

# Gallium(III) complexes based on *N,N'*-bis(salicylidene)propane-1,3-diamine and its derivatives

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## ABSTRACT

The reactions of *N,N'*-bis(salicylidene)propane-1,3-diamine (salpropH<sub>2</sub>) and its substituted derivatives with Ga(acac)<sub>3</sub> afforded the complexes [Ga(acac)(salprop)]·0.5H<sub>2</sub>O (**1**), [Ga(acac)(5ClSalprop)] (**2**), [Ga(acac)(5BrSalprop)] (**3**), [Ga(acac)(5NO<sub>2</sub>Salprop)] (**4**) and [Ga(acac)(5MeSalprop)] (**5**), in high yields. The crystal structures of all complexes have been determined by single-crystal X-ray crystallography. All complexes are mononuclear with the Ga(III) atoms being in octahedral environments surrounded by one tetradentate chelate 5Rsalprop<sup>2-</sup> ligand and one bidentate chelate acac<sup>-</sup> ligand. The free ligands exhibit photoluminescence which was found to be increased upon complex formation. The substituted derivatives of the salpropH<sub>2</sub> ligand bearing either electron-donating methyl groups or electron-withdrawing groups, such as Cl, Br and NO<sub>2</sub> at the fifth position of both salicylidene rings were found to modify the emission maximum of the free ligands and the complexes.

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## 1. Introduction

Group 13 metal complexes have emerged as leading materials for optoelectronic devices such as light emitting diodes (LEDs) since they often exhibit high fluorescence in the solid state and good thermal stability [1–17]. Alq<sub>3</sub> (qH = 8-hydroxyquinoline) is probably the best representative of this class of compounds exhibiting both photoluminescence (PL) and electroluminescence (EL) [3–6]. It has been shown that replacement of Al(III) with Ga(III) has resulted in materials with improved properties such as higher electroluminescence yields [7–9]. An alternative route to tune/modify the electronic properties of these materials is to introduce substituents on the periphery of the complexes [10–12]. It has been found that methylation of the 8-hydroxyquinoline ligand modifies/improves the physical properties (e.g. increases the glass transition temperature) and increases the operating voltages of the EL devices [13].

An alternative route to create such materials with improved properties is to partly replace the 8-hydroxyquinolate with Schiff bases bearing phenolate groups [14]. We and others have recently shown that Ga(III) complexes with the Schiff base ligand *N*-salicylidene-*o*-aminophenol (saphH<sub>2</sub>) exhibit bright luminescence [15–17]. We also demonstrated that the electronic properties of

these complexes may be tuned by attaching Electron Withdrawing chemical Groups (EWGs) or Electron Donating chemical Groups (EDGs) on the saph<sup>2-</sup> ligands.

Following the previous published work, we herein report a series of mononuclear Ga(III) complexes based on *N,N'*-bis(salicylidene)propane-1,3-diamine (salpropH<sub>2</sub>) and its substituted derivatives. In an attempt to tune/modify the emission maxima, EWGs such as Cl, Br and NO<sub>2</sub>, as well as EDGs such as methyl groups were introduced on the periphery of the Schiff base ligand.

## 2. Experimental

### 2.1. General and physical measurements

All manipulations were performed under aerobic conditions. Gallium metal, acetylacetone, salicylaldehyde, substituted salicylaldehydes, 1,3-diaminopropane and all solvents were obtained from commercial sources and used as received. Ga(acac)<sub>3</sub> was prepared following literature procedures [18]. Microanalyses (C, H, N) were performed with an EA 1108 Carlo Erba analyzer. IR spectra were recorded on a Shimadzu FT/IR IRAffinity-1 spectrometer with samples prepared as KBr pellets. TGA diagrams were recorded on a Mettler-Toledo TGA/DSC1 instrument under a N<sub>2</sub> flow of 50 ml/min. Emission and excitation spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer on powdered samples dispersed and squeezed on a quartz plate.

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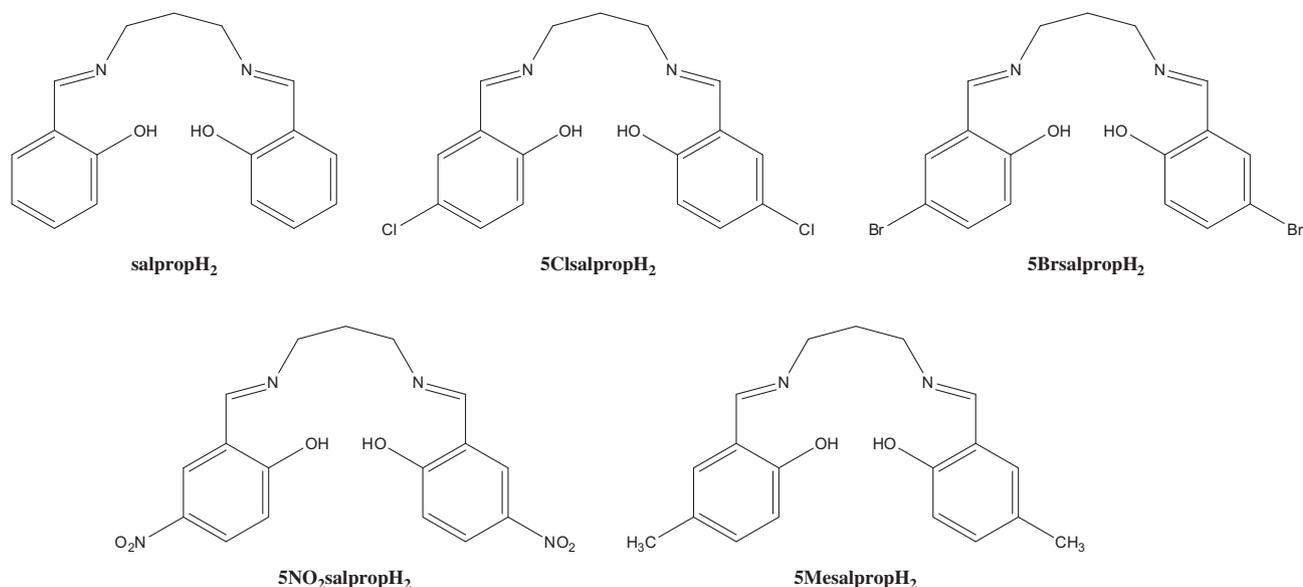


Fig. 1. The structures of the double Schiff base ligands discussed in the text.

**Table 1**  
Crystallographic data for complexes 1–5.

Compound reference	1	2	3	4	5
Chemical formula	C <sub>22</sub> H <sub>24</sub> GaN <sub>2</sub> O <sub>4.50</sub>	C <sub>22</sub> H <sub>21</sub> Cl <sub>2</sub> GaN <sub>2</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>21</sub> Br <sub>2</sub> GaN <sub>2</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>21</sub> GaN <sub>2</sub> O <sub>8</sub>	C <sub>24</sub> H <sub>27</sub> GaN <sub>2</sub> O <sub>4</sub>
Formula weight	458.15	518.03	606.95	539.15	477.20
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Unit cell dimensions					
<i>a</i> (Å)	8.1261(1)	8.4012(1)	8.7846(9)	8.361(1)	18.628(3)
<i>b</i> (Å)	14.035(2)	14.028(2)	13.850(1)	14.010(3)	8.288(1)
<i>c</i> (Å)	18.291(3)	18.851(3)	18.922(1)	18.979(4)	14.663(2)
$\alpha$ (°)	90	90	90	90	90
$\beta$ (°)	90	90	90	90	90
$\gamma$ (°)	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	2086.0(6)	2221.7(6)	2302.1(4)	2223.2(8)	2263.8(7)
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> na2 <sub>1</sub>
<i>Z</i>	4	4	4	4	4
$\mu$ (mm <sup>-1</sup> )	1.353	1.511	4.697	1.296	1.248
Reflections measured	12912	15431	19969	26186	19265
Independent reflections	4959	5020	5651	5723	5030
<i>R</i> <sub>int</sub>	0.0377	0.0378	0.0354	0.0237	0.0222
<i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0398	0.0369	0.0392	0.0263	0.0283
w <i>R</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0707	0.0752	0.0945	0.0701	0.0752
<i>R</i> <sub>1</sub> values (all data)	0.0715	0.0559	0.0546	0.0291	0.0325
w <i>R</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0793	0.0828	0.1019	0.0716	0.0775
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.002	0.917	1.041	1.013	1.012

## 2.2. Compound preparation

### 2.2.1. Synthesis of *N,N'*-bis(salicylidene)propane-1,3-diamine (salpropH<sub>2</sub>) and its substituted derivatives

SalpropH<sub>2</sub> was prepared by the condensation in absolute ethanol of 1,3-diaminopropane with salicylaldehyde in accordance with literature methods [19]. The substituted derivatives of the Schiff base were prepared by replacing salicylaldehyde with 2-hydroxy-5-chloro-benzaldehyde, 2-hydroxy-5-bromo-benzaldehyde, 2-hydroxy-5-nitro-benzaldehyde and 2-hydroxy-5-methyl-benzaldehyde. The chemical structures of the Schiff bases are shown in Fig. 1.

### 2.2.2. [Ga(acac)(salprop)]·0.5H<sub>2</sub>O (1)

**Method A:** SalpropH<sub>2</sub> (0.127 g, 0.450 mmol) and Ga(acac)<sub>3</sub> (0.165 g, 0.450 mmol) were refluxed in 20 mL toluene for 50 min. The resultant yellow solution was filtered and layered with *n*-hexane (40 mL). X-ray quality, yellow crystals of **1** were formed within a week. The crystals were isolated by vacuum filtration, washed

with *n*-hexane (2 × 5 mL) and dried in air. Yield 0.12 g, 58%. *Anal.* Calc. for C<sub>22</sub>H<sub>24</sub>GaN<sub>2</sub>O<sub>4.5</sub>: C, 57.67; H, 5.28; N, 6.11. Found: C, 57.71; H, 5.23; N, 6.17%. IR (KBr pellets, cm<sup>-1</sup>): 1620w, 1587w, 1536w, 1519w, 1466w, 1445w, 1383w, 1338w, 1315w, 1275w, 1210w, 1195w, 1146w, 1125w, 1079w, 1065w, 1015w, 923w, 898w, 797w, 762w, 738w, 604w.

**Method B:** Salicylaldehyde (0.094 mL, 0.900 mmol), 1,3-diaminopropane (0.037 mL, 0.450 mmol) and Ga(acac)<sub>3</sub> (0.165 g, 0.450 mmol) were refluxed in 20 mL toluene for 50 min. The resultant clear yellow solution was cooled to room temperature and layered with *n*-hexane (40 mL). Yellow crystals of **1** were formed within a week. The crystals were isolated by vacuum filtration, washed with *n*-hexane (2 × 5 mL) and dried in air. Yield 0.14 g, 67%. *Anal.* Calc. for C<sub>22</sub>H<sub>24</sub>GaN<sub>2</sub>O<sub>4.5</sub>: C, 57.67; H, 5.28; N, 6.11. Found: C, 57.70; H, 5.25; N, 6.15%. IR (KBr pellets, cm<sup>-1</sup>): 1620w, 1587w, 1536w, 1519w, 1466w, 1445w, 1383w, 1338w, 1315w, 1275w, 1210w, 1195w, 1146w, 1125w, 1079w, 1065w, 1015w, 923w, 898w, 797w, 762w, 738w, 604w.

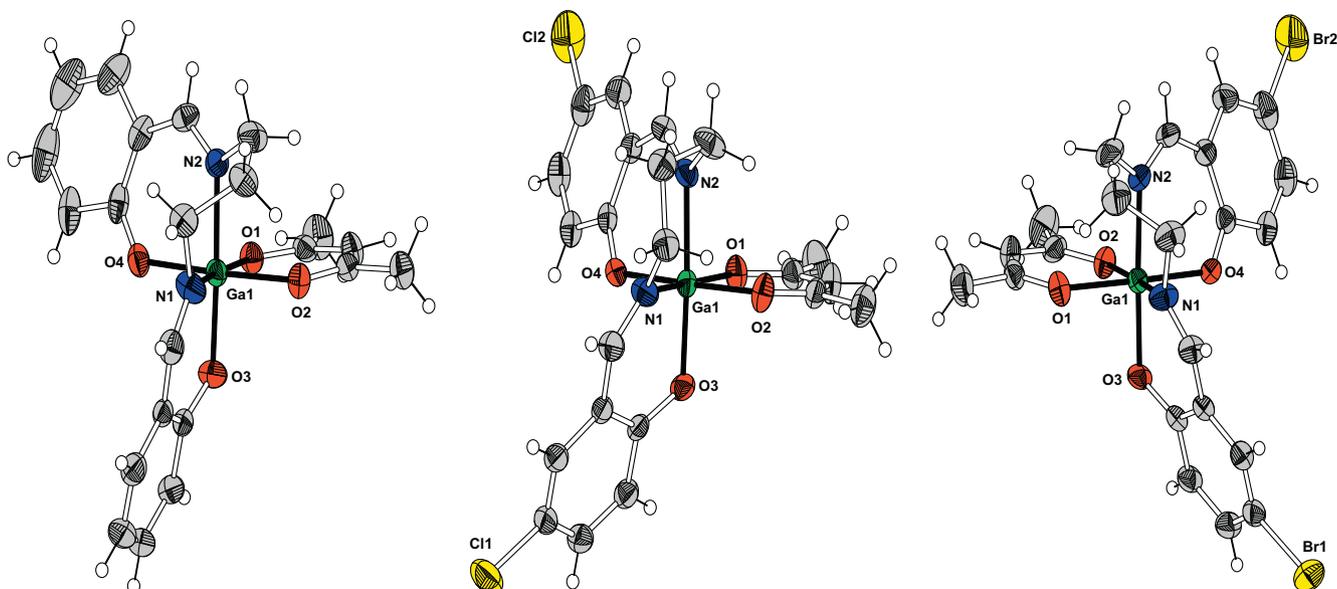


Fig. 2. ORTEP diagrams of the molecular structures of **1** (left), **2** (middle) and **3** (right). Color code: Ga, green; O, red; N, blue; Cl and Br, yellow; C, gray; H, white. (Color online.)

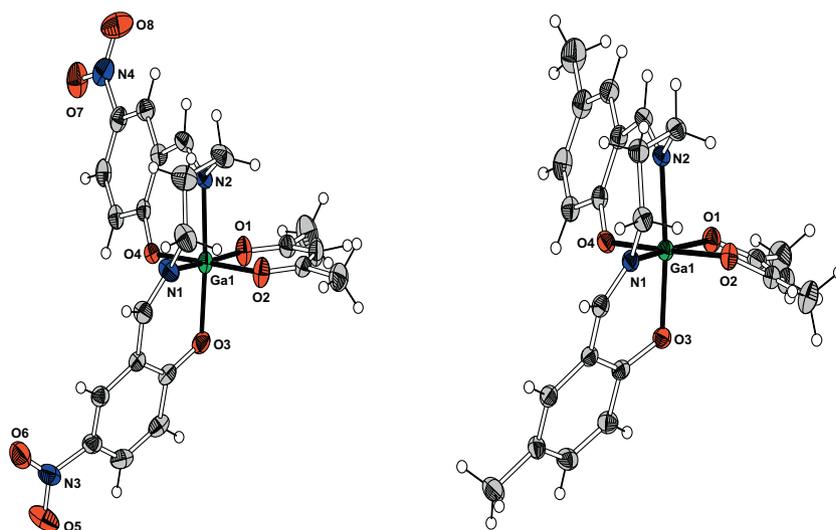


Fig. 3. ORTEP diagrams of the molecular structures of **4** (left) and **5** (right). Color code: same as in Fig. 2. (Color online.)

### 2.2.3. $[Ga(acac)(5Clisalprop)]$ (**2**)

**Method A:**  $Ga(acac)_3$  (0.102 g, 0.280 mmol) and  $5ClisalpropH_2$  (0.098 g, 0.280 mmol) were dissolved in methanol (12 mL). The solution was stirred for 30 min and left undisturbed to evaporate at room temperature. Light yellow crystals of **2** were formed over a period of two days. The crystals were isolated by vacuum filtration, washed with  $Et_2O$  ( $2 \times 5$  mL) and dried in air. Yield 0.08 g, 56%. *Anal. Calc.* for  $C_{22}H_{21}Cl_2GaN_2O_4$ : C, 51.01; H, 4.09; N, 5.41. *Found:* C, 51.05; H, 4.02; N, 5.38%. IR (KBr pellets,  $cm^{-1}$ ): 1622w, 1592w, 1525w, 1459w, 1382w, 1307w, 1175w, 822w, 800w, 708w, 414w.

**Method B:** 5-chlorosalicylaldehyde (0.088 g, 0.560 mmol), 1,3-diaminopropane (0.023 mL, 0.280 mmol) and  $Ga(acac)_3$  (0.102 g, 0.280 mmol) were refluxed in methanol (12 mL) for 50 min. The resultant clear yellow solution was left undisturbed to evaporate at room temperature. Yellow crystals of **2** were formed within four days. The crystals were isolated by vacuum filtration, washed with  $Et_2O$  ( $2 \times 5$  mL) and dried in air. Yield 0.06 g, 41%. *Anal. Calc.* for  $C_{22}H_{21}Cl_2GaN_2O_4$ : C, 51.01; H, 4.09; N, 5.41. *Found:* C, 51.07; H,

4.01; N, 5.43%. IR (KBr pellets,  $cm^{-1}$ ): 1622w, 1592w, 1525w, 1459w, 1382w, 1307w, 1175w, 822w, 800w, 708w, 414w.

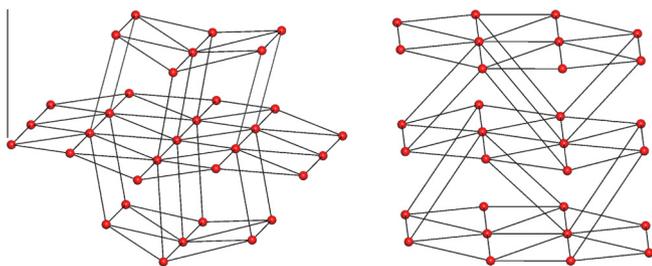
### 2.2.4. $[Ga(acac)(5Brsalprop)]$ (**3**)

**Method A:**  $Ga(acac)_3$  (0.102 g, 0.280 mmol) and  $5BrsalpropH_2$  (0.123 g, 0.280 mmol) were dissolved in methanol (10 mL). The solution was stirred for 45 min and left undisturbed to evaporate at room temperature. Orange crystals of **3** were formed over a period of a week. The crystals were isolated by vacuum filtration, washed with  $Et_2O$  ( $2 \times 5$  mL) and dried in air. Yield 0.12 g, 70%. *Anal. Calc.* for  $C_{22}H_{21}Br_2GaN_2O_4$ : C, 43.54; H, 3.49; N, 4.62. *Found:* C, 43.48; H, 3.40; N, 4.70%. IR (KBr pellets,  $cm^{-1}$ ): 1635m, 1620m, 1591m, 1525m, 1456m, 1379, 1306m, 1227w, 1172w, 1132w, 1073w, 1062w, 1020w, 846w, 822w, 799w, 774w, 685w, 641w, 557w.

**Method B:** 5-bromosalicylaldehyde (0.110 g, 0.560 mmol), 1,3-diaminopropane (0.023 mL, 0.280 mmol) and  $Ga(acac)_3$  (0.102 g, 0.280 mmol) were refluxed in methanol (15 mL) for 50 min. The resultant clear orange solution was left undisturbed to evaporate

**Table 2**  
Selected bond distances (Å) and angles (°) in **1–5**.

Compound reference	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Ga(1)–O(1)	1.994(2)	1.995(2)	1.992(3)	1.974(1)	1.994(2)
Ga(1)–O(2)	2.000(2)	1.990(2)	1.991(3)	1.958(1)	2.009(1)
Ga(1)–O(3)	1.911(2)	1.910(2)	1.901(3)	1.930(1)	1.911(2)
Ga(1)–O(4)	1.923(2)	1.908(2)	1.906(3)	1.924(1)	1.920(1)
Ga(1)–N(1)	2.059(3)	2.062(3)	2.070(4)	2.066(1)	2.058(2)
Ga(1)–N(2)	2.077(3)	2.050(3)	2.053(3)	2.064(1)	2.059(2)
O(1)–Ga(1)–O(2)	87.97(8)	88.16(1)	87.74(1)	89.90(6)	86.75(7)
O(1)–Ga(1)–O(3)	89.82(9)	91.88(1)	89.76(1)	93.64(7)	91.95(8)
O(1)–Ga(1)–O(4)	89.35(9)	89.09(9)	176.06(1)	87.38(6)	91.54(7)
O(2)–Ga(1)–O(3)	91.62(1)	90.56(1)	92.32(1)	90.17(7)	92.87(9)
O(2)–Ga(1)–O(4)	176.54(1)	177.07(1)	88.32(1)	177.13(6)	177.76(8)
O(3)–Ga(1)–O(4)	90.55(1)	90.53(1)	90.59(1)	89.08(6)	88.63(9)
O(1)–Ga(1)–N(1)	172.75(1)	173.17(1)	86.19(1)	175.38(7)	169.13(8)
O(2)–Ga(1)–N(1)	84.83(1)	85.18(1)	173.65(1)	86.60(7)	82.41(7)
O(3)–Ga(1)–N(1)	91.16(1)	89.71(1)	89.51(1)	89.39(6)	89.40(8)
O(4)–Ga(1)–N(1)	97.82(1)	97.54(1)	97.74(1)	96.16(7)	99.27(7)
O(1)–Ga(1)–N(2)	92.80(9)	91.96(1)	91.17(1)	91.93(7)	91.68(8)
O(2)–Ga(1)–N(2)	89.70(1)	90.43(1)	91.60(1)	92.08(7)	91.70(9)
O(3)–Ga(1)–N(2)	177.11(1)	176.06(1)	176.00(1)	174.00(6)	174.32(8)
O(4)–Ga(1)–N(2)	88.25(1)	88.66(1)	88.76(1)	88.93(6)	86.90(9)
N(1)–Ga(1)–N(2)	86.40(1)	86.58(1)	86.68(1)	85.19(7)	87.86(8)



**Fig. 4.** Representation of the real ( $3^6.4^{18}.5^3.6$ )-hex network (left) and the ( $3^6.4^{14}.5^8$ )-bct-8-Pccn net (right), adopted by **1** and **5**, respectively.

at room temperature. Orange crystals of **3** were formed within a week. The crystals were isolated by vacuum filtration, washed with Et<sub>2</sub>O (2 × 5 mL) and dried in air. Yield 0.10 g, 59%. *Anal. Calc.* for C<sub>22</sub>H<sub>21</sub>Br<sub>2</sub>GaN<sub>2</sub>O<sub>4</sub>: C, 43.54; H, 3.49; N, 4.62. Found: C, 43.50; H, 3.42; N, 4.68%. IR (KBr pellets, cm<sup>-1</sup>): 1635m, 1620m, 1591m, 1525m, 1456m, 1379, 1306m, 1227w, 1172w, 1132w, 1073w, 1062w, 1020w, 846w, 822w, 799w, 774w, 685w, 641w, 557w.

#### 2.2.5. [Ga(acac)(5NO<sub>2</sub>salprop)] (**4**)

*Method A:* Ga(acac)<sub>3</sub> (0.102 g, 0.280 mmol) and 5NO<sub>2</sub>salpropH<sub>2</sub> (0.104 g, 0.280 mmol) were refluxed in a mixture of ethanol (15 mL) and dichloromethane (15 mL) for 30 min. The resultant yellow solution was filtered and layered with *n*-hexane (60 mL). X-ray quality, yellow-orange crystals of **4** were formed within a week. The crystals were isolated by vacuum filtration, washed with *n*-hexane (2 × 5 mL) and dried in air. Yield 0.11 g, 73%. *Anal. Calc.* for C<sub>22</sub>H<sub>21</sub>GaN<sub>2</sub>O<sub>8</sub>: C, 49.01; H, 3.93; N, 10.39. Found: C, 49.04; H, 3.90; N, 10.32%. IR (KBr pellets, cm<sup>-1</sup>): 1649m, 1631s, 1603m, 1558s, 1532m, 1507w, 1486m, 1440w, 1379w, 1319s, 1284w, 1246w, 1217w, 1192w, 1130w, 1102m, 1016w, 955w, 946w, 836w, 798w, 755w, 699w, 691w, 650w, 576w, 515w.

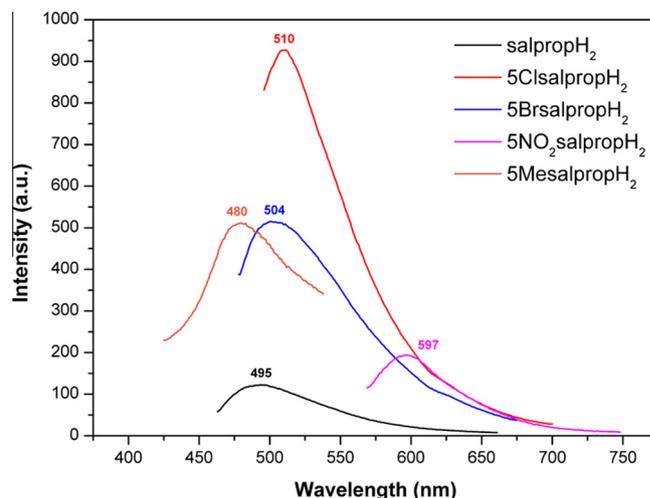
*Method B:* 5-nitrosalicylaldehyde (0.093 g, 0.560 mmol), 1,3-diaminopropane (0.023 mL, 0.280 mmol) and Ga(acac)<sub>3</sub> (0.102 g, 0.280 mmol) were refluxed in a mixture of ethanol (15 mL) and dichloromethane (15 mL) for 30 min. The resultant yellow solution was filtered and layered with *n*-hexane (60 mL). X-ray quality, yellow-orange crystals of **4** were formed within a week. The crystals were isolated by vacuum filtration, washed with *n*-hexane (2 × 5 mL) and dried in air. Yield 0.09 g, 60%. *Anal. Calc.* for C<sub>22</sub>H<sub>21</sub>

GaN<sub>4</sub>O<sub>8</sub>: C, 49.01; H, 3.93; N, 10.39. Found: C, 49.06; H, 3.88; N, 10.30%. IR (KBr pellets, cm<sup>-1</sup>): 1649m, 1631s, 1603m, 1558s, 1532m, 1507w, 1486m, 1440w, 1379w, 1319s, 1284w, 1246w, 1217w, 1192w, 1130w, 1102m, 1016w, 955w, 946w, 836w, 798w, 755w, 699w, 691w, 650w, 576w, 515w.

#### 2.2.6. [Ga(acac)(5Mesalprop)] (**5**)

*Method A:* Ga(acac)<sub>3</sub> (0.102 g, 0.280 mmol) and 5MesalpropH<sub>2</sub> (0.087 g, 0.280 mmol) were dissolved in a mixture of *n*-hexane (12 mL) and dichloromethane (6 mL). The yellow solution was stirred for 15 min and left undisturbed to evaporate at room temperature. Yellow-orange crystals of **5** were formed over a period of a week. The crystals were isolated by vacuum filtration, washed with Et<sub>2</sub>O (2 × 5 mL) and dried in air. Yield 0.07 g, 52%. *Anal. Calc.* for C<sub>24</sub>H<sub>27</sub>GaN<sub>2</sub>O<sub>4</sub>: C, 60.41; H, 5.70; N, 5.87. Found: C, 60.48; H, 5.60; N, 5.90%. IR (KBr pellets, cm<sup>-1</sup>): 2922m, 2866m, 1654m, 1638s, 1624s, 1617s, 1610s, 1595s, 1576m, 1570m, 1565w, 1560m, 1554m, 1543s, 1540s, 1534s, 1525s, 1522s, 1518s, 1507w, 1472s, 1387s, 1323m, 1308s, 1256w, 1212w, 1166m, 1072w, 954w, 926w, 806w, 777w.

*Method B:* 5-methylsalicylaldehyde (0.076 g, 0.560 mmol), 1,3-diaminopropane (0.023 mL, 0.280 mmol) and Ga(acac)<sub>3</sub> (0.102 g, 0.280 mmol) were refluxed a mixture of *n*-hexane (12 mL) and dichloromethane (6 mL) for 30 min. The resultant clear yellow



**Fig. 5.** Photoluminescence spectra of the free ligands in the solid-state.

solution was left undisturbed to evaporate at room temperature. Yellow-orange crystals of **5** were formed within a week. The crystals were isolated by vacuum filtration, washed with Et<sub>2</sub>O (2 × 5 mL) and dried in air. Yield 0.05 g, 38%. *Anal. Calc.* for C<sub>24</sub>H<sub>27</sub>GaN<sub>2</sub>O<sub>4</sub>: C, 60.41; H, 5.70; N, 5.87. *Found:* C, 60.45; H, 5.62; N, 5.92%. IR (KBr pellets, cm<sup>-1</sup>): 2922m, 2866m, 1654m, 1638s, 1624s, 1617s, 1610s, 1595s, 1576m, 1570m, 1565w, 1560m, 1554m, 1543s, 1540s, 1534s, 1525s, 1522s, 1518s, 1507w, 1472s, 1387s, 1323m, 1308s, 1256w, 1212w, 1166m, 1072w, 954w, 926w, 806w, 777w.

### 2.3. Single-crystal X-ray crystallography

The data collection for the single crystals of the compounds studied carried out at room temperature using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a SMART CCD 1 k diffractometer (for **1**) and on a Bruker SMART Apex-II diffractometer (for **2–5**). Complete crystal data and parameters for data collection and processing are reported in Table 1.

The structures were solved by direct methods using SHELXS-86 [20] and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97 [21]. The coordinates of the metal atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. All non-hydrogen atoms were refined by full-matrix techniques first in isotropic and then in anisotropic approximation. Hydrogen atoms coordinates were calculated geometrically and included into the final refinement in isotropic approximation except those for the atom C(15) in the structure of complex **4**, where the disorder in the propylene backbone made the calculation impossible for two different orientations simultaneously and the average H-atoms were found in the difference Fourier synthesis.

## 3. Results and discussion

### 3.1. Brief synthetic comments

Complexes **1–5**, can be regarded as ligand substitution products, obtained by the reaction between Ga(acac)<sub>3</sub> (acacH = 2,4,-pentanedione) and the appropriate tetradentate double Schiff base ligand 5RsalpropH<sub>2</sub> (R = H salpropH<sub>2</sub>, R = Cl 5ClisalpropH<sub>2</sub>, R = Br 5BrsalpropH<sub>2</sub>, R = NO<sub>2</sub> 5NO<sub>2</sub>salpropH<sub>2</sub> and R = Me 5MesalpropH<sub>2</sub>). This procedure involves the synthesis and isolation of the double Schiff base ligands prior to the reaction with the gallium salt. Alternatively, all complexes can be synthesized directly from the 1:2:1 reaction between 1,3-diaminopropane, the appropriate 5Rsalicylaldehyde and Ga(acac)<sub>3</sub>. Eq. (1) summarizes the preparation of the complexes

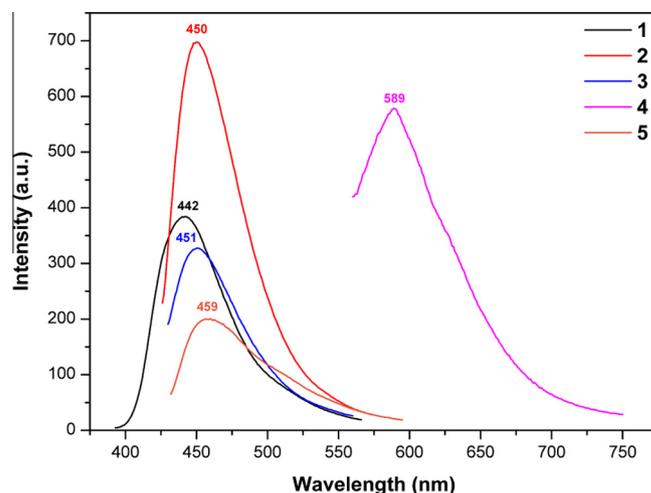
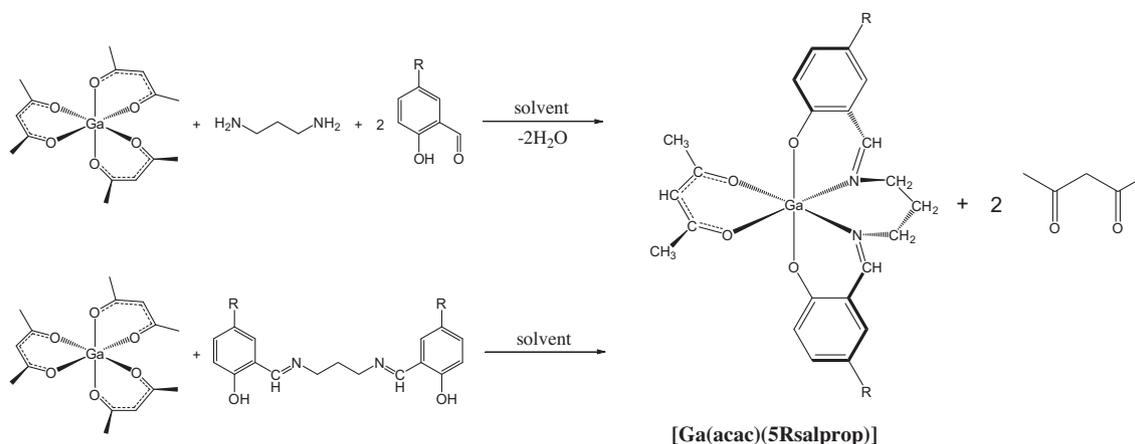


Fig. 6. Photoluminescence spectra of complexes **1–5** in the solid-state.

### 3.2. Description of structures

Complexes **1–4** crystallize in the orthorhombic space group  $P2_12_12_1$ , while complex **5** crystallizes in the orthorhombic space group  $Pna2_1$ . The molecular structures of **1–3** and **4–5** are shown in Figs. 2 and 3, respectively, while selected bond distances and angles for all complexes are listed in Table 2. The molecular structures of all complexes are very similar and therefore a general description for all complexes will follow. The Ga<sup>III</sup> ion is in a distorted octahedral geometry being surrounded by one tetradentate chelate 5Rsalprop<sup>2-</sup> ligand and a bidentate chelate acac<sup>-</sup> ligand. The 5Rsalprop<sup>2-</sup> ligand is coordinated through the imine nitrogen atoms and the deprotonated hydroxyl oxygen atoms of the phenolate groups creating three six-membered chelate rings around the Ga<sup>III</sup> atom. A bidentate chelate acac<sup>-</sup> ligand completes the octahedron and increases the number of the six-membered chelate rings around the metal atom to four. The Ga–O<sub>acac</sub> [Ga(1)–O(1) and Ga(1)–O(2)] distances are very similar in all five complexes ranging from 1.958(1) to 2.009(1) Å. The same is true for the Ga–O<sub>phenolate</sub> [Ga(1)–O(3) and Ga(1)–O(4)] and the Ga–N<sub>imine</sub> [Ga(1)–N(1) and Ga(1)–N(2)] distances, with the former ranging between 1.901(3) and 1.930(1) Å and the latter between 2.050(3) and 2.077(3) Å. A profound structural difference at the molecular level between the five complexes is the out of plane distance between the Ga<sup>III</sup> atom and the mean plane of the three carbon atoms and the two oxygen atoms of the acac<sup>-</sup> ligand. The relative distances are 0.212 Å (**1**), 0.013 Å (**2**), 0.242 Å (**3**), 0.158 Å (**4**) and 0.581 Å (**5**).

Besides the structural similarities at the molecular level, the peripheral substitution at the salicylidene rings has largely affected the supramolecular structures of the complexes. All complexes exhibit two C–H···O intermolecular interactions between one of the imine carbon atoms and one of the phenolate oxygen atoms and several C–H··· $\pi_{\text{phenolate}}$  interactions (Tables S1–S5). Complex **1** interacts with eight neighboring molecules creating a three-dimensional (3<sup>6</sup>.4<sup>18</sup>.5<sup>3</sup>.6)-**hex** network (Fig. 4) through two C–H···O<sub>phenolate</sub> (one unique) and six C–H··· $\pi_{\text{phenolate}}$  (three unique) interactions. Complexes **2** and **4** are connected to six neighboring molecules through two C–H···O<sub>phenolate</sub> (one unique) and four C–H··· $\pi_{\text{phenolate}}$  (two unique) interactions, each creating a regular two-dimensional 3<sup>6</sup> network, complex **3** interacts with four of its neighbors through two C–H···O<sub>phenolate</sub> (one unique) and two C–H··· $\pi_{\text{phenolate}}$  (one unique) interactions to create a regular two-dimensional 4<sup>4</sup> net (square-grid), while complex **5** connects to eight neighbors through two C–H···O<sub>phenolate</sub> (one unique) and six C–H··· $\pi_{\text{phenolate}}$  (three unique) interactions to create a three-dimensional (3<sup>6</sup>.4<sup>14</sup>.5<sup>8</sup>)-**bct-8-Pccn** net (Fig. 4).

### 3.3. Thermal stability

Thermogravimetric analysis (Fig. S1) reveals that complex **1** loses the solvate water molecule and degrades above 150 °C, complex **5** is also stable up to ~150 °C, while complexes **2–4** are stable up to ~225 °C.

### 3.4. Solid-state emission

Gallium complexes with Schiff bases bearing aromatic groups are known to exhibit interesting luminescence properties [15–17]. The solid-state emission spectra of the five free Schiff base ligands and complexes **1–5** are shown in Figs. 5 and 6, respectively. The emission spectra were obtained after excitation at the peak maximum of the relevant excitation spectrum, except for the spectrum of 5MesalpropH<sub>2</sub>, which was excited at 280 nm. The excitation spectra of the ligands and complexes are shown in Figs. S2 and S3, respectively. SalpropH<sub>2</sub> exhibits an emission band with a maximum at 495 nm. By attaching the EDG methyl groups at the fifth position of the salicylidene rings of the ligand a hypsochromic shift of ~15 nm of the emission maximum is observed. The exact opposite is observed when the EWG –Cl or –Br are attached on the same position of the ligand; ligands 5ClsalpropH<sub>2</sub> and 5BrsalpropH<sub>2</sub> displayed emission maxima at 510 nm and 504 nm, respectively, which are 15 nm and 9 nm bathochromically shifted with respect to the salpropH<sub>2</sub> emission. The presence of –NO<sub>2</sub> groups, which are EWG inductively and EWG by resonance, on the fifth position of the salicylidene rings results in even larger bathochromic shift of the emission maximum by 102 nm with respect to the salpropH<sub>2</sub> emission.

The maxima in the emission spectra of complexes **1–5** are less broad and hypsochromically shifted compared to that of the respective free ligands. Since the emission of the complexes is ligand-based [22–26] mainly originating from the iminophenolato chromophore, the role of the Ga<sup>III</sup> atom is to impose conformational rigidity, extending the conjugation of the ligand, thus restricting energy loss via non-radiative decay [25,26]. The unsubstituted complex **1** displayed an emission maximum at 442 nm, which is below the blue light region. All substituted complexes with either an EDG (**5**) or an EWG (**2–4**) display bathochromically shifted emission with respect to complex **1**. Complexes **2**, **3** and **5** exhibit emission maxima at 450 nm, 451 nm and 459 nm, respectively, which are all within the blue light region, while complex **4** displays an emission maximum at 589 nm which is at the border between the yellow and orange light regions. The substitution of the salicylidene rings of the ligands with either EWG or EDG does

affect the electronic properties of the both the free ligands and the respective complexes and modulates the emission maxima of the materials in the solid-state.

## 4. Conclusions

A family of mononuclear Ga(III) complexes based on *N,N'*-bis(salicylidene)propane-1,3-diamine (salpropH<sub>2</sub>) and its substituted derivatives with EDGs or EWGs at the fifth position of the salicylidene rings has been synthesized and structurally characterized. All complexes comprise an octahedral Ga<sup>III</sup> atom being surrounded by a tetradentate, tris-chelate 5Rsalprop<sup>2-</sup> (R = H, Cl, Br, Me or NO<sub>2</sub>) ligand and a bidentate chelate acac<sup>-</sup> ligand. Both free ligands and complexes display photoluminescence in the solid-state in the visible region. The peripheral substitution of the salpropH<sub>2</sub> ligand with EDGs or EWGs modulates the emission maxima of the free ligands and the complexes with the latter displaying hypsochromic shifts with respect to the emission of the free ligands.

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## Appendix A. Supplementary data

CCDC 920125–920129 contain the supplementary crystallographic data for **1–5**. 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. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2013.02.057>.

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