



Synthesis and structure of *N*-salicylidene-*o*-aminophenolato gallium(III) complexes

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Dedicated to Dr. Aris Terzis for the occasion of his retirement and for his great contribution to the advancement of inorganic chemistry in Greece through X-ray crystallography.

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ABSTRACT

The reactions of Ga(acac)₃ with *N*-salicylidene-*o*-aminophenol (saphH₂) and its 5-methyl (5MesaphH₂) and 5-bromo (5BrsaphH₂) derivatives in alcohols afforded the complexes [Ga(acac)(saph)(EtOH)] (**1**), [Ga(acac)(5Mesaph)(MeOH)] (**2**) and [Ga(acac)(5Brsaph)(EtOH)] (**3**), respectively, in good yields. The crystal structures of **1** and **2** have been solved by single-crystal X-ray crystallography. All three complexes are mononuclear with the Ga^{III} atoms being surrounded by a dianionic tridentate Schiff base ligand, one bidentate acac⁻ ligand and a terminal alcohol molecule. Characteristic IR data are discussed in terms of the nature of bonding and the structures of the three complexes.

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1. Introduction

Over the last decade we have been exploring the coordination chemistry of gallium(III) with ligands bearing N and/or O donor atoms [1–7]. Our interest in Ga(III) chemistry stems from the fact that some gallium(III) complexes have emerged as leading materials for optoelectronic devices such as light-emitting diodes (LEDs) and laser diodes in the blue/UV region [8,9] as well as potential metallo-drugs mainly due to their antiproliferative activity.

Gallium complexes [10] are considered as the most promising candidates to replace [Alq₃] as electron-transport host or emitting material [11] for small molecule light-emitting diodes (SMOLEDs) [12]. [Gaq₃] is also a promising electroluminescence (EL) material, exhibiting higher power efficiency than the aluminum analog, [Alq₃] [13,14]. The relevance of Ga(III) complexes in both materials science and biomedical developments is projected on [Gaq₃] which is of current interest in materials science [13,14] and at the same time is being evaluated in clinical trials for anticancer activity [15–17].

Focusing on SMOLED materials, such as [Alq₃] or [Gaq₃], it has been found that the ligand-centered luminescence upon ligand-

centered excitation, may be tuned by attaching Electron Withdrawing chemical Groups (EWGs) or Electron Donating chemical Groups (EDGs) on the ligands [18]. An alternative way to tune the optical properties of those materials is to substitute some of the q⁻ ligands. [Ga₂(saph)₂q₂] for example, [saph²⁻ = (*N*-salicylidene-*o*-aminophenolate)(-2) and q⁻ = 8-quinolate(-1)], is a very good candidate as a novel electron-transporting and emitting material for SMOLEDs [10].

Recently, our interest turned toward the synthesis of gallium(III) complexes based on the Schiff base ligand *N*-salicylidene-*o*-aminophenol and its derivatives. By employing Ga(acac)₃ with saphH₂ and its EWGs (5MesaphH₂ = 5-methyl-*N*-salicylidene-*o*-aminophenol) and EDGs (5BrsaphH₂ = 5-bromo-*N*-salicylidene-*o*-aminophenol) derivatives in alcohols, we have isolated three mononuclear complexes namely [Ga(acac)(saph)(EtOH)] (**1**) [Ga(acac)(5Mesaph)(MeOH)] (**2**) and [Ga(acac)(5Brsaph)(EtOH)] (**3**). All three complexes exhibit ligand-centered photoluminescence the intensity of which is extensively increased upon complex formation. All three complexes can also be for the construction of electroluminescence devices and all emitted electroluminescence [19]. In this paper, we report the *chemical* aspects of our investigation, i.e. the detailed synthesis, the single-crystal X-ray characterization of **1** and **2**, and the IR spectroscopic data for all three complexes.

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2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions. Gallium (III) acetylacetonate, $[\text{Ga}(\text{acac})_3]$, 2-aminophenol and 5-methylsalicylaldehyde (2-hydroxy-5-methyl-benzaldehyde) were obtained from Aldrich. 5-Bromosalicylaldehyde was from Fluka, while salicylaldehyde and the rest of the reagents were from Merck. All chemicals were of the best quality available and were used as received. Microanalyses (C, H and N) were performed by the University of Ioannina (Ioannina, Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. IR spectra ($4000\text{--}450\text{ cm}^{-1}$) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets.

2.2. Compound preparation

2.2.1. Synthesis of *N*-salicylidene-*o*-aminophenol (*saphH*₂) and derivatives

Synthesis of *saphH*₂ was achieved by the condensation in absolute ethanol of 2-aminophenol with salicylaldehyde in the case of the unsubstituted Schiff base, with 2-hydroxy-5-methyl-benzaldehyde in the case of methyl substituted Schiff base or with 5-bromosalicylaldehyde in the case of bromo-substituted Schiff base, in accordance with literature methods [20]. The chemical structures of the free and substituted Schiff bases are shown in Fig. 1.

2.2.2. $[\text{Ga}(\text{acac})(\text{saph})(\text{EtOH})]$ (**1**)

A yellow solution of *H*₂*saph* (0.021 g, 0.10 mmol) in EtOH (10 mL) was added to a colorless solution of $[\text{Ga}(\text{acac})_3]$ (0.037 g, 0.10 mmol) in the same solvent (10 mL). The clear yellow solution, obtained was allowed to stand undisturbed for one day at room temperature. Well-formed X-ray quality single crystals of **1** slowly appeared. The yellow crystals were isolated by vacuum filtration, washed with cold EtOH ($2 \times 3\text{ mL}$) and dried in air. The yield was 80% based on Ga. *Anal. Calc.* for $\text{C}_{20}\text{H}_{22}\text{GaNO}_5$: C, 56.37; H, 5.21; N, 3.29. Found: C, 55.78; H, 5.12; N, 3.24%. IR (KBr pellets, cm^{-1}): 3440br, 3048w, 2968w, 2790w, 1620s, 1586s, 1546m, 1526s, 1474s, 1446w, 1386s, 1342w, 1308m, 1270m, 1222w, 1176m, 1154m, 1128w, 1090w, 1042m, 928m, 876w, 836m, 774w, 742m, 678w, 626w, 610w, 526w, 538m, 490w.

2.2.3. $[\text{Ga}(\text{acac})(5\text{Mesaph})(\text{MeOH})]$ (**2**)

Solid $[\text{Ga}(\text{acac})_3]$ (0.037 g, 0.10 mmol) was added to a yellow-orange solution of *H*₂5*Mesaph* (0.023 g, 0.10 mmol) in MeOH/EtOH (1:1 v/v, 20 mL). The yellow solution obtained was filtered and layered with Et₂O/hexane (1:1 v/v, 40 mL). Slow mixing yielded well-

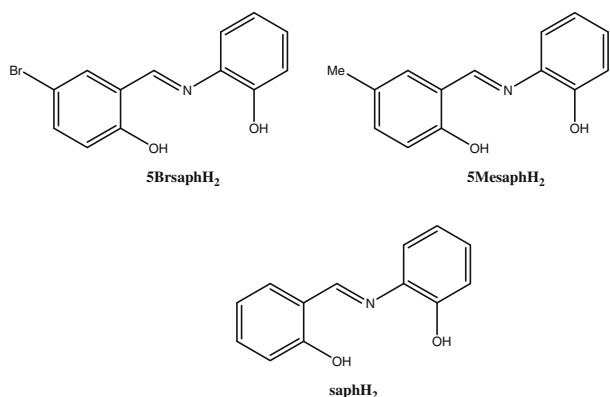


Fig. 1. The chemical structures of the ligands discussed in the text.

formed, X-ray quality yellow crystals of **2**. The crystals were isolated by vacuum filtration, washed with Et₂O ($2 \times 3\text{ mL}$) and dried in air. The yield was 78% based on Ga. *Anal. Calc.* for $\text{C}_{20}\text{H}_{22}\text{GaNO}_5$: C, 56.37; H, 5.21; N, 3.29. Found: C, 57.10; H, 5.75; N, 3.47%. IR (KBr pellets, cm^{-1}): 3450wbr, 3003w, 2760w, 2552w, 1621m, 1588s, 1537s, 1478s, 1433w, 1393m, 1378s, 1315m, 1282m, 1270m, 1252w, 1214w, 1200w, 1161m, 1147w, 1134m, 1028m, 961w, 933w, 891w, 830m, 814w, 785w, 740m, 684w, 652w, 616w, 584w, 564w, 532w, 491w, 478w, 451w.

2.2.4. $[\text{Ga}(\text{acac})(5\text{Brsaph})(\text{EtOH})]$ (**3**)

A colorless solution of $[\text{Ga}(\text{acac})_3]$ (0.037 g, 0.10 mmol) in EtOH (10 mL) was added to a yellow solution of *H*₂5*Brsaph* (0.058 g, 0.20 mmol) in the same solvent (10 mL). The yellow solution obtained was filtered and allowed to stand undisturbed in the refrigerator for thirteen days. Well-formed X-ray quality single crystals of **3** slowly appeared. The yellow crystals were isolated by vacuum filtration, washed with Et₂O ($2 \times 3\text{ mL}$) and dried in air. The yield was 60% based on Ga. *Anal. Calc.* for $\text{C}_{20}\text{H}_{21}\text{GaNO}_5\text{Br}$: C, 47.56; H, 4.20; N, 2.77. Found: C, 48.79; H, 5.94; N, 2.84%. IR (KBr pellets, cm^{-1}): 3460br, 2348w, 2284br, 1658w, 1619s, 1589m, 1524s, 1475s, 1458s, 1377s, 1307m, 1261m, 1248m, 1209w, 1169s, 1137w, 1114w, 1087w, 1045w, 875w, 826m, 744s, 678m, 648m, 620w, 580w, 544w, 518w, 493w.

2.3. Single-crystal X-ray crystallography

Crystals of **1** and **2** were mounted in capillary. Diffraction measurements were made on a Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu radiation. Complete crystal data and parameters for data collection and processing are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $22 < 2\theta < 54^\circ$ for **1** and

Table 1
Crystallographic data for complexes **1** and **2**.

Parameter	1	2
Formula	$\text{C}_{40}\text{H}_{44}\text{Ga}_2\text{N}_2\text{O}_{10}$	$\text{C}_{20}\text{H}_{22}\text{GaNO}_5$
Formula weight	852.21	426.11
Crystal color, habit	yellow, plates	yellow, plates
Crystal dimensions (mm)	$0.10 \times 0.20 \times 0.30$	$0.13 \times 0.15 \times 0.40$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	12.8150(18)	10.912(5)
<i>b</i> (Å)	16.826(3)	10.065(5)
<i>c</i> (Å)	18.170(3)	11.164(6)
α (°)	90	76.35(2)
β (°)	90.888(6)	61.66(2)
γ (°)	90	63.54(2)
<i>V</i> (Å ³)	3917.3(11)	965.7(8)
<i>Z</i>	8	2
ρ_{calc} (g cm^{-3})	1.445	1.465
Radiation, λ (Å)	Cu $K\alpha$, 1.54180	Cu $K\alpha$, 1.54180
<i>T</i> (K)	293	293
$2\theta_{\text{max}}$ (°)	110	118
μ (mm^{-1})	2.184	2.215
Reflections collected/unique (R_{int})	5060/4882 (0.0280)	2928/2772 (0.0205)
Data with $I > 2\sigma(I)$	3557	2674
Parameters refined	543	293
$(\Delta\rho)_{\text{max}}$, $(\Delta\rho)_{\text{min}}$ (e Å^{-3})	0.419, −0.511	1.212, −0.398
Goodness-of-fit (GOF) (on F^2)	1.024	1.060
R_1^a , wR_2^b (all data)	0.0740, 0.1360	0.0370, 0.1000
R_1^a , wR_2^b ($I > 2\sigma(I)$)	0.0486, 0.1186 ^c	0.0361, 0.0991 ^d

^a $R_1 = \sum (|F_o| - |F_c|) / \sum (|F_o|)$.

^b $wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$.

^c For 3579 reflections with $I > 2\sigma(I)$.

^d For 2674 reflections with $I > 2\sigma(I)$.

2. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86 [21] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [22]. For **1**, all hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. For **2**, the hydrogen atoms were either located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Brief synthetic comments

Eq. (1) summarizes the synthesis of the ligands. Complexes **1–3** were obtained by ligand substitution reactions between $\text{Ga}(\text{acac})_3$ ($\text{acacH} = 2,4\text{-pentanedione}$) and 5XsaphH_2 ($\text{X} = \text{H}$, saphH_2 ; $\text{X} = \text{Me}$, 5MesaphH_2 and $\text{X} = \text{Br}$, 5BrsaphH_2) in alcoholic solutions as yellow crystals. Eq. (1) summarizes the preparation of the representative complex **1**. The ligand substitution reactions can be realized on the basis of the different coordination strength of the acacH and the 5XsaphH_2 ligands.

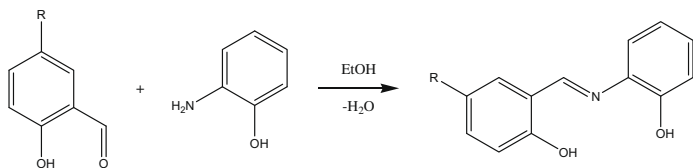
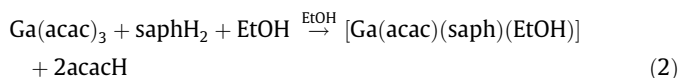


Table 2
Selected bond distances (Å) and angles ($^\circ$) in **1**.

Ga(1)–O(1)	1.894(4)	Ga(2)–O(11)	1.910(4)
Ga(1)–O(2)	1.923(4)	Ga(2)–O(12)	1.927(4)
Ga(1)–O(3)	1.925(4)	Ga(2)–O(13)	1.925(4)
Ga(1)–O(4)	1.984(4)	Ga(2)–O(14)	1.977(4)
Ga(1)–O(5)	2.067(4)	Ga(2)–O(15)	2.062(4)
Ga(1)–N(1)	1.966(2)	Ga(2)–N(11)	2.045(2)
O(1)–Ga(1)–O(2)	171.4(2)	O(11)–Ga(2)–O(12)	172.2(2)
O(1)–Ga(1)–O(3)	92.0(2)	O(11)–Ga(2)–O(13)	91.7(2)
O(1)–Ga(1)–O(4)	93.9(2)	O(11)–Ga(2)–O(14)	93.5(2)
O(1)–Ga(1)–O(5)	88.6(2)	O(11)–Ga(2)–O(15)	90.2(2)
O(1)–Ga(1)–N(1)	98.2(6)	O(11)–Ga(2)–N(11)	95.2(6)
O(2)–Ga(1)–O(3)	93.7(2)	O(12)–Ga(2)–O(13)	94.3(2)
O(2)–Ga(1)–O(4)	92.3(2)	O(12)–Ga(2)–O(14)	91.4(2)
O(2)–Ga(1)–O(5)	85.5(2)	O(12)–Ga(2)–O(15)	85.4(2)
O(2)–Ga(1)–N(1)	76.3(6)	O(12)–Ga(2)–N(11)	78.8(6)
O(3)–Ga(1)–O(4)	90.7(2)	O(13)–Ga(2)–O(14)	90.3(2)
O(3)–Ga(1)–O(5)	87.0(2)	O(13)–Ga(2)–O(15)	85.7(2)
O(3)–Ga(1)–N(1)	169.6(6)	O(13)–Ga(2)–N(11)	173.1(6)
O(4)–Ga(1)–O(5)	176.7(2)	O(14)–Ga(2)–O(15)	174.7(2)
O(4)–Ga(1)–N(1)	86.8(4)	O(14)–Ga(2)–N(11)	89.0(5)
O(5)–Ga(1)–N(1)	95.0(4)	O(15)–Ga(2)–N(11)	94.6(5)

Complex **1** crystallizes in the monoclinic space group $P2_1/n$, while there are two crystallographically independent mononuclear



3.2. Description of structures

Complexes **1** and **2** were characterized by X-ray crystallography, while preliminary X-ray characterization of complex **3** revealed that it is isostructural to **1** and therefore we did not performed full X-ray characterization.

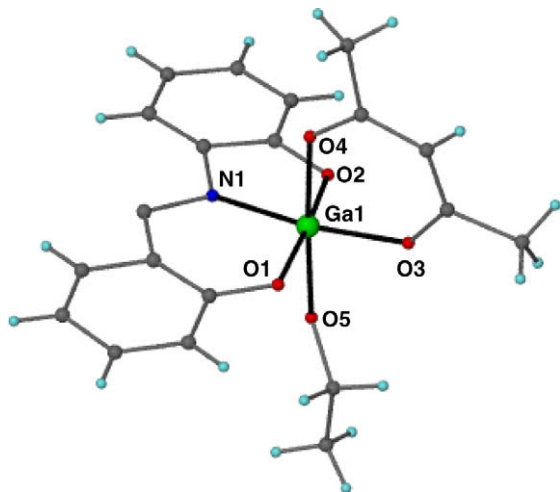


Fig. 2. Ball and stick representation of the molecular structure of **1**.

complexes in the unit cell. Fig. 2 shows the molecular structure of one monomer of **1**, while selected bond distances and angles are listed in Table 2. The Ga^{III} ion adopts a six-coordinate distorted octahedral geometry. The saph^{2-} ligand chelates the Ga^{III} ion through the imine nitrogen atom and the deprotonated hydroxyl oxygen atoms all on the equatorial plane of the octahedron. The acac^- ligand also chelates the Ga^{III} atom with one O atom completing the equatorial plane of the octahedron and the other on one of the axial positions. The ethanol O atom occupies the second axial position. Although the EtOH hydroxyl hydrogen atom was not located, it appears that each $[\text{Ga}(\text{acac})(\text{saph})(\text{EtOH})]$ is hydrogen

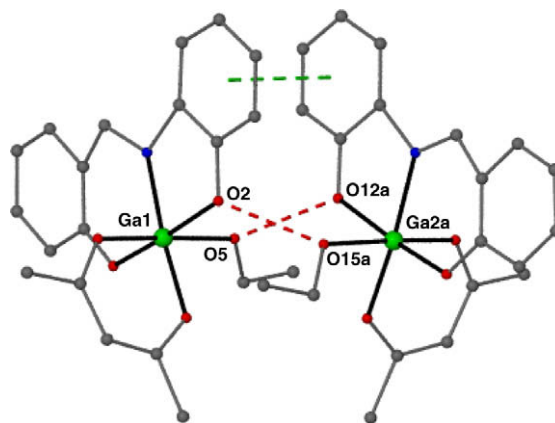


Fig. 3. The hydrogen bonding and the π – π stacking interactions that form the dimer in **1**. All hydrogen atoms have been omitted for clarity. Symmetry code: a, $x-1/2, 3/2-y, 1/2+z$.

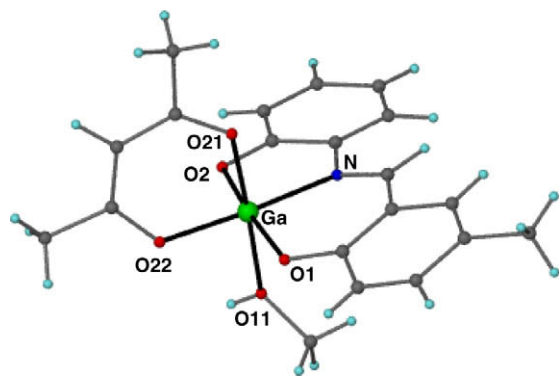


Fig. 4. Ball and stick representation of the molecular structure of **2**.

Table 3
Selected bond distances (Å) and angles (°) in **2**.

Ga–O(1)	1.896(2)	Ga–O(11)	2.060(2)
Ga–O(2)	1.960(2)	Ga–O(21)	1.982(2)
Ga–N	2.032(3)	Ga–O(22)	1.920(2)
O(1)–Ga–O(2)	170.8(1)	O(2)–Ga–O(22)	89.7(1)
O(1)–Ga–N	91.5(1)	N–Ga–O(11)	92.5(1)
O(1)–Ga–O(11)	87.5(1)	N–Ga–O(21)	89.5(1)
O(1)–Ga–O(21)	93.0(1)	N–Ga–O(22)	171.5(1)
O(1)–Ga–O(22)	96.8(1)	O(11)–Ga–O(21)	177.9(1)
O(2)–Ga–N	81.8(1)	O(11)–Ga–O(22)	85.7(1)
O(2)–Ga–O(11)	86.6(1)	O(21)–Ga–O(22)	92.2(1)
O(2)–Ga–O(21)	93.3(1)		

bonded to the other crystallographically independent monomer (Fig. 3) through two hydrogen bonds that involve the EtOH oxygen [O5 and O15] and the deprotonated hydroxyl oxygen [O12 and O2] atoms of the saph²⁻ ligand with the O...O distances equal to 2.618 and 2.650 Å for O5...O12a and O2...O15a (a: $x-1/2$, $3/2-y$, $1/2+z$), respectively. A π - π stacking interaction (centroid...centroid distance: 3.638 Å) between the aminophenolate rings of the two monomers assists the hydrogen bonding in forming the dimer (Fig. 3).

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **2** is shown in Fig. 4, while selected bond distances and angles are listed in Table 3. The mononuclear complex **2** is very similar to **1**, with the Ga^{III} ion adopting a distorted octahedral environment. A tridentate 5Mesaph²⁻ ligand chelates to the Ga^{III} ion through the imine nitrogen atom and the deprotonated hydroxyl oxygen atoms. A bidentate chelating acac⁻ ligand and a MeOH molecule complete the octahedron around the metal centre. The NO₂ donor set from the 5Mesaph²⁻ ligand and one oxygen atom from the acac⁻ ligand are situated on the equatorial plane, while the other acac⁻ oxygen atom and the methanolic oxygen atom occupy the axial positions of the octahedron. Two

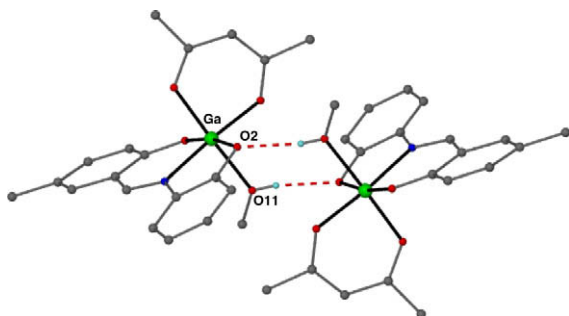


Fig. 5. The hydrogen bonding that form the dimer in **2**. All hydrogen atoms have been omitted for clarity.

[Ga(acac)(5Mesaph)(MeOH)] complexes assemble to form a hydrogen bonded dimer (Fig. 5) through the O11–H011...O2a [O11...O2a 2.627 Å, a: $1-x, -y, 1-z$] hydrogen bond (and its symmetry related) which involves the methanolic oxygen atom O11 and one of the deprotonated hydroxyl oxygen atoms O2 of the 5Mesaph²⁻ ligand.

3.3. Spectroscopic characterization

The IR spectra of all complexes are similar. In the $\nu(\text{O-H})$ region, the IR spectra of the complexes exhibit medium-intensity bands at 3440 (**1**), 3450 (**2**) and 3460 (**3**) cm^{-1} , assignable to $\nu(\text{O-H})_{\text{alcohol}}$ [23]. The broadness and the relatively low frequency of these bands are both indicative of hydrogen bonding. The $\nu(\text{C=N})$ in spectra free ligands appears at 1632, 1628 and 1630 cm^{-1} for saphH₂, 5MesaphH₂ and 5BrsaphH₂, respectively [24]. These bands are shifted to lower wavenumbers in the spectra of **1** (1620 cm^{-1}), **2** (1621 cm^{-1}) and **3** (1619 cm^{-1}) due to complexation. The $\nu(\text{C=C})$ and $\nu(\text{C=O})$ modes [25] of the acetylacetonate ligand at 1586 and 1532 cm^{-1} in the spectrum of Ga(acac)₃ have not shifted significantly in the spectra of **1** (1586 and 1526 cm^{-1}), **2** (1588 and 1537 cm^{-1}) and **3** (1589 and 1524 cm^{-1}), respectively.

4. Conclusions and perspectives

In this manuscript, we presented the chemical aspects of our first results from the exploitation of the Ga(III)/5XsaphH₂ reaction system. The Ga(acac)₃/saphH₂, 5MesaphH₂ and 5BrsaphH₂ reaction systems provided access to three mononuclear Ga(III) complexes. Two of the complexes were characterized by single-crystal X-ray crystallography, while the identity of the third was confirmed by crystal cell determination and IR data. All three complexes are surrounded by a tridentate-chelate 5Xsaph²⁻ ligand, a chelate acac⁻ ligand and a terminal alcohol molecule. The optical properties of this series indicated [19] that all three complexes emitted light upon photo- or electro-excitation. Efforts are being devoted to change the acac⁻ and alcohol molecules with other electron rich molecules.

5. Supplementary data

CCDC 725905 and 725906 contain the supplementary crystallographic data for **1** and **2**. 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

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