

# Synthesis, characterization and luminescence study of dimethyl[2-(arylmethyleneimino)phenolato]gallium complexes: Crystal structure of dimethyl[*N*-(4-*N,N'*-dimethylamino)phenylmethyleneiminophenolato]gallium

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## Abstract

Three dimethylgallium complexes of type  $\text{Me}_2\text{GaL}$  [ $\text{L} = 2\text{-methoxyphenylmethyleneiminophenolato}$  (**1**),  $N\text{-(4-}N,N'\text{-dimethylamino)phenylmethyleneiminophenolato}$  (**2**),  $N\text{-(2-naphthyl)methyleneiminophenolato}$  (**3**)] have been synthesized by the reaction of trimethylgallium with appropriate *N*-arylmethyleneiminophenol. The complexes obtained have been characterized by elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR, IR and mass spectroscopy, respectively. The solid structure of **2** has been determined by X-ray single crystal analysis. The gallium atom was bonded by an oxygen atom and coordinated by an imine nitrogen atom forming one five-membered ring. The stable dimer was formed by the coordination of bridging oxygen atom of phenolate to another gallium atom. The photoluminescence of complexes **1–3** were studied. The maximum emission wavelengths of **1–3** are between 305 and 320 nm upon radiation by UV light. The electroluminescent properties of diodes using **1–3** as emitting material were measured. The blue/green electroluminescence has been observed.

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**Keywords:** Trimethylgallium; Arylmethyleneiminophenol; X-ray crystallography; Electroluminescence

## 1. Introduction

Since the first observation of electroluminescence (EL) in 1965 [1], EL devices have been extensively studied due to their potential application to full color 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]. Schiff base, which could be obtained by condensation of salicylaldehyde and amines, have been widely used in the prepara-

tion of various metallic complexes [7–9]. Their reactions with Group 13 metal trialkyls have received much attention during the decade [10–13]. Although the Schiff bases based on 2-aminophenol and aldehydes have been known for many years [7–9], their application in the preparation of Group 13 organometallic complexes has not been investigated up to our knowledge. So development of various electroluminescent materials and study the relationship between structure and electroluminescence property are in great need. Recently, we have reported some light-emitting materials based on *N*-arylmethylenethiobenzahydrazone and beta-ketoimine group 13 organometallic complexes [14,15]. In order to search for the new electroluminescent materials, the synthesis and characterization of various bis[dimethyl[2-(arylmethyleneimino)phenolato]gallium] complexes (**1–3**) have been described in this paper. The crystal structure of **2** has been determined by X-ray

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analysis. The photoluminescent and electroluminescent properties of the complexes prepared have been measured and discussed as well.

## 2. Experimental

### 2.1. 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 2-hydroxylaniline with *p*-methoxybenzaldehyde, *p*-*N,N'*-dimethylaminobenzaldehyde, and 2-naphthalaldehyde. Trimethylgallium was provided by the National 863 Program Advanced Material MO Precursors R&D Center of China.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR data were collected on Bruker ARX-300 spectrometer.  $^1\text{H}$  chemical shifts were reported in units (ppm) and referenced to  $\text{SiMe}_4$  as 0.00 (solvent:  $\text{C}_6\text{D}_6$ ). Infrared spectra were obtained as KBr pellets with a 5DX-FT-2 spectrometer. Mass spectra were measured on VG-ZAB-HS spectrometer (electron impact ionization), luminescent spectra was determined with AMINCO. BOWMAN luminance spectrometer, Elemental analysis was performed on a Perkin–Elmer 240C elemental analyzer. Melting point was observed in sealed capillaries and was uncorrected.

### 2.2. Preparation of bis[*dimethyl*[2-(2-methoxyphenylmethyleneimino)phenolato]gallium] (1)

A solution of trimethylgallium (0.24 g, 2.1 mmol) in 10 mL of cyclohexane was added over a period of 10 min dropwise with stirring to a solution of 2-(2-methoxyphenylmethyleneimino)phenol (0.45 g, 2 mmol) in 10 mL of cyclohexane and 2 mL of benzene. On addition of the solution of trimethylgallium, methane gas was evolved immediately from the mixture and the reaction was exothermic. After the reaction mixture was stirred for an additional 30 min at room temperature, all volatiles were removed in oil-pump vacuo and the yellow powder was recrystallized from cyclohexane/benzene solution, giving cardinal crystals. Yields: 0.56 g (85.2%, based on TMGa).

M.p.: 175–177 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{NO}_2\text{Ga}$ : C, 58.94; H, 5.57; N, 4.30. Found: C, 58.53; H, 5.32; N, 4.56%.  $^1\text{H}$  NMR data:  $-0.18$  (s, 6H,  $\text{GaMe}_2$ ), 3.91 (s, 3H,  $-\text{OCH}_3$ ), 6.67–7.74 (m, 8H, Ar–H), 8.72 (s, 1H,  $-\text{CH}=\text{N}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  164.1 (s,  $\text{N}=\text{C}-$ ), 161.7 (s, Ar–C), 158.5 (s, Ar–C), 134.6 (s, Ar–C), 132.5 (s, Ar–C), 131.5 (s, Ar–C), 125.9 (s, Ar–C), 119.9 (s, Ar–C), 116.6 (s, Ar–C), 116.2 (s, Ar–C), 115.3 (s, Ar–C), 114.7 (s, Ar–C), 56.1 (s,  $\text{OCH}_3$ ),  $-5.5$  (s, GaMe). IR data ( $\text{cm}^{-1}$ ): 3072 (w), 3009 (w), 2968 (m), 2933 (w), 1601 (vs), 1589 (m), 1517 (m), 1479 (s), 1302 (m), 1300 (s), 1171 (m), 1020 (m), 743 (w), 528 (w). MS data: 327 (4.8%),

325 (6.9%), 312 (54.8%), 311 (13.2%), 310 (77.7%), 228 (9.6%), 227 (65.7%), 226 (100.0%), 183 (15.3%), 156 (2.6%), 155 (5.3%), 154 (7.4%), 134 (11.6%), 112 (31.5%), 108 (11.4%), 71 (25.5%), 69 (37.6%), 65 (21.1%).

### 2.3. Preparation of bis[*dimethyl*[2-(*p*-*N,N'*-dimethylaminophenylmethyleneimino)phenolato]gallium] (2)

Prepared as described for **1** from 2-(*p*-*N,N'*-dimethylaminophenylmethyleneimino)phenol (0.48 g, 2 mmol) and trimethylgallium (0.24 g, 2.1 mmol). Complex **2** was isolated as brown crystal. Yields: 0.57 g (84.6%, based on TMGa).

M.p.: 210–212 °C. Anal. Calc. for  $\text{C}_{17}\text{H}_{21}\text{N}_2\text{OGa}$ : C, 60.22; H, 6.24; N, 8.26. Found: C, 60.53; H, 6.31; N, 7.86%.  $^1\text{H}$  NMR data:  $-0.17$  (s, 6H,  $\text{GaMe}_2$ ), 3.11 (s, 6H,  $-\text{NMe}_2$ ), 6.62–7.64 (m, 8H, Ar–H), 8.56 (s, 1H,  $-\text{CH}=\text{N}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  161.2 (s,  $\text{N}=\text{C}-$ ), 158.6 (s, Ar–C), 153.8 (s, Ar–C), 135.3 (s, Ar–C), 132.9 (s, Ar–C), 130.3 (s, Ar–C), 120.2 (s, Ar–H), 119.3 (s, Ar–C), 116.4 (s, Ar–C), 115.9 (s, Ar–C), 111.9 (s, Ar–C), 40.4 (s,  $\text{N}(\text{CH}_3)_2$ ),  $-5.7$  (s, GaMe). IR data ( $\text{cm}^{-1}$ ): 3063 (w), 2966 (w), 2907 (w), 2860 (w), 1611 (m), 1593 (vs), 1579 (vs), 1563 (s), 1531 (vs), 1479 (s), 1379 (vs), 1284 (m), 1195 (m), 1166 (s), 814 (m), 748 (s), 588 (m), 518 (w). MS data: 340 (12.2%), 338 (11.6%), 326 (12.7%), 325 (66.3%), 324 (18.5%), 323 (100%), 310 (7.3%), 309 (6.1%), 308 (8.3%), 307 (5.7%), 240 (57.1%), 239 (80.9%), 228 (9.8%), 223 (18.9%), 215 (5.9%), 204 (10.9%), 148 (3.4%), 147 (8.7%), 146 (5.8%), 145 (9.2%), 121 (27.9%), 120 (25.8%), 101 (10.8%), 99 (14.2%), 78 (11.2%), 77 (11.5%), 71 (27.1%), 69 (40.9%).

### 2.4. Preparation of bis[*dimethyl*[2-(2-naphthylmethyleneimino)phenolato]gallium] (3)

Prepared as described for **1** from 2-(2-naphthylmethyleneimino)phenol (0.49 g, 2 mmol) and trimethylgallium (0.24 g, 2.1 mmol). Complex **3** was isolated as yellow crystal. Yields: 0.60 g (86%, based on TMGa).

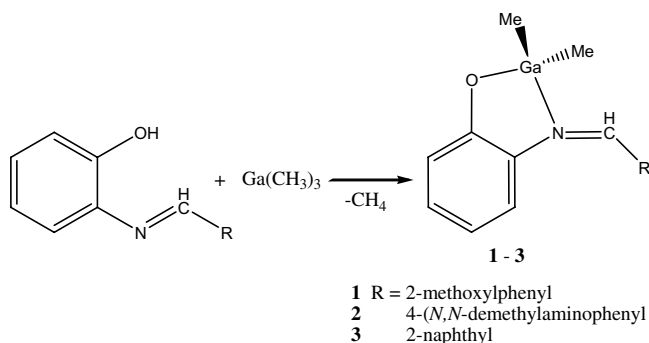
M.p.: 174–176 °C. Anal. Calc. for  $\text{C}_{19}\text{H}_{18}\text{NOGa}$ : C, 65.94; H, 5.24; N, 4.05. Found: C, 65.47; H, 5.03; N, 4.13%.  $^1\text{H}$  NMR data:  $-0.15$  (s, 6H,  $\text{GaMe}_2$ ), 6.72–8.28 (m, 10H, Ar–H), 8.99 (s, 1H,  $-\text{CH}=\text{N}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  162.2 (s,  $\text{N}=\text{C}-$ ), 158.9 (s, Ar–C), 135.7 (s, Ar–C), 134.5 (s, Ar–C), 133.1 (s, Ar–C), 132.3 (s, Ar–C), 130.7 (s, Ar–C), 129.7 (s, Ar–C), 129.6 (s, Ar–C), 129.5 (s, Ar–C), 128.5 (s, Ar–C), 128.0 (s, Ar–C), 124.5 (s, Ar–C), 120.3 (s, Ar–C), 116.7 (s, Ar–C), 116.4 (s, Ar–C),  $-5.1$  (s, GaMe). IR data ( $\text{cm}^{-1}$ ): 3065 (w), 2963 (w), 2911 (w), 1602 (m), 1584 (m), 1481 (s), 1467 (m), 1298 (m), 1283 (s), 1261 (s), 746 (s), 588 (m). MS data: 347 (3.3%), 345 (4.4%), 333 (15.8%), 332 (74.5%), 331 (21.5%), 330 (100%), 317 (2.1%), 316 (3.2%), 315 (3.1%), 314 (3.5%), 247 (25.4%), 246 (33.5%), 71 (1.6%), 69 (2.2%).

### 3. Results and discussion

#### 3.1. Synthesis and characterization

Reaction of 2-(arylmethyleneimino)phenols, which were obtained by condensation of 2-aminophenol with *p*-methoxybenzaldehyde, *p*-*N,N'*-dimethylaminobenzaldehyde, and 2-naphthaldehyde, with trimethylgallium proceeded smoothly at room temperature afforded the corresponding dimethylgallium complexes (Scheme 1). The complexes were isolated as cardinal or brown solid in high yields. Although gallium alkyls are extremely moisture and oxygen sensitive, the complexes obtained, however, are fairly stable on exposure to air. The complexes could be left at ambient atmosphere for months without obvious decomposition. The complexes are nearly insoluble in cold saturated hydrocarbons such as pentane or petroleum and very soluble in unsaturated hydrocarbons such as benzene or THF. All products obtained gave satisfactory elemental analysis results as expected for the stoichiometric structure  $\text{Me}_2\text{GaL}$  [ $\text{L} = 2$ -(2-methoxyphenylmethyleneimino)phenolato (**1**), 2-(*p*-*N,N'*-dimethylaminophenylmethyleneimino)phenolato (**2**), 2-(2-naphthylmethyleneimino)phenolato (**3**)]. The complexes obtained have also been characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR and MS spectroscopy.

Comparing the IR spectra of the complexes with those of the free ligands, appearance of medium to strong C–H stretch vibration bands is distinctive accompanying with the disappearance of the O–H signals. The CH=N stretch vibration bands (between  $1598$  and  $1611\text{ cm}^{-1}$ ) in the complexes are red shifted comparing with those of the free ligands (around  $1620\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectra, the signals of gallium bonded methyl protons in the complexes **1–3** ( $-0.15$  to  $-0.18$  ppm) shift upfield comparing with the signals of trimethylgallium ( $-0.10$  ppm). It is believed that the coordination of nitrogen atom to the gallium atom is responsible for the upfield shifting of the proton signals [16]. Although monomeric ion peaks of the complexes **1–3** were all visible in their MS spectra, there are some peaks appeared in the higher  $m/e$  region in some of the complexes. It may be the sign of the presence of the dimeric species. Fairly strong intensity peaks of the fragments eliminating one methyl from monomeric species are observed



Scheme 1. Synthesis of complexes **1–3**.

for almost all the complexes. The relative intensities of peaks for the metal containing species agrees well with the isotopic distribution of the metals [ $^{69}\text{Ga}$ (ca. 60%);  $^{71}\text{Ga}$ (ca. 40%)].

#### 3.2. Solid state structure of **2**

In order to confirm the structure of the complexes, especially for determination of whether they are in monomeric or dimeric form, the molecular structure of **2** has been determined by X-ray single crystal analysis.

ORTEP drawing of **2** is shown in Fig. 1 with selected bond lengths and angles listed in Table 1. Complex **2** can be regarded as a centrosymmetric dimer of “ $\text{Me}_2\text{GaL}$ ” units bridged by two  $\mu_2$ -oxygen atoms. Each ligand chelates a gallium atom via the bridging phenolic-oxygen atom and the nitrogen atom, forming five-membered chelate ring ‘ $\text{Ga}(1)\text{–O}(1)\text{–C}(1)\text{–C}(6)\text{–N}(1)$ ’. The gallium atom is five-coordinate with two methyl carbon atoms, two bridging oxygen atoms and a nitrogen atom. The  $\text{Ga}(1)\text{–O}(1)$  distance ( $1.911(2)\text{ \AA}$ ) is comparable to that in dimethylgallium *N*-methylsalicylaldiminate ( $1.904(7)\text{ \AA}$ ) [17] and dimethyl(2-hydroxybenzaldehydato)gallium ( $1.927(3)\text{ \AA}$ ) [18], just belonging to covalent bonds, whereas the

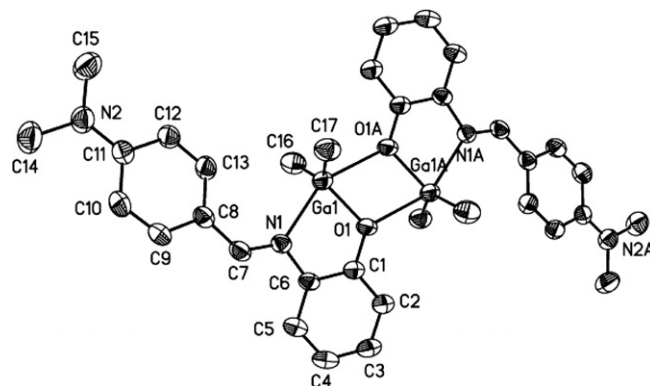


Fig. 1. ORTEP drawing of **2**, showing 30% probability displacement ellipsoids. The hydrogen atoms are omitted for clarity.

Table 1  
Selected bond distances and angles of **2**

Bond distances ( $\text{\AA}$ )			
$\text{Ga}(1)\text{–O}(1)$	1.911(2)	$\text{Ga}(1)\text{–C}(16)$	1.952(3)
$\text{Ga}(1)\text{–O}(1)^\#$	2.321(2)	$\text{Ga}(1)\text{–C}(17)$	1.955(4)
$\text{Ga}(1)\text{–N}(1)$	2.227(2)	$\text{O}(1)\text{–C}(1)$	1.330(4)
$\text{N}(1)\text{–C}(6)$	1.420(4)	$\text{C}(1)\text{–C}(6)$	1.399(4)
Bond angles ( $^\circ$ )			
$\text{O}(1)\text{–Ga}(1)\text{–C}(16)$	113.9(1)	$\text{O}(1)\text{–Ga}(1)\text{–C}(17)$	112.5(1)
$\text{C}(16)\text{–Ga}(1)\text{–C}(17)$	131.9(1)	$\text{O}(1)\text{–Ga}(1)\text{–N}(1)$	79.0(1)
$\text{C}(16)\text{–Ga}(1)\text{–N}(1)$	99.7(1)	$\text{C}(17)\text{–Ga}(1)\text{–N}(1)$	100.9(1)
$\text{O}(1)\text{–Ga}(1)\text{–O}(1)^\#$	72.0(1)	$\text{N}(1)\text{–Ga}(1)\text{–O}(1)^\#$	150.9(1)
$\text{C}(7)\text{–N}(1)\text{–Ga}(1)$	132.8(2)	$\text{C}(6)\text{–N}(1)\text{–Ga}(1)$	107.2(2)
$\text{C}(1)\text{–O}(1)\text{–Ga}(1)$	118.9(2)	$\text{C}(1)\text{–O}(1)\text{–Ga}(1)^\#$	132.0(2)
$\text{Ga}(1)\text{–O}(1)\text{–Ga}(1)^\#$	108.0(1)		

Symmetry code #:  $1/2 - x, 1/2 - y, 2 - z$ .

Ga(1)–O(1)<sup>#</sup> distance (2.321(2) Å) is obviously longer than that of bis[dimethyl(2-methoxyphenolato)gallium] (2.046(4) Å) [19], bis(pyridine-2-methanolatodimethylgallium) (2.073(3) Å) [20], just falling in the range of coordinate bonds. The Ga(1)–N(1) distance is 2.227(3) Å, slightly longer than those in complex *N,N*-ethylenebis(salicylideneiminato)bis[dimethylgallium] (2.026(3)–2.035(3) Å) [21], [<sup>t</sup>Bu<sub>2</sub>Ga(μ-NHPh)]<sub>2</sub> (2.103(9) Å) [17] and Me<sub>3</sub>GaNH<sub>2</sub><sup>t</sup>Bu (2.12(1) Å) [22]. The central four-member planar ring is constructed by two gallium atoms and two bridging oxygen atoms, which demonstrates that the dimeric species are formed by coordination of bridging oxygen to gallium between the two monomeric species. The O(1)–Ga(1)–O(1)<sup>#</sup> is 72.0(1)° which is smaller than that of [Me<sub>2</sub>In{μ-O-CH<sub>2</sub>CH<sub>2</sub>(2-C<sub>5</sub>H<sub>4</sub>N)}]<sub>2</sub> 75.4(2)° [23]. The O(1)–Ga(1)–N(1) angle 79.0(1)° is comparable to that of dimethyl[1-(2-pyridyl)methyleneimino-2-naphthonato]gallium 78.9(2)° [24].

### 3.3. Photoluminescence study

Photoluminescence emission spectra of the complexes **1**–**3** (solid state) have been measured at room temperature as shown in Fig. 2. It shows that the emission bands are located in the ultraviolet region. Their emission maximums are at 305 nm with the intensities of 68 a.u. (**1**), 310 nm with the intensities of 102 a.u. (**2**), and 320 nm with the intensities of 32 a a.u. (**3**). Complex **2** exhibits a relatively stronger PL intensity, which will be attributed to the stronger electron repelling capability of dimethylamino substituent. The emission wavelength of **3** shifted red-ward comparing to **1** as well as **2**, indicating that the large conjugation system of **3** will be responsible for this shifting. The stronger luminescence observed may be attributed to the coordination or bridging of the ligands to the gallium center, which increases the rigidity of the ligand and reduces the loss of energy via un-radiation pathway, thus enhancing the π\*–π irradiation probability.

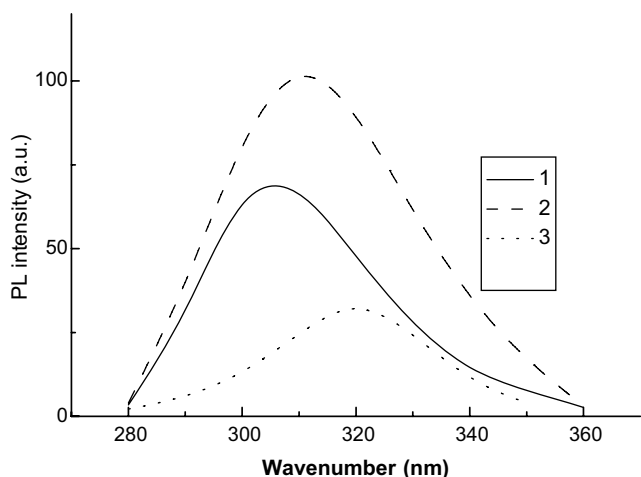


Fig. 2. Photoluminescence spectra of complexes **1**–**3** in solid state.

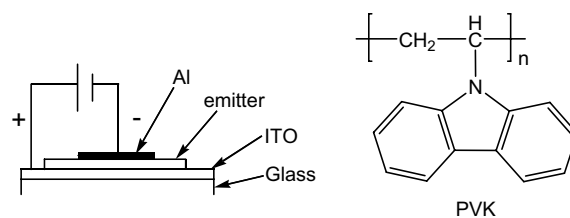


Fig. 3. Configuration of devices and PVK structure.

### 3.4. Electroluminescence studies

The gallium complexes were used as light emitting materials and a series of EL diodes were prepared (Fig. 3). The devices were prepared on indium–tin–oxide (ITO) coated glass substrate, which were cleaned by ultrasonic in a mixture of isopropyl alcohol and water (1:1) and degreased in toluene vapor, with a sheet resistance of near 80 Ω/. Polymer poly (vinylcarbazole) (PVK) was added to the emitter layers used both as a hole injected material to improve the balance of current carrier and to improve the quality of the film-formation. The complexes and the PVK were mixed (10:1 in molar ratio) by dissolving them in chloroform at the concentration of 10 mg/mL (gallium complexes). The thickness of the emitting layers for all the samples was controlled to be the same (~700 Å). A device structure of (–)Al/emitter/ITO(+) was employed. High-quality film can be obtained by spin-casting of PVK and organogallium complex mixture with 2500 r/min. Electron injecting electrode Al was deposited on top by vacuum evaporation at pressure below  $2 \times 10^{-5}$  Torr with a deposition rate of 10–15 Å/s. The emitting area was  $5 \times 8$  mm<sup>2</sup>.

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. Current density increasing rate is proportional to the bias voltage. It increases from 0.01 to 2.53 mA/mm<sup>2</sup> for complex **1** (1–24 V), from 0.025 to 2.23 mA/mm<sup>2</sup> for complex **2** (1–20 V), from 0.025 to 3.63 mA/mm<sup>2</sup> for complex **3** (1–19 V). The current density

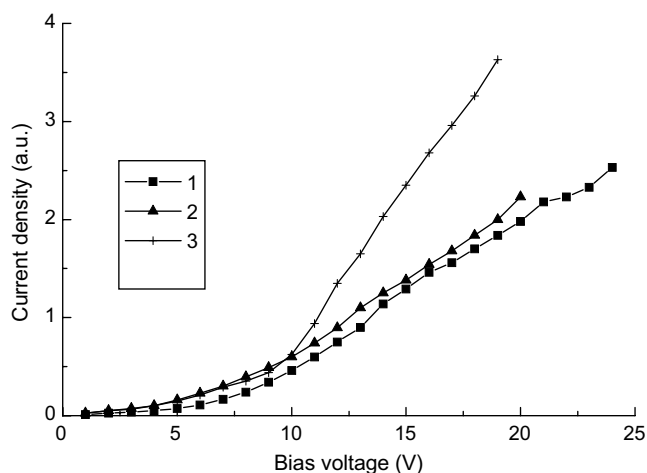


Fig. 4. The relationship of current density and voltage of diodes with the emitter of complexes **1**–**3**.

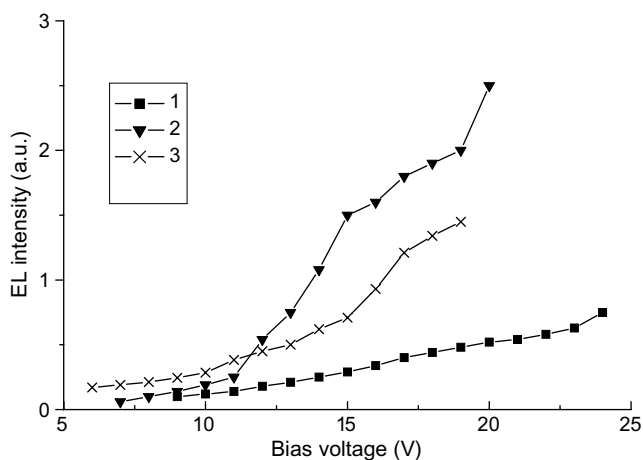


Fig. 5. EL intensity–voltage curves of diodes with the emitter of complexes 1–3.

increasing rate for complex 3 is bigger than those of the other complexes. It should be attributed to the existence of the large delocalized conjugated system, which exhibit a good electric conductivity.

The EL emission intensity–voltage relationships of the EL devices have been measured as shown in Fig. 5. The light output of the EL diodes is proportional to the input voltage in the voltage range. The complex 2 has large EL emission intensities, showing that the dimethylamino groups, which are very stronger electronic repelling group, are beneficial to EL emission. The emission of 3 is not so good as expected. That may be due to the poor coplanar configuration of the naphthyl and the phenyl planes in the complex due to the relatively steric hindrance of naphthyl group.

The EL luminescence spectra of the diodes were measured as shown in Fig. 6. Their EL bands are located from blue/green region. The EL emission maximums are 473 nm for 1 (22 V), 465 nm for 2 (16 V), 510 nm for 3 (17 V). Seen from Fig. 6, the substitutes on the phenyl ring have an

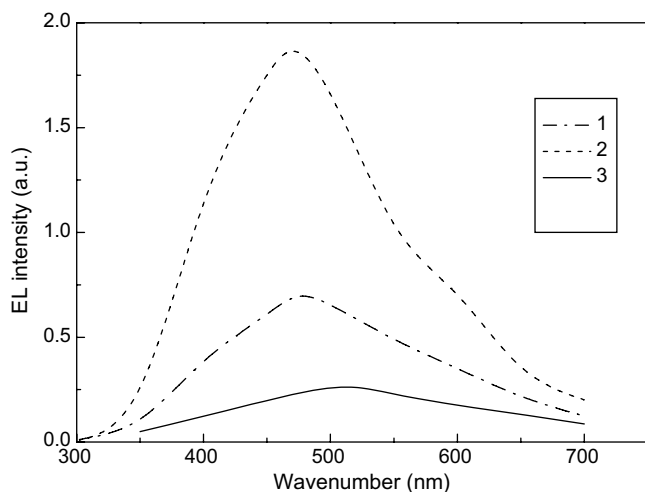


Fig. 6. Electroluminescence spectra of complexes 1–3.

influence on emission wavelength. It is interesting to see that the emission maximum wavelength of 3 appears at the longest wavelength. This will be attributed to the large conjugation of naphthyl group, which reduced the energy gap between HOMO and LUMO of the complexes.

In general, the EL emission bands will be similar to those of the photoluminescence emission spectra, [21] because the EL spectra are independent of the driving voltage and current. The result also indicates that the radiative recombination of injected electrons and holes takes place in the gallium complexes. The EL maximum emission wave number, however, are significantly red-shifted compared to those in PL measurement, this may be due to the energy loss during the exciton recombination and decrease the energy gap between HOMO and LUMO of the complexes. The role of gallium atom in the blue/green luminescence of complexes is considered to be twofold. First, the formation of covalent bond between the gallium and the oxygen atom and of the donor-acceptor bond between the gallium and the nitrogen atom which may contribute to the perturbation of the  $\pi$  energy level, thus change the  $\pi^* \rightarrow \pi$  transition

Table 2  
Crystallographic data and structure refinement details for 2

Formula	C <sub>17</sub> H <sub>21</sub> GaN <sub>2</sub> O
Formula weight	339.08
Crystal colour	Brown
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	16.259(3)
<i>b</i> (Å)	15.101(3)
<i>c</i> (Å)	14.420(3)
$\alpha$ (°)	90
$\beta$ (°)	111.68(3)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	3290.1(11)
<i>Z</i> value	8
<i>D</i> <sub>calc</sub> (g/cm <sup>-3</sup> )	1.369
Index ranges	−19 ≤ <i>h</i> ≤ 13, −13 ≤ <i>k</i> ≤ 17, −16 ≤ <i>l</i> ≤ 17
<i>F</i> (000)	1408
$\mu$ (mm <sup>-1</sup> )	1.673
Crystal size (mm)	0.4 × 0.3 × 0.2
Temperature (K)	293
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71073
$2\theta_{\min}/2\theta_{\max}$ (°)	3.82/50.00
Number of reflections measured	5992
Independent reflections	2900
Independent reflections observed	1965
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	
parameters	194
<i>R</i> <sub>int</sub>	0.0283
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]/all <sup>a</sup>	0.0335/0.0679
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]/all <sup>b</sup>	0.0830/0.0951
Goodness-of-fit on <i>F</i> <sup>2c</sup>	1.017
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	−0.44/0.41
( $\Delta/\sigma$ ) <sub>mean</sub> /( $\Delta/\sigma$ ) <sub>max</sub>	0.000/0.002

<sup>a</sup>  $R_1 = \sum(\|F_o\| - |F_c|)/\sum|F_o|$ ;  $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$ .

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.8008P]$ ,  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>c</sup>  $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$ , *n* = number of reflections, *p* = parameters used.



energy of the ligand. The second, the binding of 2-arylmethyleneiminophenato to the gallium atom increases the rigidity of the ligand, thus reducing the loss of energy via un-radiation vibration motions and increasing the emission efficiency. The effect of substitutes on ligands as well as the different alkyl substitutes of gallium atom on electroluminescence is being investigated in detail in our laboratory.

### 3.5. Crystal structure determination of complex 2

Single crystal of complex 2 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, removed from the glove box, then flame sealed. Data were collected at 293 K on a Siemens P4 imaging plate area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) radiation. CAD-4 software [25] was used for data collection and cell refinement. Data were corrected for Lorentz and Polarization effects during data reduction. The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  with SHELXTL-PC package [26]. All nonhydrogen atoms were refined anisotropically and the hydrogen atoms were located geometrically and refined isotropically. The graphical representation of the crystal structure was produced with ORTEPII [27]. Crystallographic data and refinement details are presented in Table 2.

## 4. Conclusion

Three dimethyl[2-(arylmethyleneimino)phenolato]gallium complexes have been prepared and characterized. Single crystal structure of dimethyl[*N*-(4-*N,N'*-dimethylamino)phenylmethyl eneiminophenolato]gallium has been determined by using X-ray single crystal structure analysis. The electroluminescent properties of 1–3 have been studied. The blue/green EL properties have been observed.

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## Appendix A. Supplementary material

CCDC 616654 contains the supplementary crystallographic data for this paper. These data can be obtained free

of charge via <http://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; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.08.022](https://doi.org/10.1016/j.jorganchem.2007.08.022).

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