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

Sotiria Tella, Vlasoula Bekiari, Vadim G. Kessler, Giannis S. Papaefstathiou

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]. Alq3 (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) results in materials with improved properties such as higher luminescence efficiency and improved thermal stability [7–9]. An alternative route to tune/modify the electronic properties of these materials is to introduce substitute chemical Groups (EWGs) or Electron Donating chemical Groups (EDGs) on the saphH2 ligand. This method 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-hydroxyquinoline 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 (saphH2) 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 saphH2 ligand.

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 (salpropH2) and its substituted derivatives. An attempt to tune/modify the emission maxima, EWGs such as Cl, Br and NO2, 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-dimino propane and all solvents were obtained from commercial sources and used as received. Ga(acac)3 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 N2 flow of 50 ml/min. Emission and excitation spectra were recorded on a Shimadzu RF-5301PC spectrophotofluorometer on powdered samples dispersed and squeezed on a quartz plate.
2.2. Compound preparation

2.2.1. Synthesis of \(N,N\)-bis(salicylidene)propane-1,3-diamine (salpropH2) and its substituted derivatives

SalpropH2 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. \([\text{Ga(acac)}(\text{salprop})]/\text{C1}_{0.5}\text{H2O (1)}\)

Method A: SalpropH2 (0.127 g, 0.450 mmol) and Ga(acac)3 (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 (2 × 5 mL) and dried in air. Yield 0.12 g, 58%. Anal. Calc. for \(\text{C}_{22}\text{H}_{24}\text{GaN}_{2}\text{O}_{4.5}\): C, 57.67; H, 5.28; N, 6.11. Found: C, 57.71; H, 5.23; N, 6.17%. IR (KBr pellets, cm\(^{-1}\)): 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)3 (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 \(\text{C}_{22}\text{H}_{24}\text{GaN}_{2}\text{O}_{4.5}\): C, 57.67; H, 5.28; N, 6.11. Found: C, 57.70; H, 5.25; N, 6.15%. IR (KBr pellets, cm\(^{-1}\)): 1620w, 1587w, 1536w, 1519w, 1466w, 1445w, 1383w, 1338w, 1315w, 1275w, 1210w, 1195w, 1146w, 1125w, 1079w, 1065w, 1015w, 923w, 898w, 797w, 762w, 738w, 604w.

Table 1: Crystallographic data for complexes 1–5.

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Fig. 1. The structures of the double Schiff base ligands discussed in the text.
2.2.3. $[\text{Ga(acac})(\text{5Clsalprop})] \text{ (2)}$

**Method A:** $\text{Ga(acac)}_3$ (0.102 g, 0.280 mmol) and 5ClsalpropH$_2$ (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$_2$O (2/5 mL) and dried in air. Yield 0.08 g, 56%. Anal. Calc. for C$_{22}$H$_{21}$Cl$_2$GaN$_2$O$_4$: 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 $\text{Ga(acac)}_3$ (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$_2$O (2 × 5 mL) and dried in air. Yield 0.06 g, 41%. Anal. Calc. for C$_{22}$H$_{21}$Cl$_2$GaN$_2$O$_4$: 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. $[\text{Ga(acac})(\text{5Brsalprop})] \text{ (3)}$

**Method A:** $\text{Ga(acac)}_3$ (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$_2$O (2 × 5 mL) and dried in air. Yield 0.12 g, 70%. Anal. Calc. for C$_{22}$H$_{21}$Br$_2$GaN$_2$O$_4$: 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 $\text{Ga(acac)}_3$ (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.

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<td>1.995(2)</td>
<td>1.993(3)</td>
<td>1.974(1)</td>
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<tr>
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<td>1.990(2)</td>
<td>1.991(3)</td>
<td>1.958(1)</td>
<td>2.009(1)</td>
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2.2.5. [Ga(acac)(5NO2salprop)] (4)

Method A: Ga(acac)3 (0.102 g, 0.280 mmol) and 5NO2salpropH2 (0.104 g, 0.280 mmol) were refluxed in a mixture of ethanol (15 mL) and dichloromethane (6 mL). The crystals were isolated by vacuum filtration, washed with n-hexane (60 mL). Yield 0.09 g, 60%. Anal. Calc. for \( C_{22}H_{21}GaN_{4}O_{8} \): C, 49.01; H, 3.93; N, 10.39. Found: C, 49.06; H, 3.88; N, 10.30. IR (KBr pellets, cm−1): 1649m, 1631s, 1603m, 1558s, 1532m, 1507w, 1486m, 1440w, 1379w, 1319s, 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)3 (0.102 g, 0.280 mmol) were refluxed in a mixture of ethanol (15 mL) and dichloromethane (6 mL) for 30 min. The yellow solution was filtered, washed with n-hexane (60 mL). X-ray quality yellow-orange crystals of 4 were formed within a week. Yield 0.09 g, 60%. Anal. Calc. for \( C_{22}H_{21}GaN_{4}O_{8} \): C, 49.01; H, 3.93; N, 10.39. Found: C, 49.06; H, 3.88; N, 10.30. IR (KBr pellets, cm−1): 1649m, 1631s, 1603m, 1558s, 1532m, 1507w, 1486m, 1440w, 1379w, 1319s, 1246w, 1217w, 1192w, 1130w, 1102m, 1016w, 955w, 946w, 836w, 798w, 755w, 699w, 691w, 650w, 576w, 515w.

Fig. 4. 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 Et₂O (2 × 5 mL) and dried in air. Yield 0.05 g, 38%. Anal. Calc. for C₂₄H₂₇GaN₂O₄: C, 60.41%; H, 5.70%; N, 5.87. Found: C, 60.45%; H, 5.62%; N, 5.92%. IR (KBr pellets, cm⁻¹): 2922m, 2866m, 1654m, 1638s, 1624s, 1617s, 1610s, 1595s, 1576m, 1570m, 1565w, 1560m, 1545m, 1540m, 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 Kα radiation (λ = 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 SHELX-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)₃ (acacH = 2,4-pentanedione) and the appropriate tetradeятenate double Schiff base ligand 5RsalpropH₂ (R = H salpropH₂, R = Cl 5ClsalpropH₂, R = Br 5BrsalpropH₂, R = NO₂ 5NO₂salpropH₂ and R = Me 5MesalpropH₂). 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)₃. Eq. (1) summarizes the preparation of the complexes

![Chemical reaction image]

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 P2₁2₁2₁, while complex 5 crystallizes in the orthorhombic space group Pna2₁. 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 GaIII ion is in a distorted octahedral geometry being surrounded by one tetradeятenate chelate 5Rsalprop⁻² ligand and a bidentate chelate acac⁻² ligand. The 5Rsalprop⁻² 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 GaIII atom. A bidentate chelate acac⁻² ligand completes the octahedron and increases the number of the six-membered chelate rings around the metal atom to four. The Ga–O_acac [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_phenolate [Ga(1)–O(3) and Ga(1)–O(4)] and the Ga–N_amine [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 GaIII atom and the mean plane of the three carbon atoms and the two oxygen atoms of the acac⁻² 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).

![Molecular structure image]
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⋯N phenolate interactions (Tables S1−S5). Complex 1 interacts with eight neighboring molecules creating a three-dimensional (3\(\text{d}^4\text{r}^5\text{p}^6\))-hex network (Fig. 4) through two C-H⋯O phenolate (one unique) and six C-H⋯N phenolate (three unique) interactions. Complexes 2 and 4 are connected to six neighboring molecules through two C-H⋯O phenolate (one unique) and four C-H⋯N phenolate (two unique) interactions, each creating a regular two-dimensional 3\(\text{d}\) network, complex 3 interacts with four of its neighbors through two C-H⋯O phenolate (one unique) and two C-H⋯N phenolate (one unique) interactions to create a regular two-dimensional 4\(\text{d}\) net (square-grid), while complex 5 connects to eight neighbors through two C-H⋯O phenolate (one unique) and six C-H⋯N phenolate (three unique) interactions to create a three-dimensional (3\(\text{d}^4\text{r}^5\text{p}^6\))-bct-8-Pccn net (Fig. 4).

3.3. Thermal stability

Thermogravimetric analysis (Fig. S1) reveals that complex 1 looses 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 5MesalpropH2, which was excited at 280 nm. The excitation spectra of the ligands and complexes are shown in Figs. S2 and S3, respectively. SalpropH2 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 5CsalpropH2 and 5BrsalpropH2 display emission maxima at 510 nm and 504 nm, respectively, which are 15 nm and 9 nm bathochromically shifted with respect to the salpropH2 emission. The presence of –NO2 groups, which is observed when the EWG –Cl or –Br are attached on the same position of the salicylidene rings results in even larger bathochromic shift of the emission maximum by 102 nm with respect to the salpropH2 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 framework, the role of the Ga\(^{3+}\) ion 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 salicylideno 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 (salpropH2) 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\(^{3+}\) ion being surrounded by a tetradentate, tris-chelate 5SrSalprop\(^2\)- (R = H, Cl, Br, Me, or NO\(_2\)) ligand and a bidentate chelate acac\(^-\) ligand. Both free ligands and complexes display photoluminescence in the solid-state in the visible region. The peripheral substitution of the salpropH2 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.

Acknowledgements

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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.

References