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Synthesis, characterization and luminescence study of dialkyl[1-arylmethyleneimino-2-naphthonato]gallium complexes: Crystal structure of dimethyl[1-(2-pridyl) methyleneimino-2-naphthonato]gallium

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Abstract

Eight dialkylgallium complexes of type R_2GaL [(M = Me, L = 1-(2-pyridyl)methyleneimino-2-naphthonato (**1**), M = Et, L = 1-(2-pyridyl)methyleneimino-2-naphthonato (**2**), M = Me, L = 1-phenylmethyleneimino-2-naphthonato (**3**), M = Et, L = 1-phenylmethyleneimino-2-naphthonato (**4**), M = Me, L = 1-(*p*-methoxylphenyl)methyleneimino-2-naphthonato (**5**), M = Me, L = 1-(3,4-dimethoxylphenyl)methyleneimino-2-naphthonato (**6**), M = Me, L = 1-naphthylmethyleneimino-2-naphthonato (**7**), M = Me, L = 1-naphthylmethyleneimino-2-naphthonato (**8**)) have been synthesized by reaction of trialkylgallium with appropriate 1-arylmethyleneimino-2-naphthols. The complexes have been characterized by elemental analysis, ^1H NMR, IR and mass spectrometry. Structure of dimethyl[1-(2-pyridyl)methyleneimino-2-naphthonato]gallium (**1**) has been determined by X-ray single crystal analysis. Ga atom is five coordinate in the structure. Photoluminescent properties have been measured. The maximum emission wavelengths are in the range of 358 and 412 nm with the intensity of 13–325 a.u. The electroluminescent properties of **3**, **5**, **7** and **8** have been measured. The maximum emission wavelengths are in the range of 450 and 480 nm.

Keywords: Trialkylgallium; Electroluminescent; X-ray crystal structure

1. Introduction

Since the first observation of electroluminescence (EL) in 1965 [1], EL devices have been extensively studied due to their potential application to fullcolor flat panel displays, a high performance device fabricated by Tang and VanSlyke using two-layer light-emitting diodes (LEDS) with organic fluorescent dyes was a breakthrough in this field [2]. Then a number of organic materials have been developed as luminescent materials including small molecular systems and aromatic organic polymer [3–6]. Organometallic complexes are very promising candidates as emitting materials in the OLEDs. Although quite a few metallic complexes such as 8-hydroxyquinoline or azomethine coordinated Al(III), Be(II), Zn(II) complexes have been studied [7–10], few group 13 organometallic complexes-based electroluminescent diodes were known [11,12]. So development of various electroluminescent materials and study the relationship between structure and electroluminescence property are in great need. Recently, we reported some light-emitting materials based on group 13 organometallic complexes [13–16]. In order

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to search for the new electroluminescent materials, we report here the synthesis and characterization of various dialkyl[1-arylmethyleneimino-2-naphthonato]gallium complexes, Both the photoluminescent and electroluminescent properties of the complexes have been measured and discussed as well.

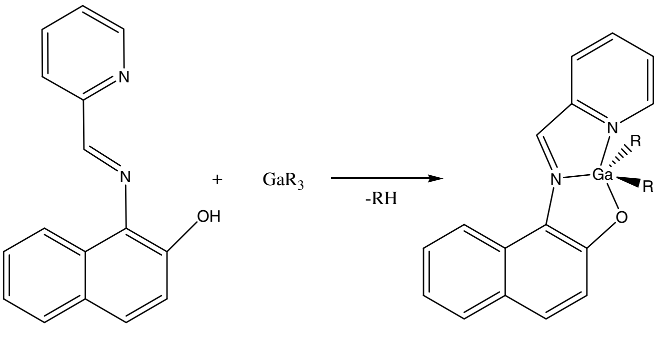
2. Results and discussion

2.1. Synthesis and characterization

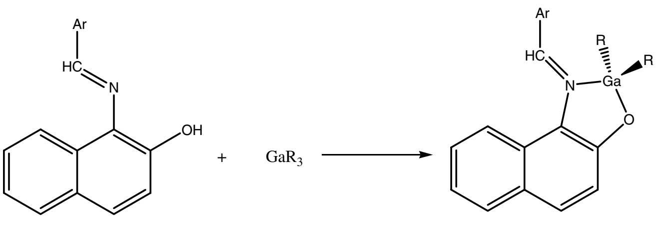
Reaction of 1-arylmethyleneimino-2-naphthols, which were obtained by condensation of 1-amino-2-naphthol with 2-pridylaldehyde, benzaldehyde, *p*-methoxybenzaldehyde, 3,4-dimethoxy-benzaldehyde, 1-naphthalaldehyde and 9-anthralaldehyde, with trimethyl- or triethylgallium proceeded smoothly at room temperature and afforded the corresponding dialkylgallium complexes in almost quantitative yields (Schemes 1, 2 and Table 1). The complexes isolated are deep red or brown solids. Although trialkylgallium is extremely moisture and oxygen sensitive, the complexes obtained are fairly stable on exposure to air and they could be left in ambient atmosphere for months without obvious decomposition. The complexes are nearly insoluble in cold saturated hydrocarbons such as pentane or petroleum and are fairly soluble in unsaturated hydrocarbons such as benzene or toluene. All the products obtained gave satisfactory elemental analysis results as expected for the stoichiometric structure R_2GaL. The compounds obtained have been characterized by IR, ^{1}H NMR and MS spectroscopy, respectively. In the IR spectra of the complexes, appearance of visible alkyl C–H vibration from the gallium-bonded alkyl groups and the disappearance of O–H vibration comparing with the free ligands prove the reaction of trialkylgallium with the hydroxyl group of the ligands. The stretch vibration of C=N bond appeared at higher frequency than those of the free ligands, suggesting in some extent the coordination of imino nitrogen atom to the gallium metal. The chemical shifts of the gallium–bonded methyl or methylene protons in their ^{1}H NMR spectra appeared at higher field compared with those of the free gallium trialkyls, implying the coordination of the nitrogen atom to gallium, as the coordination of nitrogen atom to gallium should increase the electron density around the metal center. The molecule ion peaks of the complexes were all visible in their MS spectra and the fragments eliminating one methyl or ethyl group appeared in high intensity. The relative intensity of the gallium-containing peaks in the MS spectra agrees well with the isotopic distribution of the gallium atom [^{69}Ga (ca. 60%); ^{71}Ga(ca. 40%)]. These indicate that the complexes exist as intramolecularly coordinated monomeric species.

Table 1
Synthesis of complexes **1**–**8**

Compound number	R	Ar
1	Me	2-Pyridyl
2	Et	2-Pyridyl
3	Me	Phenyl
4	Et	Phenyl
5	Me	*p*-Methoxylphenyl
6	Me	3,4-Dimethoxylphenyl
7	Me	1-Naphthyl
8	Me	9-Anthryl



Scheme 1. Synthesis of complexes **1**–**2**.



Scheme 2. Synthesis of complexes **3**–**8**.

2.2. Solid-state structure of *1*

Single crystals of **1** was obtained by recrystallization of a saturated benzene solution containing **1** at −20 °C. The

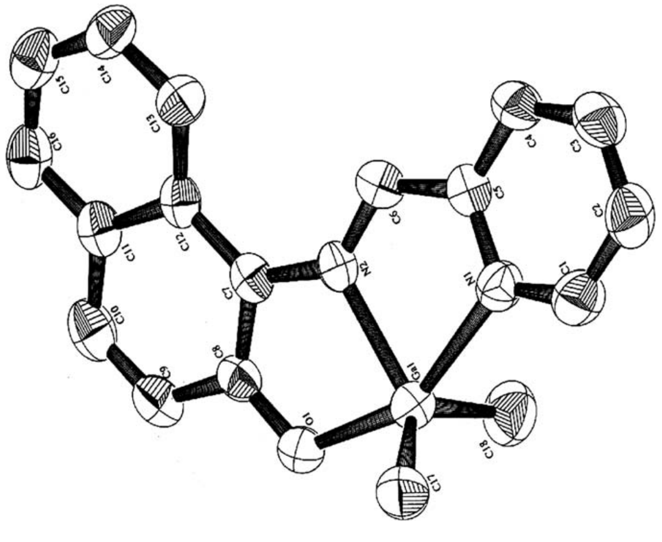


Fig. 1. Molecular structure of **1**, showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Crystal data, collection parameters, and refinements for **1**

Formula	$C_{18}H_{17}GaN_2O$
Formula weight	347.07
Crystal color	Deep red
Crystal dimensions (mm)	1.00 × 0.80 × 0.80
Crystal system	Monoclinic
Space group	*P*21/*c* (#14)
a (Å)	14.800 (2)
b (Å)	7.344 (5)
c (Å)	15.809 (3)
β (°)	110.35 (1)
V (Å^3)	1611.0300
Z value	4
D_{calc} (g/cm^3)	1.431
F_{000}	712.00
μ (Mo Kα) (cm^{-1})	17.10
Diffractometer	RAXIS-IV
Radiation	Mo Kα ($\lambda = 0.71070$ Å)
Temperature (K)	288
$2\theta_{max}$ (°)	55.0
Number of reflections measured	2496
Independent reflections observed (I) > 3.00 ($\sigma(I)$)	1867
Number of variables	251
Correction	Lorentz polarization
R (*F*)	0.052
wR	0.077
Goodness-of-fit indicator	1.24
$\Delta\rho_{max}$ (e Å^{-3})	0.55
$\Delta\rho_{min}$ (e Å^{-3})	−0.54
$(\Delta/\sigma)_{max}$	0.00

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$; $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.00490P)^2], P = (F_o^2 + 2F_c^2)/3$.
[c] $S = [\sum w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$. *n*, number of reflections; *p*, parameters used.

result of the X-ray structure analysis of **1** is depicted in Fig. 1. Crystal data, collection and refinement parameters are summarized in Table 2 and selected bond length (Å) and angles (°) are given in Table 3. Complex **1** crystallizes in the monoclinic space group *P*21/*c* (#14). In compound **1**, the nitrogen atom in the pyridyl group coordinates to the gallium atom, apart from the coordination of the imino nitrogen, to form another intramolecularly coordinated five-membered ring. It shows clearly the coordination of two nitrogen atoms to the gallium with formation of two new five-membered rings. Gallium atom is five coordinate in the compound in the geometry of trigonal bipyramidal. The naphthyl plane and the pyridyl plane are almost coplanar connected by a C=N bridge, suggesting that a good conjugation π-electrons system is formed in the structure. The compound exists as a monomer in the solid state, in spite of quite a few dimethylgallium alkoxides and phenoxides were found to be dimeric with a planar Ga_2O_2 ring [17–19]. Ga–O1 distance (2.002(4) Å) in **1** is longer than those reported in *N*,*N*-ethylenbis(salicylideneiminato)[dimethylgallium] (1.869(2) and 1.874(2) Å, respectively) [20], dimethylgallium *N*-methylsalicylaldiminate (1.904(7) Å) [21] and dimethylgallium[2-(*N*,*N*-dimethylaminomethyl)-4-methyl]phenoxide 1.890(4) Å) [22]. The Ga–N distances (2.303(4) Å for Ga–N1 and 2.115(5) Å for Ga–N2 are also longer than those reported for Ga–N covalent and coordinative bond lengths as in (α-pyridyl)acetophenone Ga–N (2.027(2) Å) [23], $Me_3GaNH_2{}^t Bu$ (2.12(1) Å) [24] and dimethylgallium-[2-(*N*,*N*-dimethylaminomethyl)-4-methyl]-phenoxide (2.096(6) Å) [22]. The apparent difference in Ga–O and Ga–N length between the present compound (**1**) with other known compounds should be caused by the steric requirements of formation of the two rigid five-membered rings.

Table 3
Selected bond distances (Å) and angles (°) for **1**

Bond distances			
Ga–O1	2.002 (4)	Ga–N1	2.303 (4)
Ga–N2	2.115 (5)	O1–C8	1.303 (6)
C5–C6	1.456 (8)	N1–C5	1.353 (7)
C7–C12	1.451 (7)	N2–C7	1.394 (6)
C9–C10	1.341 (9)	C7–C8	1.412 (7)
C11–C12	1.435 (8)		
Bond angles			
O1–Ga1–N1	153.2 (2)	N1–Ga1–N2	78.9 (2)
Ga1–O1–C8	115.0 (3)	Ga1–N1–C5	111.5 (3)
Ga1–N2–C6	117.2 (4)	C17–Ga1–N2	112.7 (3)
N1–C5–C6	114.9 (54)	C17–Ga1–C18	126.9 (4)
N2–C6–C5	120.0 (5)	C1–N1–C5	118.3 (5)
O1–C8–C7	121.3 (5)	Ga1–N2–C7	112.7 (3)
O1–Ga1–N2	78.9 (2)	N2–C7–C8	111.9 (5)

3. Photoluminescence study

Photoluminescence (PL) emission spectra of the complexes **1**–**8** were measured as shown in Fig. 2. It shows that the emission bands are located in ultraviolet to violet-blue region from 377 to 412 nm and most of them appeared as multi-peaks. The emission maximum wavelengths and intensities are summarized in Table 4. The emission strength of the pyridyl containing complexes is obviously lower than those of the phenyl- or naphthyl-containing ones, implying that the electro-withdrawing pyridyl group is disadvantageous to light-emission. Emission wavelength

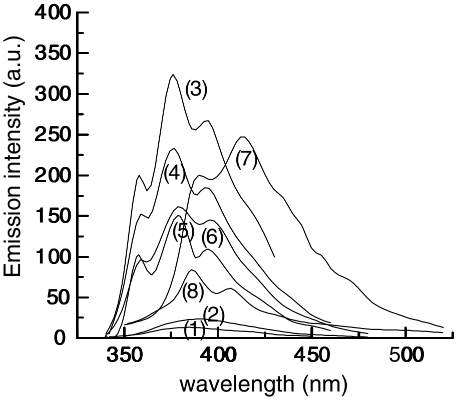


Fig. 2. PL emission spectra of **1**–**8** in solid state.

Table 4
Wavelength and emission intensity of the complexes **1**–**8**

Compound number	Wavelength (cm^{-1}) (intensity, a.u.)		
1	385 (13)		
2	396 (23)		
3	370 (267)	380 (325)	395 (267)
4	370 (200)	377 (233)	383 (200)
5	358 (102)	380 (150)	395 (109)
6	359 (97)	379 (162)	396 (145)
7	390 (250)	412 (247)	
8	386 (84)	407 (61)	

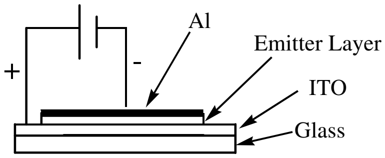


Fig. 3. Configuration of EL cell.

of the compound **7** is longer than that of **8**, and the emission intensity of the compound **7** is also relatively better than that of **8**. The difference in emission wavelengths and intensities between the compound **7** and **8** should reflect their difference in structure. Considering the π-system of anthryl group is larger than that of the naphthyl group, the abnormal blue-ward shift of emission wavelength and the poor emission intensity should imply that the anthryl group in the compound **8** may not conjugate very well with other part π-system of the compound. The poor coplanarity of the compound may be caused by the steric repellency between the anthryl group and the other part of the compound. Energy optimized molecular modeling shows clearly that the two naphthyl groups in the compound **7** is almost coplanar, while the naphthyl group and the anthryl group in the compound **8** is impossible to locate in one plane. There is a strong steric repellency between the anthryl group and the dimethylgallium group in **8**.

4. Electroluminescence study

Compounds **3**, **5**, **7** and **8** were selected as light emitting material. The electroluminescence device structure is shown in Fig. 3. The gallium complexes were used as light-emitting layer. The complexes were dissolved in dichloromethane. The device was prepared on patterned indium–tin-oxide (ITO) coated on glass substrate, which was cleaned by ultrasonic in a mixture of isopropanol and water (1:1) and degreased in toluene vapor, with a sheet resistance of near 80 Ω/□ . Due to the poor film-forming properties of the complexes, a very small quantity of poly(methylmethacrylate) (PMMA), which is inert to light and electricity, was used to improve the film-forming properties by mixing it with the organogallium complexes. A device structure of ITO/emissive layer/Al was employed. High-quality film can be obtained by spin-cast of PMMA and gallium complexes mixture dissolved in dichloromethane. An electron injecting electrode Al was deposited on top by vacuum evaporation at pressure below 2×10^{-5} Torr with a deposition rate of 10–15 Å/s. The emitting area was $2 \times 3\ mm^2$. The luminance of the EL devices was measured with a Perkin–Elmer LS 50B fluorescence spectraphotometer. Meanwhile, the current density was recorded with a digital multimeter. All measurements were carried out at room temperature under DC bias conditions.

The current–voltage relationship of the EL device is shown in Fig. 4. The forward bias current can be obtained when the ITO electrode is positively biased and the Al electrode negatively. The current density, increasing proportional to the bias voltage, increases from 1 to 185 mA/cm^2 for complex **3** (1–18 V), from 1 to 105 mA/cm^2 for complex **5** (1–23 V), from 4 to 206 mA/cm^2 for complex **7** (1–16 V), and from 16 to 128 mA/cm^2 for complex **8** (1–30 V). The current density increasing rate for complex **3** and **7** are much larger than those of the complexes **5** and **8**, implying that there is a stronger electron interaction between the molecules in **3** and **7**. This is reasonable considering the nature of substitutes on the phenyl ring or the coplanarity of the molecules. The break down voltage is 18, 23, 20 and 30 V for complexes **3**, **5**, **7** and **8**, respectively.

The EL intensity-voltage relationship of the EL devices for the complexes **3**, **5**, **7** and **8** was measured as shown in Fig. 5. The light output of the EL diodes is proportional to the input voltage in the voltage range of 8–18 V (**3**), 18–23 V (**5**), 10–20 V (**7**) and 20–30 V (**8**). Complexes **5** and **7** exhibit relatively higher EL intensities than the other two. Good luminescent characteristic of the complex **5** may attribute to the methoxyl group on the phenyl ring. Steric hindrance of the methyl group decreases electron-interaction between the molecules, then subdues thermo-quenching of excitons. For complex **7**, it should be due

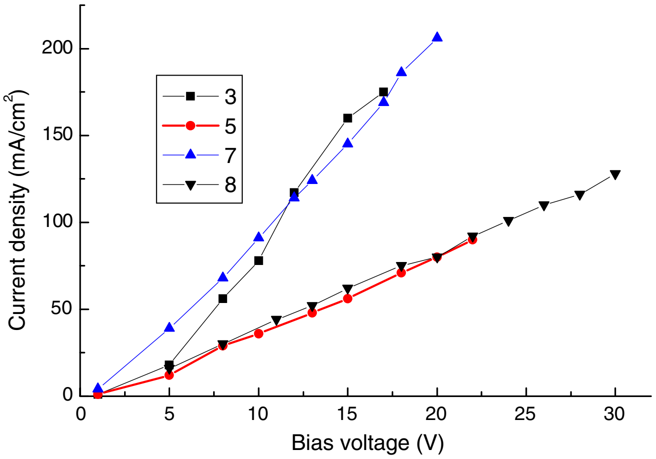


Fig. 4. The relationship of current density and voltage of diodes with the emitter of complexes **3**, **5**, **7** and **8**.

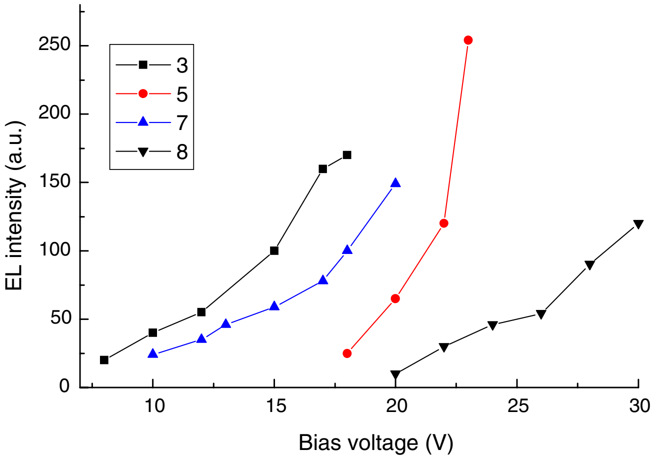


Fig. 5. EL intensity–voltage curves the emitter of complexes **3**, **5**, **7** and **8**.

to the large π-delocalized system formed between the two naphthyls. Lower EL intensity of complex **8** than that of complex **7** is shown as expected due to the poor coplanarity of the anthryl plane and the naphthyl plane. The result demonstrates that the different substitutes on the Schiff-base ligands have different effect on the EL characteristics of the EL diodes. The turn-on voltage of complexes **3**, **5**, **7** and **8** are 8, 18, 10, 20 V, respectively, which are much lower than that of tri(1,3-diphenyl-1,3-propanediono) of diodes with monophenathroline)-europium(III) (25 V) [25].

The EL spectra of the complexes **3**, **5**, **7** and **8** were shown in Fig. 6. Their emission wavelengths are located in the blue region from 450 to 478 nm (450, 469, 475 and 478 nm for the complexes **3**, **5**, **7** and **8**, respectively). The emission wavelengths of the EL diodes are obviously related to the structure of the ligands. Different substitutes have different effects on the emission wavelength. The role of gallium atom for the EL emission is considered to be the twofold. Firstly, the formation of covalent bonds between the gallium and oxygen or nitrogen atoms changes the levels of the transition energy. Secondly, the binding of ligand to gallium atom increases the rigidity of the complexes, thus reduces the loss of energy via vibration motions, i.e., thermo-quenching process and then increases the emission efficiency.

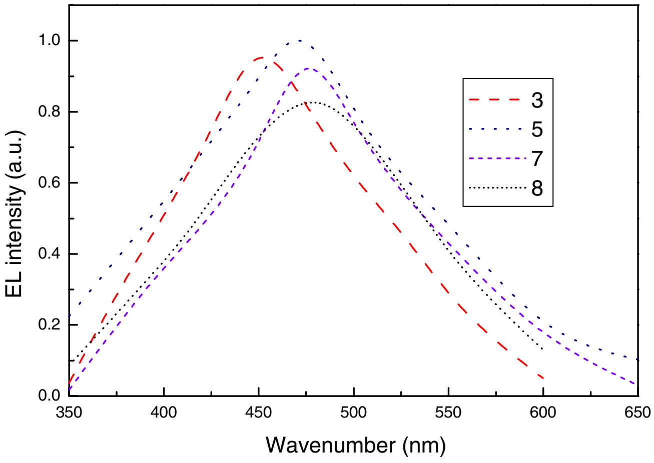


Fig. 6. EL spectra of diodes with the emitter of complexes **3**, **5**, **7** and **8**.

5. Experimental

5.1. General comments

All reactions were performed in a glove box under purified nitrogen. The solvents were refluxed with sodium benzophenone and distilled under nitrogen prior to use. The Schiff-base ligands were prepared by condensation of salicylaldehyde with 1-amino-2-naphthol. Trimethylgallium and triethylgallium were provided by the National 863 Program Advanced Material MO Precursors R&D Center of China. ^{1}H NMR data were collected on a Bruder ARX-300 spectrometer with TMS as internal Standard. Infrared spectra were collected as KBr pellets on a Shimadzu IR 408 instrument. Mass spectra were measured on VG-ZAB-HS spectrometer (electron impact ionization), luminescent spectra was determined with Shimadzu F-5000 fluorescence spectrophotometer, Elemental analysis was performed on a Perkin–Elmer 240C elemental analyzer. Melting point was observed in sealed capillaries and was uncorrected.

The photoluminescence (PL), electroluminescence (EL) and the relative emission intensity were measured with Shimadzu F-5000 fluorescence spectra-photometer, and the absorption spectra were measured with Shimadzu UV2010 spectra-photometer. The current density was recorded with a digital multimeter.

*5.2. Preparation of dimethyl[1-(2-pyridyl)methyleneimino-2-naphtha onato]gallium (**1**)*

A solution of trimethylgallium (1.15 g, 10 mmol) in 10 mL of cyclohexane was added dropwise over a period of 10 min with stirring to a solution of 1-(2-pridyl)methyleneimino-2-naphthol (2.48 g, 10 mmol) in 10 mL of cyclohexane and 2 mL of benzene. After stirring the reaction mixture for an additional 15 min at room temperature, all volatiles are removed in oil-pump vacuo and the yellow powder was recrystallized from cyclohexane/benzene solution, giving cardinal crystals. Yield: 3.1 g (89.3% based on TMGa).

M.p.: 148–150 °C (dec). Anal. Calc. for $C_{18}H_{17}N_2OGa$: C, 62.29; H, 4.94; N, 8.07. Found: C, 62.16; H, 4.59; N, 8.15%. IR data (cm^{-1}): 3051 (vw), 2959 (w), 1610 (m), 1595 (s), 1554 (m), 1530 (m), 1502 (s), 1480 (m), 1449 (vs), 1440 (vs), 1390 (m), 1364 (w), 1344 (s), 1311 (m), 1261 (w), 1208 (m), 1150 (s), 1138 (vs), 1081 (w), 1006 (w), 829 (w), 766 (m), 751 (m), 725 (m), 577 (w). ^{1}H NMR data (ppm): 9.31 (s, 1H, $-C\mathit{H}{=}N$) 7.12–8.63 (m, 10H, Ar–*H*) 0.25 (s, 6H, $Ga(C\mathit{H}_3)_2$). MS data: 347.9 (M^+, 4.56%), 346.0 (6.72%), 334.0 (13.45%), 333.0 (69.52%), 332.0 (20.37%), 331.0 (100.00%), 317.8 (4.16%), 316.8 (7.97%), 315.9 (6.85%), 314.8 (8.48%), 301.7 (4.23%), 247.0 (19.34%), 239.9 (3.72%), 237.9 (4.85%), 219.0 (3.97%), 100.9 (4.82%), 98.9 (6.52%), 79.0 (1.11%), 78.1 (3.59%), 70.9 (20.82%), 68.9 (31.31%).

*5.3. Preparation of diethyl[1-(2-pyridyl)methyleneimino-2-naphthonato]gallium (**2**)*

Prepared and purified in the method as described for **1** from 1-(2-pridyl)methyleneimino-2-naphthol (2.48 g, 10 mmol) and triethylgallium (1.57 g, 10 mmol). The compound was isolated as orange crystal. Yield: 3.05 g (81.5% based on TEGa).

M.p.: 109–110 °C. Anal. Calc. for $C_{20}H_{21}N_2OGa$: C, 64.04; H, 5.64; N, 7.47. Found: C, 64.25; H, 5.79; N, 7.74%. IR data (cm^{-1}): 3052 (w), 2931 (w), 2895 (w), 2857 (w), 1613 (m), 1594 (m), 1553 (s), 1529 (m), 1504 (s), 1444 (vs), 1393 (m), 1343 (m), 1333 (m), 1311 (m), 1259 (w), 1209 (m), 1147 (m), 1139 (s), 1080 (w), 1006 (w), 829 (w), 764 (m), 741 (m), 557 (m), 499 (w). ^{1}H NMR data (ppm): 9.34 (s, 1H, –C*H*=N), 7.14–8.65 (m, 10H, Ar–*H*), 0.87 (q, 4H, $\mathrm{Ga}\mathit{CH}_2\mathrm{CH}_3$), 0.46 (t, 6H, $\mathrm{GaCH_2}\mathit{CH}_3$), MS data: 374.8 (M$^+$, 1.05%), 347.9 (13.70%), 346.9 (67.74%), 345.9 (21.59%), 344.8 (100.00%), 332.8 (3.18%), 330.9 (4.73%), 317.9 (7.49%), 316.9 (13.33%), 315.9 (11.08%), 314.9 (14.13%), 291.3 (3.78%), 298.8 (3.37%), 248.0 (6.82%), 247.0 (18.85%), 246.0 (14.27%), 239.9 (5.45%), 237.9 (8.20%), 219.0 (8.89%), 170.0 (5.24%), 115.0 (5.94%), 114.0 (5.71%), 79.0 (4.01%), 70.9 (29.03%), 68.9 (44.33%).

*5.4. Preparation of dimethyl[1-benzylideneimino-2-naphthonato]gallium (**3**)*

Prepared and purified in the same manner as described for **1** from 1-benzylideneimino-2-naphthol (3.46 g, 10 mmol) and trimethylgallium (1.15 g, 10 mmol). The compound was isolated as orange crystal. Yield: 3.07 g (88.5% based on TMGa).

M.p.: 120–121 °C. Anal. Calc. for $C_{19}H_{18}NOGa$: C, 65.94; H, 5.24; N, 4.05. Found: C, 63.87; H, 5.63; N, 4.06%. IR data (cm^{-1}): 3055 (vw), 2921 (m), 2844 (w), 1617 (w), 1593 (s), 1574 (w), 1508 (m), 1462 (s), 1449 (w), 1430 (w), 1253 (m), 1282 (s), 1256 (s), 1224 (w), 1200 (m), 1001 (m), 853 (vw), 810 (m), 758 (s), 744 (s), 727 (m), 689 (m). ^{1}H NMR data (ppm): 9.31 (s, 1H, –C*H*=N), 7.17–8.41 (m, 11H, Ar–*H*), 0.23 (s, 6H, $\mathrm{GaC}\mathit{H}_3$). MS data: 347.9 (M$^+$, 2.57%), 346.9 (12.37%), 345.9 (5.54%), 344.9 (18.03%), 332.9 (13.55%), 332.0 (67.70%), 330.9 (20.52%), 330.0 (100.00%), 317.9 (4.35%), 317.0 (16.45%), 316.0 (10.07%), 315.0 (23.75%), 314.0 (5.80%), 247.0 (15.82%), 246.0 (40.16%), 245.0 (6.26%), 243.9 (5.42%), 242.9 (4.84%), 241.9 (8.12%), 240.9 (6.11%), 228.9 (7.37%), 227.9 (5.31%), 226.9 (11.30%), 225.9 (5.42%), 211.9 (4.03%), 150.9 (4.13%), 115.01 (4.94%), 114.0 (5.68%), 100.9 (14.45%), 98.9 (19.75%), 70.9 (42.11%), 68.9 (63.11%).

*5.5. Preparation of diethyl[1-benzylideneimino-2-naphthonato]gallium (**4**)*

Prepared and purified in the same manner as described for **1**. The compound was isolated as orange crystal. Yield: 3.11 g (82.3% based on TEGa).

M.p.: 180–182 °C. Anal. Calc. for $C_{21}H_{22}NOGa$: C, 67.42; H, 5.93; N, 3.74. Found: C, 66.43; H, 6.24; N, 3.78%. M.p.: 153–154 °C. IR data (cm^{-1}): 3057 (w), 2934 (m), 2859 (m), 1612 (m), 591 (s), 1574 (m), 1507 (m), 1461 (s), 1429 (m), 1362 (m), 1351 (m), 1283 (s), 1257 (m), 1225 (w), 1000 (m), 817 (m), 809 (m), 759 (m), 745 (m), 729 (m), 691 (w), 643 (m). ^{1}H NMR data (ppm): 8.30 (s, 1H, –C*H*=N) 7.17–8.01 (m, 11H, Ar–*H*) 0.94 (q, 4H, $\mathrm{Ga}\mathit{CH}_2\mathrm{CH}_3$), 0.43 (t, 6H, $\mathrm{GaCH_2C}\mathit{H}_3$). MS data: 374.9 (M$^+$, 5.32%), 372.9 (7.74%), 346.9 (15.51%), 345.9 (69.24%), 344.9 (20.88%), 343.9 (100.00%), 317.9 (6.04%), 317.0 (27.34%), 316.0 (11.81%), 315.0 (40.55%), 314.0 (5.48%), 290.6 (5.34%), 288.6 (7.92%), 247.0 (6.62%), 246.0 (26.61%), 211.9 (5.30%), 115.0 (8.70%), 70.9 (53.28%), 68.9 (79.88%).

*5.6. Preparation of dimethyl[1-(4-methoxy)benzylideneimino-2-naphthonato]gallium (**5**)*

Prepared and purified in the same manner as described for **1** from 1-(4-methoxy)-benzylideneimino-2-naphthol (2.77 g, 10 mmol) and trimethylgallium (1.15 g, 10 mmol). The compound was isolated as orange crystal. Yield: 3.16 g (84.1% based on TEGa).

M.p.: 197–198 °C. Anal. Calc. for $C_{20}H_{20}NO_2Ga$: C, 63.87; H, 5.36; N, 3.72. Found: C, 63.87; H, 5.63; N, 3.26%. IR data (cm^{-1}): 3064 (vw), 2969.3 (w), 2959.3 (w), 1614.5 (w), 1592.7 (s), 1571.7 (m), 1511 (vs), 1461 (m), 1422 (w), 1362 (m), 1271 (vs), 1256 (s), 1199 (s), 1173 (w), 1142 (m), 1023 (m), 998 (m), 863 (w), 814 (m), 752 (m), 677 (m). ^{1}H NMR data (ppm): 9.11 (s, 1H, –C*H*=N), 7.06–7.95 (m, 10H, Ar–*H*), 3.94 (s, 3H, $-\mathrm{OCH_3}$), 0.23 (s, 6H, $\mathrm{Ga(CH_3)_2}$). MS data: 378.0 (M$^+$, 3.18%), 377.0 (14.68%), 376.0 (5.18%), 374.9 (21.77%), 363.0 (13.87%), 362.0 (67.11%), 361.0 (23.12%), 360.0 (100.00%), 348.1 (6.59%), 347.0 (16.54%), 346.0 (12.03%), 345.0 (23.78%), 344.0 (5.62%), 330.7 (4.17%), 276.9 (12.97%), 275.9 (36.37%), 274.9 (5.44%), 233.0 (6.32%), 211.8 (4.70%), 204.0 (4.27%).

*5.7. Preparation of dimethyl[1-(3,4-dimethoxy)-benzylideneimino-2-naphthonato]gallium (**6**)*

Prepared and purified in the same manner as described for **1** from 1-(3,4-dimethoxy)benzylideneimino-2-naphthol (3.07 g, 10 mmol) and trimethylgallium (1.15 g, 10 mmol). The compound was isolated as orange crystal. Yield: 3.51 g (85.1% based on TMGa).

M.p.: 200–201 °C. Anal. Calc. for $C_{21}H_{22}NO_3Ga$: C, 62.21; H, 5.47; N, 3.46. Found: C, 62.42; H, 5.66; N, 3.35%. IR data (cm^{-1}): 3051 (w), 2967 (w), 2900 (w), 2833 (w), 1607 (m), 1585 (s), 1547 (w), 1511 (m), 1462 (m), 1429 (w), 1375 (m), 1350 (m), 1315 (m), 1187 (s), 1148 (s), 999 (w), 926 (m), 851 (m), 797 (w), 780 (s), 759 (s). ^{1}H NMR data (ppm): 9.09 (s, 1H, –C*H*=N), 7.02–7.96 (m, 9H, Ar–*H*), 3.99–4.02 (d, 6H, –OC*H*$_3$), 0.188 (s, 6H, GaC*H*$_3$). MS data: 407.1 (M$^+$, 15.05%), 405.2 (21.03%), 393.7 (16.34%), 392.8 (73.37%), 391.8 (24.09%), 390.8 (100.00%), 378.1 (13.84%), 377.0 (10.29%), 376.1 (20.43%), 375.0 (6.11%), 307.1 (10.77%), 306.1 (23.35%), 290.1 (7.06%), 221.0 (4.11%), 100.9 (6.77%), 98.9 (9.50%), 70.9 (17.97%), 68.9 (26.79%).

5.8. Preparation of dimethyl[1-(1-naphthyl)-methylenenimino-2-naphthonato]gallium (7)

Prepared and purified in the same manner as described for **1** from 1-(1-naphthyl)-methyleneimino-2-naphthol (2.97 g, 10 mmol) and trimethylgallium (1.15 g, 10 mmol). The compound was isolated as orange red crystal. Yield: 3.31 g (83.4% based on TMGa).

M.p.: 116–117 °C. Anal. Calc. for $C_{23}H_{20}NOGa$: C, 69.74; H, 5.09; N, 3.54. Found: C, 69.94; H, 5.09; N, 3.47%. IR data (cm^{-1}): 3058 (w), 2957 (w), 1685 (w), 1615 (m), 1591 (vs), 1573 (m), 1506 (vs), 1461 (w), 1433 (m), 1371 (m), 1353 (m), 1336 (s), 1162 (vw), 1000 (m), 968 (s), 820 (m), 807 (w), 790 (s), 768 (vs), 711 (m), 694 (m). ^{1}H NMR data (ppm): 10.04 (s, 1H, –C*H*=N), 7.2–8.12 (m, 13H, Ar–*H*), 0.33 (s, 6H, Ga(CH$_3$)$_2$). MS data: 397.1 (M$^+$, 13.52%), 396.1 (5.28%), 395.1 (19.40%), 383.3 (17.09%), 382.4 (70.95%), 381.4 (26.67%), 380.4 (100.00%), 368.4 (5.45%), 367.4 (10.08%), 366.4 (22.54%), 365.4 (14.25%), 364.4 (27.08%), 351.7 (9.31%), 349.9 (7.22%), 348.4 (8.40%), 297.0 (8.67%), 296.0 (31.81%), 115.0 (9.62%), 100.9 (8.40%), 98.9 (12.23%), 70.9 (29.92%), 68.9 (43.97%).

5.9. Preparation of dimethyl[1-(9-anthryl)methyleneimino-2-naphthonato]gallium (*8*)

Prepared and purified in the same manner as described for **1** from 1-(9-anthryl)-methylenenimino-2-naphthol (3.64 g, 10 mmol) and trimethylgallium (1.15 g, 10 mmol). The compound was isolated as orange crystal. Yield: 3.62 g (78.7% based on TMGa).

M.p.: >200 °C (dec.). Anal. Calc. for $C_{27}H_{22}NOGa$: C, 72.68; H, 4.97; N, 3.14. Found: C, 72.48; H, 4.67; N, 3.44%. IR data (cm^{-1}): 3050 (w), 2997 (w), 2904 (w), 1617 (m), 1591 (s), 1508 (m), 1462 (s), 1431 (m), 1372 (w), 1351 (m), 1283 (s), 1255 (s), 1209 (w), 1169 (m), 1155 (w), 1144 (w), 996 (m), 886 (m), 818 (m), 750 (s), 732 (vs), 701 (w), 646 (m). ^{1}H NMR data (ppm): 10.23 (s, 1H, –C*H*=N), 7.26–8.69 (m, 16H, Ar–*H*), 0.86 (s, 6H, Ga(CH$_3$)$_2$). MS data: 447.0 (M$^+$, 11.51%), 446.0 (5.16%), 445.1 (15.98%), 433.3 (20.20%), 432.3 (68.42%), 431.3 (30.76%), 430.3 (100.00%), 417.3 (8.06%), 416.2 (22.23%), 415.3 (11.14%), 414.3 (27.37%), 399.8 (18.43%), 347.0 (10.69%), 346.0 (36.09%), 262.9 (5.81%), 261.0 (9.00%), 203.0 (7.64%), 178.0 (7.76%), 177.0 (4.92%), 115.0 (5.08%), 101.0 (5.36%), 198.9 (7.89%), 70.9 (23.34%), 68.9 (35.95%).

5.10. Crystal structure determination of compound *1*

Single crystal of compound **1** was obtained by recrystallization from benzene solution. A single crystal suitable for X-ray determination was mounted in a thin-walled capillary tube in a glove box, plugged with resin then flame sealed. Data were collected at 288 K on a Rigaku-Raxis IVP imaging plate area detector with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation to a maximum 2θ value 55.0°. Read out was performed in the 0.100 mm pixel mode. A total of 2496 reflections were collected, the intensity data were corrected for Lorentz-polarization factors as well as for absorption. The structure was solved by direct methods [26] expanded using Fourier technique [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [28].

6. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis has been deposited with the Cambridge Crystallographic Center (Deposition No. CCDC 269755) Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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