OMe-3)-CH=N-(C_6H_4)-O-)]$ (2h)	316, 362, 432	350, 500	554, 580	1
$[EtIn(-O-(C_6H_4)-CH=N-(C_6H_4)-S-)]$ (3d)	254, 280, 364, 418	388, 480	630	1



Figure 5. Emission spectra from complexes (a) 2f and (b) 2h in dichloromethane. Excitation wavelength is 355 nm.

(Figure 6b). Some of the optimized geometrical parameters are given in Supporting Information. It is clear that the In–L bond distances are always larger as compared to the Ga–L distance because of the larger size of In. For form **B** M–N bond distances are larger for both In and Ga. Bond lengths from X-ray crystal structure of Ga-form **A** (E = O) are given in Tables 1 and 2. The bridging M–O bond distances



Figure 6. Optimized structure of (a) M-form A and (b) M-form B complexes, where M = Ga/In and E = O/S.

are 2.018 and 1.984 Å, while M–N, M–O, and M–C bond distances are 2.059, 1.891, and 1.930 Å, respectively. For obtaining the complexation energy value of a particular complex, we have considered the total energy of the complex, ligands, and the metal ion, which are involved in the formation of that complex. The calculated complexation Table 4. Calculated Complexation Energies (eV) for In and Ga Complexes Using the def2-TZVP/BP86 Method

complex name	complexation energy
Ga-form $A (E = O) (2a)$	-129.03
Ga-form \mathbf{A} (E = S)	-127.83
Ga-form \mathbf{B} (E = O)	-128.68
Ga-form B $(E = S)$ $(3a)$	-127.94
In-form $\mathbf{A} (\mathbf{E} = \mathbf{O}) (\mathbf{2e})$	-118.06
In-form \mathbf{A} (E = S)	-117.36
In-form B ($E = O$)	-117.90
In-form B ($E = S$) (3c)	-117.41

energy values and charge values on the metal and donor centers are also given in the Supporting Information.

CONCLUSION

Air- and moisture-stable, photoemissive monoorgano-gallium and -indium complexes derived from dianionic tridentate Schiff bases have been isolated conveniently. They are dimeric molecules with phenolate bridges in the solid state. The gallium complexes exist as a mixture of monomeric and dimeric forms in dichloromethane solution. These complexes are emissive in solution at room temperature, and the emission peaks are red-shifted with respect to the peaks for corresponding free ligands. The complexes derived from $O^N ^O$ ligands comprise a bridged structure with four-, five-, and six-membered rings lying one after another, while complexes containing $O^N ^S$ ligands adopt a structure with four-, six-, and fivemembered rings one after another.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All experiments involving organo-gallium/ -indium compounds were carried out in anhydrous conditions under a nitrogen atmosphere using Schlenk techniques. Solvents were dried using standard methods. The $R_3Ga\cdotOEt_2$ (R = Me, Et) were prepared using a gallium–magnesium alloy and alkyl iodide in diethyl ether, while $R_3In\cdotOEt_2$ (R = Me or Et) were obtained by a reaction between anhydrous InCl₃ and RMgI in diethyl ether.⁹ Ether contents in each preparation were evaluated by ¹H NMR integration. The ligands were prepared by condensation reaction between a salicyaldehyde and an equivalent amount of *o*-aminophenol or *o*-aminothiophenol in refluxing benzene as described in the literature.^{22,27,28}

Infrared spectra were recorded as KBr plates on a Jasco FT-IR 6100 spectrometer. The NMR spectra were recorded on a Bruker Avance-II 300 MHz spectrometer in 5 mm tubes as $CDCl_3$ or DMSO- d_6 solutions. Chemical shifts were referenced to internal chloroform or dimethyl sulfoxide peak. Electronic spectra were recorded in dichloromethane on a UV–vis Jasco V-630 spectrophotometer. All luminescence measurements were carried out at room temperature by using an Edinburgh Instruments FLSP 920 system, having a 450W Xe lamp as the excitation source for steady-state measurements. Red-sensitive PMT was used as the detector. 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.

Quantum-Chemical Calculations. Geometries of all the bare dianionic ligands and the resulting complexes involving Ga³⁺ and In³⁺ ions have been optimized fully using the Turbomole 6.0 program.²⁹ For this purpose we have used density functional theory with Becke's exchange functional³⁰ in conjunction with Perdew's correlation functional³¹ (BP86). Standard def2-TZVP basis sets have been used for all the atoms at the allelectron level except for In. For the In atom, 28 core electrons have been considered using an effective core potential, and the remaining electrons have been treated explicitly.

Synthesis of Monoorgano-Gallium and -Indium Complexes. [$MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-$)] (2a). To a benzene solution (25 mL) of trimethylgallium etherate (0.56 g,

containing 0.24 g (2.12 mmol) of Me₃Ga) was added a solution of (2-hydroxyphenyl)salicylideneimine (450 mg, 2.11 mmol) with stirring, which continued for 3 h. The solvent was evaporated under reduced pressure to give a yellow, crystalline solid (600 mg, 96% yield), which was recrystallized from dichloromethane-hexane as a colorless crystalline solid, mp 260 °C. The compound could not be sublimed at 200 °C at 34 mm/Hg. Anal. Calcd for $C_{14}H_{12}GaNO_2 \cdot 0.5(CH_2Cl_2)$: C, 51.45; H, 3.87; N, 4.13. Found: C, 51.77; H, 3.78; N, 4.18. IR (v in cm⁻¹): 1614 (C=N); 580 (Ga-C). ¹H NMR in DMSO-d₆: -0.62 (s, MeGa); 5.74 (CH₂Cl₂); 6.56 (t, ³J_{HH} = 7.3 Hz, 1H); 6.70 (dd, 8.5 Hz, 3H); 7.04 (t, ${}^{3}J_{HH} =$ 7.8 Hz, 1H); 7.27 (t, ${}^{3}J_{HH} =$ 7.3 Hz, 1H); 7.40 (d, ${}^{3}J_{HH} =$ 7.3 Hz, 1H); 7.55 (d, ${}^{3}J_{HH} =$ 7.7 Hz, 1H); 8.87 (s, -CH=N-, 1H) [¹H NMR in CD_2Cl_2 : -0.36 (s, MeGa); -0.03 (s, MeGa); 6.69 (t, ${}^{3}J_{HH} = 7.2$ Hz, 1H); 6.86 (m, 3H); 7.04 (m, 3H); 7.22 (m, 2H); 7.39 (m, 5H); 7.54 (m, 2H); 7.63 (d, ${}^{3}J_{HH} = 8.1$ Hz, 1H); 8.48 (s, -CH=N-, 1H); 8.77 (s, -CH=N-, 1H]. ¹³C{¹H} NMR in DMSO- d_6 : -7.1 (s, MeGa); 115.4, 115.6, 116.5, 117.6, 120.3, 122.3, 130.0, 132.6, 134.4, 134.8, 157.7, 159.5, 166.9 (s, -CH=N-).

[*MeGa*(−*O*(2-*C*₆*H*₃*OMe*-3)-*CH*=*N*(2-*C*₆*H*₄)-*O*−)] (2*b*). 2*b* was prepared similarly to 2*a* in (720 mg) 91% yield and recrystallized from dichloromethane. Mp: 275 °C. Anal. Calcd for C₁₅H₁₄GaNO₃·CH₂Cl₂: C, 46.76; H, 3.92; N, 3.41. Found: C, 47.26; H, 3.94; N, 3.54. IR (ν in cm⁻¹): 1613 (C=N); 582 (Ga−C). ¹H NMR in DMSO-*d*₆: −0.65 (*s*, MeGa); 3.73 (*s*, OMe); 5.72 (CH₂Cl₂) 6.52−6.58 (m, 1H); 6.64 (t ³*J*_{HH} = 8.0 Hz, 2H); 6.92 (d, ³*J*_{HH} = 7.6 Hz, 1H); 6.98−7.05 (m, 3H); 7.53 (d, ³*J*_{HH} = 7.8 Hz, 1H); 8.84 (*s*, −CH=N−, 1H) [¹H NMR in CD₂Cl₂: −0.36 (*s*, MeGa); −0.00 (*s*, MeGa); 3.91 (*s*, OMe); 3.99 (*s*, OMe); 6.62 (d, ³*J*_{HH} = 7.5 Hz, 1H); 6.80 (m, 3H); 7.05 (m, 5H); 7.33 (m, 2H); 7.54 (m, 2H); 7.92 (d, ³*J*_{HH} = 8.1 Hz, 1H); 8.46 (*s*, −CH=N−, 1H); 8.77 (*s*, −CH=N−, 1H)]. ¹³C{¹H} NMR in DMSO-*d*₆: −7.2 (*s*, MeGa); 55.9 (*s*, OMe); 115.3, 115.6, 117.6, 119.7, 125.7, 130.0, 132.6, 152.0, 157.4, 157.7, 159.4 (*s*, −CH=N−).

[*EtGa*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)$] (*2c*). *2c* was prepared similarly to **2a** in (360 mg) 97% yield. Mp: 220 °C. Anal. Calcd for C₁₅H₁₄GaNO₂·0.5H₂O: C, 56.48; H, 4.74; N, 4.39. Found: C, 57.14; H, 4.55; N, 4.54. IR (ν in cm⁻¹): 1615 (C=N); 575 (Ga-C). ¹H NMR in DMSO- d_6 : 0.12 (q, ³J_{HH} = 7.6 Hz, $-CH_2Ga$); 0.75 (t, ³J_{HH} = 7.8 Hz, CH₃CH₂Ga); 6.57–6.74 (m, 5H); 7.04 (t, ³J_{HH} = 7.1 Hz, 1H); 7.27 (t, ³J_{HH} = 8.0 Hz, 1H); 7.37 (d, ³J_{HH} = 6.3 Hz, 1H); 7.55 (d, ³J_{HH} = 7.5 Hz, 1H); 8.89 (s, -CH=N-, 1H). ¹³C{¹H} NMR in DMSO- d_6 : 4.4 (s, $-CH_2Ga$); 10.2 (s, CH₃CH₂Ga); 115.5, 116.5, 117.6, 120.5, 122.2, 122.3, 130.0, 132.9, 134.4, 134.8, 157.8, 167.4 (s, -CH=N-).

[*EtGa*($-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-$)] (2d). 2d was prepared similarly to 2a in (350 mg) 92% yield. Mp: 175 °C (dec). Anal. Calcd for C₁₆H₁₆GaNO₃·0.5H₂O: C, 55.05; H, 4.90; N, 4.01. Found: C, 54.84; H, 4.73; N, 3.81. IR (ν in cm⁻¹): 1613 (C=N); 578 (Ga-C). ¹H NMR in DMSO- d_6 : 0.10 (q, ³ J_{HH} = 8.0 Hz, $-CH_2Ga$); 0.74 (t, ³ J_{HH} = 8.0 Hz, CH₃CH₂Ga); 3.75 (s, OMe); 6.57–6.67 (m, 3H); 7.01–6.92 (m, 3H); 7.54 (d, ³ J_{HH} = 7.8 Hz, 1H); 8.89 (s, -CH=N-).¹³C{¹H} NMR in DMSO- d_6 : 4.3 (s, $-CH_2Ga$); 10.2 (s, CH₃CH₂Ga); 56.1 (s, OMe); 115.2, 115.5, 117.5, 120.1, 125.6, 129.9, 132.9, 152.0, 157.8, 159.9 (s, -CH=N-).

[*Meln*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-$)] (2e). 2e was prepared similarly to 2a in (590 mg) 91% yield. Mp: 270 °C (dec). Anal. Calcd for C₁₅H₁₂InNO₂·0.5C₆H₆: C, 53.68; H, 3.97; N, 3.68. Found: C, 53.64; H, 4.04; N, 4.07. IR (ν in cm⁻¹): 1603 (C=N); 524 (In–C). ¹H NMR in DMSO-d₆: -0.28 (s, MeIn); 6.43 (t, ³J_{HH} = 7.3 Hz, 1H); 6.51 (t, ³J_{HH} = 7.2 Hz, 1H); 6.60 (t, ³J_{HH} = 7.3 Hz, 2H); 6.96 (t, ³J_{HH} = 7.5 Hz, 1H); 7.18 (t, ³J_{HH} = 7.7 Hz, 1H); 7.38 (d, ³J_{HH} = 7.3 Hz, 1H); 7.47 (d, ³J_{HH} = 7.8 Hz, 1H); 8.78 (s, -CH=N-, 1H). ¹³C{¹H} NMR in DMSO-d₆: -4.3 (s, MeIn); 113.5, 113.8, 115.7, 119.1, 120.4, 122.9, 128.6, 128.8 (benzene), 133.7, 134.2, 136.1, 159.2, 161.2, 171.4 (s, -CH=N-).

[*Meln*($-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-$)] (2f). 2f was prepared similarly to 2a in (500 mg) 97% yield). Mp: 280 °C (dec). Anal. Calcd for C₁₅H₁₄InNO₃: C, 48.55; H, 3.80; N, 3.77. Found: C, 47.61; H, 4.25; N, 3.47. IR (ν in cm⁻¹): 1603 (C=N); 526 (In-C). ¹H

NMR in DMSO- d_6 : -0.27 (s, MeIn); 3.69 (s, OMe); 6.45 (m, 2H); 6.58 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 1H); 6.81 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 1H); 6.93–7.02 (m, 2H); 7.45 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 1H); 8.75 (s, -CH=N-, 1H) [¹H NMR in CD₂Cl₂: -0.02 (s, MeIn); 4.00 (s, OMe); 6.56 (t, ${}^{3}J_{HH}$ = 7.5 Hz, 1H); 6.62 (d, ${}^{3}J_{HH}$ = 8.4 Hz, 1H); 6.96 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 1H); 7.06 (m,3H); 7.34 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 1H); 8.71 (s, -CH=N-, 1H]. 1³C{¹H} NMR in DMSO- d_6 : -4.2 (s, MeIn); 55.6 (s, OMe); 112.8, 113.7, 114.5, 115.7, 118.9, 119.6, 127.7, 128.6, 134.8, 152.4, 159.5, 160.8 (s, -CH=N-).

[*Etin*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-$)] (**2g**). **2g** was prepared similarly to **2a** in (510 mg) 96% yield. Mp: 215 °C (dec). Anal. Calcd for C₁₅H₁₄NO₂In·2H₂O: C, 46.06; H, 4.63; N, 3.58. Found: C, 46.24; H, 3.30; N, 1.90. IR (ν in cm⁻¹): 1610 (C=N); 525 (In-C). ¹H NMR in DMSO- d_6 : 0.56 (q, ³J_{HH} = 8.1 Hz, $-CH_2$ In); 1.24 (t, ³J_{HH} = 8.0 Hz, CH₃CH₂In); 6.42–6.53 (m, 3H); 6.59 (d, ³J_{HH} = 8.4 Hz, 1H); 6.96 (t, ³J_{HH} = 7.7 Hz, 1H); 7.18 (t, ³J_{HH} = 7.7 Hz, 1H); 7.37 (d, ³J_{HH} = 7.8 Hz, 1H); 7.45 (d, ³J_{HH} = 8.1 Hz, 1H); 8.75 (s, -CH=N-). ¹³C{¹H} NMR in DMSO- d_6 : 8.2 (s, $-CH_2$ In); 12.4 (s, CH₃CH₂In); 113.7, 113.9, 115.8, 119.1, 120.4, 123.0, 133.8, 134.3, 136.1, 159.3, 160.4, 161.0, 171.4 (s, -CH=N-).

[*Etln*($-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-$)] (2h). 2h was prepared similarly to 2a in (450 mg) 95% yield. Mp: 250. Anal. Calcd for C₁₆H₁₆InNO₃: C, 49.90; H, 4.19; N, 3.64. Found: C, 49.70; H, 4.60; N, 3.84. IR (ν in cm⁻¹): 1605 (C=N); 524 (In-C). ¹H NMR in CDCl₃: 0.90-0.99 (m, $-CH_2$ In); 1.08 (t, ³J_{HH} = 7.7 Hz, CH₃CH₂In); 3.98 (s, OMe); 6.51 (t, ³J_{HH} = 7.5 Hz, 1H); 6.67 (d, ³J_{HH} = 8.4 Hz, 1H); 6.81 (t, ³J_{HH} = 7.8 Hz, 1H); 6.94-7.02 (m, 3H); 7.30 (d, ³J_{HH} = 7.8 Hz, 1H); 8.60 (s, -CH=N-). ¹³C{¹H} NMR in CDCl₃: 5.6 (s, $-CH_2$ In); 11.5 (s, CH₃CH₂In); 56.2 (s, OMe); 114.5, 114.6, 115.0, 118.1, 120.0, 121.8, 126.1, 130.2, 132.6, 149.8, 156.9, 161.7 (s, -CH=N-).

[*MeGa*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-S-)$] (*3a*). 3a was prepared similarly to 2a in (1.13 g) 97% yield. Mp: 255 °C. Anal. Calcd for C₁₄H₁₂GaNOS.H₂O: C, 50.98; H, 4.28; N, 4.25. Found: C, 50.87; H, 4.05; N, 5.23. IR (ν in cm⁻¹): 1620 (C=N); 598 (Ga-C). ¹H NMR in DMSO- d_6 : -0.55 (s, MeGa); 6.75 (t, ³J_{HH} = 7.7 Hz, 1H); 7.05 (m); 7.33 (br); 7.46 (d, ³J_{HH} = 7.2 Hz); 7.59 (d, ³J_{HH} = 7.2 Hz); 8.73 (s, -CH=N-, 1H). ¹³C{¹H} NMR in DMSO- d_6 : -4.2 (s, MeGa); 117.0, 117.2, 120.4, 122.3, 124.1, 128.5, 131.0, 135.1, 135.5, 140.0, 142.5, 161.0, 166.0 (s, -CH=N-).

[*EtGa*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-S-$)] (**3b**). **3b** was prepared similarly to **2a** in (250 mg) 94% yield. Mp: 207 °C (dec). Anal. Calcd for C₁₅H₁₄GaNOS·0.5H₂O: C, 53.77; H, 4.51; N, 4.18. Found: C, 53.69; H, 4.41; N, 3.76. IR (ν in cm⁻¹): 1620 (C=N); 598 (Ga-C). ¹H NMR in DMSO- d_6 : 0.17 (q, ³J_{HH} = 7.6 Hz, $-CH_2Ga$); 0.70 (t, ³J_{HH} = 7.7 Hz, CH₃CH₂Ga); 6.73 (t, ³J_{HH} = 6.0 Hz, 2H); 6.80 (d, ³J_{HH} = 8.1 Hz, 1H); 7.03 (m, 3H); 7.45 (d, ³J_{HH} = 7.0 Hz, 1H); 7.60 (d, ³J_{HH} = 6.0 Hz, 1H); 8.79 (s, -CH=N-, 1H). ¹³C{¹H} NMR in DMSO- d_6 : 7.2 (s, $-CH_2Ga$); 10.4 (s, CH₃CH₂Ga); 116.8, 117.0, 122.1, 122.3, 123.9, 128.4, 130.9, 135.0, 135.4, 143.2, 161.2, 161.5, 166.4 (s, -CH=N-).

[*Meln*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-S-$)] (**3c**). **3c** was prepared similarly to **2a** in (920 mg) 97% yield. Mp: 290 °C (dec). Anal. Calcd for C₁₅H₁₂InNOS.2(H₂O): C, 42.74; H, 4.10; N, 3.56. Found: C, 41.68; H, 3.45; N, 3.42. IR (ν in cm⁻¹): 1603 (C=N); 537 (In–C). ¹H NMR in DMSO- d_6 : -0.30 (s, MeIn); 6.55 (t, ³J_{1HH} = 7.3 Hz, 1H); 6.63 (d, ³J_{HH} = 8.3 Hz, 1H); 6.98 (d, ³J_{1HH} = 7.3 Hz, 2H); 7.21–7.34 (m, 3H); 7.41 (d, ³J_{1HH} = 7.8 Hz, 1H); 8.26 (d, ³J_{1HH} = 2.7 Hz); 8.56 (s, -CH=N-, 1H). ¹³C{¹H} NMR in DMSO- d_6 : -2.1 (s, MeIn); 114.2, 119.3, 120.6, 123.1, 123.4, 126.7, 132.5, 134.7, 136.4, 141.1, 146.2, 165.1, 171.8 (s, -CH=N-).

[*Etln*($-O(2-C_6H_4)-CH=N(2-C_6H_4)-S--)$] (3*d*). 3*d* was prepared similarly to 2*a* in (0.28 g) 96% yield. Mp: 210 °C (dec). Anal. Calcd for C₁₅H₁₄InNOS: C, 48.54; H, 3.80; N, 3.77. Found: C, 48.35; H, 3.84; N, 3.49. IR (ν in cm⁻¹): 1616 (C=N); 539 (In-C). ¹H NMR in DMSO- d_6 : 0.52(q, ³J_{HH} = 8.0 Hz, $-CH_2$ In); 1.11 (t, ³J_{HH} = 7.6 Hz, CH₃CH₂In); 6.54 (t, ³J_{HH} = 6.7 Hz, 1H); 6.63 (d, ³J_{HH} = 8.4 Hz); 7.21-7.43 (m,); 8.58 (s, -CH=N-). ¹³C{¹H} NMR in DMSO- d_6 : 10.0 (s, $-CH_2$ In); 12.4 (S, CH₃CH₂In); 114.1, 119.2, 120.6, 123.0,

123.4, 126.7, 132.7, 134.6, 136.3, 141.2, 146.4, 164.9, 172.0 (s, – CH=N–).

X-ray Crystallography. Intensity data for $[MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)]$ (2a) and $[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)]$ (2b) crystallized from dichloromethane (both triclinic) were collected at room temperature on a Rigaku AFC 7S diffractometer using graphite-monochromated Mo K α radiation. The structures were solved using direct methods³² and refined by full matrix least-squares method on $F^{2,33}$ using data corrected for absorption effects using empirical procedures.³⁴ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in their geometrically idealized positions with coordinates and thermal parameters riding on host atoms. The molecular structures are drawn using ORTEP.³⁵ Crystallographic and structural determination data are given in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

CCDC-Nos. 848250 and 848251 contain the supplementary crystallographic data for $[MeGa(-O(2-C_6H_4)-CH=N(2-C_6H_4)-O-)]$ (2a) and $[MeGa(-O(2-C_6H_3OMe-3)-CH=N(2-C_6H_4)-O-)]$ (2b), respectively, for this paper. This material is available free of charge via the Internet at http:// pubs.acs.org. These data can also 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: deposit@ccdc.cam.ac.uk]. Optimized structures of the ligands and the selected geometricla parameters of the complexes.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Drs. T. Mukherjee and D. Das for encouragement of this work.

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