Characterization of 2-methyl-8-quinolinolato gallium (III) chelates

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CHARACTERIZATION OF 2-METHYL-8-QUINOLINOLATO GALLIUM (III) CHELATES

by

Sanjini Ushika Nanayakkara

Bachelor of Science
University of Colombo, Sri Lanka
1999

A thesis submitted in partial fulfillment of the requirements for the

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Master of Science

Examination Committee Chair

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Examination Committee Member

Graduate College Faculty Representative
ABSTRACT

Characterization of 2-Methyl-Quinolinolato Gallium (III) Chelates

by

Sanjini U. Nanayakkara

Dr. Linda S. Sapochak, Examination Committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas.

We present a detailed photophysical (absorption and emission), thermal and X-ray absorption (NEXAFS) study of gallium (III) bis(2-methyl-8-quinolinolato) carboxylate (2Meq₂GaOR) chelates, where OR= acetato (OAc), trifluoroacetato (OTF) and dimethylpropianato (ODMP). These materials are compared with aluminum (III) tris(8-quinolinolato) (Alq₃) chelates. We show that regardless of changing the carboxylato ligand the 2Meq₂GaOR chelates have similar unoccupied (LUMO) states. This implies that charge injection should be constant in these materials when used as emitter materials in organic light emitting devices. We also present the first detailed evaluation in to the mer/fac isomerization of gallium (III) tris(2-methyl-8-quinolinolato) (2Meq₃Ga) chelate in both solution and solid state, using ¹H NMR and thermal studies. Unlike in Alq₃, where the fac-isomer is not present in detectable amounts in a thin film, in 2Meq₃Ga the fac-isomer is present approximately four times in excess. We infer that the mer- isomer interconverts to the fac-isomer in the solid state and in the gas phase.
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CHAPTER 1

INTRODUCTION

1.1 Organic Electroluminescence Technology

Recently, the use of organic materials as active components of electronic devices has been encouraged by advancements in the development of organic light emitting devices (OLED's) based on electroluminescence.\(^{(1)}\) Since the report by Kodak researchers on efficient, green electroluminescence (EL) from aluminum tris(8-quinolinolato) (Alq\(_3\)), the technology has advanced rapidly and other metal chelate systems have been found to produce EL throughout the visible spectrum.\(^{(2,3)}\)

Organic electroluminescence technology is now a strong competitor for the flat panel display market, where the goal is to replace bulky, higher energy consuming cathode ray tubes (CRT).\(^{(4)}\) Even though liquid crystal displays (LCD) have partially substituted the CRT, the manufacturing costs remain high and since displays based on LCDs operate by reflecting light, they have poor viewing angles and require a high energy consuming backlight. On the other hand, OLED's based on organic EL are relatively easy to fabricate by thermal vapor deposition on almost any substrate (i.e., glass and plastic sheets), have high brightness, and require low drive voltages (<10 V). Since they are based on emissive technology, light is generated in all directions resulting
in excellent viewing angles. Finally, organic materials can be synthetically modified to produce colors throughout the visible spectrum. These advantages allow the production of low cost, lightweight consumer products. Presently, the electronics giant SONY, is producing computer monitors that are "credit card" thin. Based on OLED technology these products will be released to the market in 2002. (5)

1.2 Mechanism of Organic Electroluminescence

OLED's are composed of thin films of organic materials sandwiched between a cathode (i.e., Mg/Ag or Al) and an indium tin oxide (ITO) coated substrate serving as the anode. Light emission or “luminescence” is caused by electrical excitation of the organic layers. Since organic materials are insulating, very thin layers (<600 Å) are required for injecting and transporting charges (electrons and holes) through the device. A proper balance of electrons and holes introduced into each organic layer is crucial for efficient production of electroluminescence. The basic structure of an OLED is shown in Figure 1.1.

![Figure 1.1. Basic structure of an organic light emitting device.](image-url)
Most organic electronic materials are hole transporting, where the term "hole" refers to the removal of an electron from the highest occupied molecular orbital (HOMO). The result is an organic radical cation produced by oxidation at the anode. Tertiary aromatic amines (TAA) are typically used as the hole transporting layer (HTL) and have been well developed because of their use in xerography applications. There are fewer known electron transporting organic materials. Alq₃ and its derivatives however have been shown to be preferentially electron transporting. Therefore, a common device structure consists of thin layers of Alq₃, serving as both the emissive and electron transporting layer (ETL), and a TAA, serving as the HTL (Figure 1.2).

Figure 1.2. Mechanism of EL in an OLED.
Electroluminescence occurs when electrons are injected into Alq₃ from the cathode (reduction) and holes are injected into the TAA layer (oxidation) from the anode. The applied voltage causes these charges to move in opposite directions where they interact at the Alq₃/TAA interface to form an exciton in the Alq₃ layer. This exciton is a molecular excited state similar in energy to the excited state of the molecule produced by light excitation. Therefore when it relaxes the energy is released as light emission, similar to photoluminescence (Figure 1.2).

Since the organic emissive layer serves a dual purpose in the device, the design of efficient electroluminescence materials requires optimization of several material properties for practical device applications. These material properties can be divided into two categories; those which affect: (1) long-term stability; and (2) EL efficiency of the device. For long-term stability, the organic materials composing the device must sublime without chemical degradation and form morphologically stable films. The EL efficiency depends on the photoluminescence (PL) efficiency in addition to charge injection and charge transport efficiencies through the film layers. More specifically, EL materials must have: (1) good PL efficiency in the solid state; (2) appropriate energy level matching of the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energies with the metal electrode work functions for efficient charge injection; and (3) the ability to efficiently transport either electrons or holes. All of these properties are strongly coupled to the molecular and electronic structure of the organic molecule, as well as the bulk packing characteristics of molecules in vapor deposited films. Therefore, systematic studies of the thermal and photophysical (absorption and emission) properties and electronic structure of similar materials are
crucial for establishing structure/function relationships in organic electroluminescent materials.

1.3 Properties of Alq3

Alq3 is the most thoroughly studied organic EL material for OLED's (Figure 1.1). This organic metal chelate has the best balance of the material properties required for efficient EL, which has been attributed mainly to its spherical shape and the nature of the 8-quinolinolato (q) ligand. First, the hexacoordinate Alq3 chelate has a distorted octahedral geometry providing a spherical shape to the molecule, which is partly responsible for the morphological stability of vapor deposited films and high PL efficiency in the solid state. Second, its unique preference for electron transport is believed to arise because of the preferential overlap of the electron deficient pyridyl ring portion of the ligand. This is known to be the location of the LUMO and likely site of electron injection.

In addition, Alq3 can exist as two geometric isomers, meridional (mer) and facial (fac) (Figure 1.3). The mer- or "trans" isomer of Alq3 has no symmetry (C1), whereas the fac- or "cis" isomer has C3v symmetry. Thus, fac-Alq3 and mer-Alq3 have different energies and different physical properties. The mer-Alq3 isomer is lower in energy, has a smaller dipole moment and been shown to be the dominant form in both the solution (1H NMR studies) and the solid state (x-ray diffraction studies). Theoretical studies have suggested that if present, fac-Alq3 may act as an electron trap in OLEDs. In the fac isomer the unoccupied states are more delocalized in the entire molecule, hence stabilize the incoming electron. This would decrease the electron transport efficiency and increase...
turn on voltages. However, the relative amounts of these two isomeric forms in vapor deposited films used in OLEDs has not been determined because of the difficulties associated with studying very thin amorphous films. Therefore, although Alq$_3$ is the most studied EL material for OLED applications, the establishment of distinct structure-function relationships still eludes researchers because the exact structure of the material in vapor deposited films is not well understood.

![Figure 1.3. Geometric isomers of Alq$_3$.](image)

1.3.1 Systematic Studies of Alq$_3$ derivatives

In an attempt to better understand the structure/function relationships of Alq$_3$ and the electroluminescence phenomenon, previous research focused on the effects of EL efficiency caused by small synthetic modifications to the 8-quinolinolato ligand (q) of metal tris-chelates. Specifically, how the chemical structure of a series of methyl (Me) substituted Group III metal tris(8-quinolinolato) chelates (nMe$q$$_3$M: n = 3, 4, 5; M = Al$^{3+}$, Ga$^{3+}$) was related to their photoluminescence efficiencies ($\phi_{PL}$), electroluminescence efficiencies ($\eta_{EL}$), and thermal properties (Figure 1.4). Consistent with previous reports by Schmidbauer, the mer-isomer was the preferred form for all methylated derivatives of Alq$_3$ and Gaq$_3$ based on $^1$H NMR studies. Similar to Alq$_3$
however, the relative amount of the \textit{mer} and \textit{fac} isomers in vapor deposited films is not known.

For the nMeq$_3$Al and nMeq$_3$Ga chelates, it was shown that although $\phi_{PL}$ and $\phi_{EL}$ were increased by C-4 methylation of the 8-quinolinol ligand for both series, a higher device operating voltage was required due to a decrease in pyridyl ring overlap, thus leading to poorer electron transport efficiency.

![Structure of nMeq$_3$Al and nMeq$_3$Ga chelates.](image)

These results were explained by correlating the thermal properties of the methylated metal tris-chelates and the OLED device performance characteristics. The thermal analysis studies were important for understanding how the synthetic modifications affected the physical properties, like intermolecular interactions, of the metal chelates. It was also proposed that in order to achieve a balance between high $\phi_{PL}$, charge injection efficiency and charge transport ability, and therefore improve overall EL.
efficiency of metal tris(8-quinolinolato) chelates, a judicious choice of both the type of substituent group and the position on the 8-quinolinol ligand should be carried out.

Although this systematic study demonstrated an important relationship between structure and charge transport efficiency in Alq₃ type molecules, methylation of the ligand and metal ion substitution significantly altered absorption and emission energies, as well as PL efficiencies. Therefore, it was evident that a large number of variables were affecting the device performance and it was difficult to judge the relative importance of each of these material properties. Hence, by studying a series of related metal chelates while holding one or more of the mentioned material properties constant, differentiation of their relative importance could be determined.

1.4 Systematic Studies of Pentacoordinate Gallium bis(2-methyl-8-quinolinolato) Carboxylato Chelates

Previously, Sapochak, et al., reported a systematic study of the photophysical and electroluminescence properties of gallium (III) bis(2-methyl-8-quinolinolato) carboxylato chelates (2Meq₂Ga-OR), where R = acetato (OAc), dimethylpropionato (ODMP) or benzoato (OBz) (Figure 1.5). The presence of the methyl group at the C-2 position of the 2-methyl-8-quinolinol ligand (2Meq) introduces steric hindrance and it is not possible to make the tris-chelate of the Al⁺³ ion (2Meq₃Al). In contrast, 2Meq₃Ga can be isolated because of the larger size of the Ga⁺³ ion. As described by Schmidbauer, the addition of a large excess of a monodentate carboxylate salt competes efficiently with the 2Meq ligand resulting in pentacoordinate, trigonal bipyramidal, mixed ligand chelates of the Ga⁺³ ion.

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Figure 1.5. Structures and OLED device properties of 2Meq₂GaOR chelates previously studied. \(^{(13)}\)

It was reported, that regardless of the nature of the monodentate ligand, absorption and emission energies for all 2Meq₂GaOR chelates were identical and PL efficiencies reported relative to Alq₃ varied by only a small percentage. \(^{(13)}\) This suggests that the photophysical properties of these metal chelates are dominated by the 2Meq ligand, and that there is little or no electronic communication with the monodentate carboxylato ligand through the Ga\(^{³⁺}\) ion. Therefore, since the absorption and emission energies are identical, these chelates should have similar HOMO and LUMO energies and as a consequence, charge injection efficiencies should also be identical. On the other hand, the size and electronic nature of the monodentate ligand, although having no effect on the photophysical properties of the 2Meq₂GaOR chelates, should have significant effects on intermolecular interactions in the solid state, and thus charge transport efficiencies. Therefore, differences in charge transport efficiencies and their relative importance to overall EL efficiencies can be evaluated since both PL and charge injection efficiencies are similar. Furthermore, unlike Alq₃ and other metal tris-chelates of 8-quinolinol, the 2Meq₂GaOR chelates do not exist in different isomeric forms and a better evaluation of structure-function relationships can be established.
In this thesis, a detailed study of the structural, photophysical, thermal and electronic properties of pentacoordinate 2Meq₃GaOR chelates with monodentate ligands (OR) capable of imparting significantly different intermolecular interactions is presented. Chelates with OR = acetate (OAc), dimethylpropionate (ODMP), trifluoroacetate (OTF), trichloroacetate (OTCl), and hydroxide (OH) were synthesized and characterized (Chapter 2). Evaluation of their electronic structures by near-edge x-ray absorption fine structure (NEXAFS) is presented in Chapter 5 and detailed photophysical studies in solution are presented in Chapter 4. The properties of these materials are compared to the prototypical EL material, Alq₃, as well as the gallium tris-chelates, Gaq₃ and 2Meq₃Ga. Our study of the 2Meq₃Ga chelate provides the link between pentacoordinate chelates and hexacoordinate chelates and allows investigation of the effect of C₂-methylation of 8-quinolinolato ligand on the properties of metal tris-chelates, which has not previously been evaluated. Furthermore, unlike Alq₃, Gaq₃ and their methylated derivatives reported previously, the presence of both the mer and fac isomers of 2Meq₃Ga in solution and solid state have been identified. Therefore, the first detailed study of the effects of purification on the ratio of these two isomers present in the solid state is presented, including evidence for solid-state isomeric (Chapter 3) interconversion. The implications of these systematic studies on the understanding of electroluminescence performance is discussed in Chapter 6.
Reference


5. www.SONY.com


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CHAPTER 2

MATERIAL SYNTHESIS AND CHARACTERIZATION

2.1 Synthesis of Gallium (III) bis(2-methyl-8-quinolinolato) carboxylato chelates

The gallium bis (2-methyl-8-quinolinolato) acetato (2Meq²GaOAc), trifluoroacetato (2Meq²GaOTF), and dimethylpropionato (2Meq²GaODMP) have been synthesized previously and were prepared here with some modifications to the published procedures. All starting materials were obtained from Aldrich Chemical Co. 2-Methyl-8-quinolinol (2Meq) was recrystallized from 95% ethanol and the other reagents were used as received. The synthesis of gallium bis(2-methyl-8-quinolinolato) trichloroacetato (2Meq²GaOTCl) and hydroxide (2Meq²GaOH) have not been previously reported. Pentacoordinate gallium chelates were obtained by combining Ga(NO₃)₃ hexahydrate in a ~1:2 molar ratio with 2Meq and a large excess of the monodentate carboxylic acid and ammonium carboxylate salt, which acts as a buffer. When an appropriate buffer salt was not available, 2N solution of NH₄OH was added dropwise to the reaction solution to induce precipitation of the product.

The presence of the methyl group at the C-2 position of 2Meq introduces steric hindrance, thus allowing the formation of pentacoordinate chelates when a large excess
of the smaller monodentate carboxylato species is present. However, the hexacoordinate chelate, gallium tris(2-methyl-8-quinolinolato) (2MeqGa) can form as a by-product.

All chelates were recrystallized from either methanol or benzene and further purified by high-vacuum gradient-temperature sublimation over a three day period before analysis. A general synthetic scheme is shown in Figure 2.1.

![Diagram showing the general synthetic route for the pentacoordinate gallium(III) chelates.]

Figure 2.1. General synthetic route for the pentacoordinate gallium(III) chelates.

The formation of 2MeqGaOTCl was most sensitive to the pH of the reaction solution. Since NH4TCIOAc was not commercially available. A 2N solution of NH4OH was added to the reaction solution to induce precipitation and the yellow 2MeqGaOTCl
was isolated immediately at ~pH 4-5. However, when the yellow precipitate was stirred for 15 minutes or more, the pH of the solution increased to ~8 and the precipitate turned white. $^1$H NMR and FT-IR analysis of this white precipitate supported the formation of 2Meq$_2$GaOH. This also was observed, but less efficiently, with prolonged stirring during the synthesis of 2Meq$_2$GaOTF, but was not observed for 2Meq$_2$GaOAc.

\[ \text{Figure 2.2. Synthesis of 2Meq}_2\text{GaOH.} \]

2.2 Material Characterization

2.2.1 Experimental

The structures of all chelates were confirmed by $^1$H NMR, $^{13}$C NMR, and FT-IR spectroscopies, as well as elemental analysis obtained from NuMega Resonance Laboratories. Both $^1$H and $^{13}$C NMR experiment were run in CDCl$_3$ on a Bruker 400 MHz NMR spectrometer and FT-IR spectra were obtained on a Nicolet 210 FT-IR spectrometer both as KBr pellets and as vapor-deposited films of thickness 1500 – 2000 Angstroms grown on NaCl plates.

Thermal analysis was determined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) performed simultaneously using a Netzsch Simultaneous Thermal Analyzer (STA) system. Pure polycrystalline samples (5-10 mg)
were placed in aluminum pans and analyzed at a rate of 20°C/min under N₂ gas at a flow rate of 50 mL/min. Indium metal was used as the temperature standard. The melted samples were cooled at a rate of 20°C/min to form glasses. The glass transition (Tₜₐₜ) and the crystallization point (Tₖₜ) were measured from a second heating of the glassy state. The maximum weight loss temperature (decomposition temperature) was determined for each sample run without a lid and reported as the maximum peak of the DTGA (derivative of the TGA curve).

2.2.2 Results and Discussion

2.2.2.1 Characterization of 2Meq₂GaOR chelates

2.2.2.1(a) 'H and ¹³C N.M.R. Spectroscopic Results

The 'H NMR results of the purified chelates were consistent with published values and are presented in section 2.3. The ¹³C NMR results, previously not reported, are tabulated in Table 2.1.

The chemical shift values of the 2Meq for all chelates followed a similar trend, while differences were observed for the monodentate carboxylate ligand. The most prominent difference was in the chemical shift value of the carbon atom of C=O, which decreased in the order 2Meq₂GaODMP > 2Meq₂GaOAc > 2Meq₂GaOTCl > 2Meq₂GaOTF. As expected, α-halogenation of the carboxylato moiety causes a shielding effect on the C=O carbon by pulling electron density towards the carbonyl functionality.
Table 2.1. $^{13}$C N.M.R characterization of 2Meq$_2$GaOR.

<table>
<thead>
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<th>$\delta$C (ppm)</th>
<th>2Meq$_2$GaOAc</th>
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<th>2Meq$_2$GaODMP</th>
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<tr>
<td>$\delta$C7</td>
<td>113.0</td>
<td>113.0</td>
<td>113.1</td>
<td>113.2</td>
</tr>
<tr>
<td>$\delta$C8</td>
<td>156.2</td>
<td>156.7</td>
<td>156.1</td>
<td>156.7</td>
</tr>
<tr>
<td>$\delta$C9</td>
<td>137.5</td>
<td>137.2</td>
<td>137.5</td>
<td>137.3</td>
</tr>
<tr>
<td>$\delta$C10</td>
<td>128.3</td>
<td>126.9</td>
<td>127.1</td>
<td>126.9</td>
</tr>
<tr>
<td>$\delta$CH$_3$$^{3Meq}$</td>
<td>22.2</td>
<td>23.0</td>
<td>23.2</td>
<td>23.2</td>
</tr>
<tr>
<td>$\delta$C=O</td>
<td>175.6</td>
<td>159.3$^\text{(1)}$</td>
<td>183.4</td>
<td>163.3</td>
</tr>
<tr>
<td>$\delta$CH$_3$$^\text{GaAc}$</td>
<td>21.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$CF$_3$</td>
<td>-</td>
<td>115.5$^\text{(2)}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$CCl$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>113.2</td>
</tr>
<tr>
<td>$\delta$C(CH$_3$)$_3$</td>
<td>-</td>
<td>-</td>
<td>38.7</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$CH$_3$$^\text{ODMP}$</td>
<td>-</td>
<td>-</td>
<td>27.0</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) The C=O carbon was split into a quartet by a coupling constant of 155 Hz.
(2) The CF$_3$ carbon was split into quartet by 1145 Hz.

2.2.2.1(b) FT-IR Spectroscopic Results

The infrared spectra for all the 2Meq$_2$GaOR chelates, with the exception of 2Meq$_2$GaOTCl showed no significant change when comparing the crystalline material (KBr pellet) and vapor deposited film. This suggests that no degradation of the chelates occurred upon vapor deposition. Due to the poor thermal stability of 2Meq$_2$GaOTCl attempts were not made to obtain a thin film IR spectra.
Figure 2.3. FT-IR spectra of $\text{2Meq}_2\text{GaOAc}$ as: (a) vapor deposited film on a NaCl plate; and (b) KBr pellet.

In both, the KBr pellet and thin film on NaCl plate of $\text{2Meq}_2\text{GaOAc}$ (Figure 2.3) a splitting of the carbonyl stretch was observed. This may be due to Fermi resonance caused by the mechanical coupling of the carbonyl stretch with that of the C-H out-of-plane-bends (o.o.p.b.) of the aromatic ring structure. The carbonyl stretch of $\text{2Meq}_2\text{GaOAc}$ is observed at $1664 \text{ cm}^{-1}$ and the C-H o.o.p.b. is observed at $832 \text{ cm}^{-1}$. In the case of $\text{2Meq}_2\text{GaOTF}$, (Figure 2.2) additional peaks are seen between $1125 \text{ cm}^{-1}$ and $1250 \text{ cm}^{-1}$, not seen in $\text{2Meq}_2\text{GaOAc}$, which are attributed to C-F stretches. X-ray crystallography studies on a single crystal of $\text{2Meq}_2\text{GaOAc}$ has shown that the acetate ligand was bound to the Ga$^{+3}$ metal ion through the oxygen atom of the C-O bond.\(^{(1)}\)

In $\text{2Meq}_2\text{GaOTF}$ (Figure 2.4), additional peaks were seen between $1125 \text{ cm}^{-1}$ and $1250 \text{ cm}^{-1}$, not seen in $\text{2Meq}_2\text{GaOAc}$, which are attributed to C-F stretches.
Figure 2.4. FT-IR spectra of 2Meq₂GaOTF as: (a) vapor deposited film on a NaCl plate; and (b) KBr pellet.

Figure 2.5. FT-IR spectra of 2Meq₂GaOH; (a) crude; (b) recrystallized; and (c) purified.

In the case of 2Meq₂GaOH a sharp free OH stretch was observed at 3526 cm⁻¹. In the recrystallized (from benzene) and purified forms of 2Meq₂GaOH the OH stretch is very broad indicating strong hydrogen bonding (Figure 2.5). The FT-IR spectra of the other chelates are presented in Appendix II. Major peak assignments are tabulated in Table 2.2.
Table 2.2. Assignments of FT-IR peaks (cm\(^{-1}\)) for the 2Meq\(_2\)GaOR chelates.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>2Meq(_2)GaOAc</th>
<th>2Meq(_2)GaOTf</th>
<th>2Meq(_2)GaODMP</th>
<th>2Meq(_2)GaOTCl</th>
<th>2Meq(_2)GaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O str</td>
<td>1664</td>
<td>1729</td>
<td>1650</td>
<td>1715</td>
<td></td>
</tr>
<tr>
<td>CO(_{OR})</td>
<td>1269</td>
<td>1268</td>
<td>1271</td>
<td>1270</td>
<td>1276</td>
</tr>
<tr>
<td>C(_{sp2})H ring</td>
<td>3047</td>
<td>3056</td>
<td>3073</td>
<td>3040</td>
<td>3040</td>
</tr>
<tr>
<td>CH(_{16+})Meq</td>
<td>832</td>
<td>836</td>
<td>832</td>
<td>834</td>
<td>839</td>
</tr>
<tr>
<td>CO(_{2Meq})</td>
<td>1116</td>
<td>1117</td>
<td>1114</td>
<td>1115</td>
<td>1112</td>
</tr>
<tr>
<td>C-N str</td>
<td>1342</td>
<td>1342</td>
<td>1343</td>
<td>1341</td>
<td>1344</td>
</tr>
<tr>
<td>C-F str</td>
<td>-</td>
<td>1125-1250</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>OH str</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C(_{sp3})H str</td>
<td>2932(^*)</td>
<td>2928(^*)</td>
<td>2966(^{hi.})</td>
<td>2928(^*)</td>
<td>2920(^*)</td>
</tr>
</tbody>
</table>

* "w" denotes weak and "h.i." denotes high intensity.

2.2.2.1(c) Thermal Analysis Results

All 2Meq\(_2\)GaOR chelates exhibited asymmetric or multiple melting transitions. \(T_m\) was assigned to the peak of the highest intensity melting (endotherm) transition. (Figure 2.6a) The source of the additional thermal transitions is not currently understood, but based on the \(^1\)H NMR and elemental analysis data, the presence of an impurity is unlikely. However, for the pentacordinate chelates the possibility that the labile carboxylato group cleaves in the process of the heating cycle cannot be ruled out. On the other hand, since 2Meq\(_2\)Ga is known to exist in two isomeric forms, the additional transitions for that compound were further investigated and are discussed in Chapter 3.
Table 2.3. Thermal Analysis Results.

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_{fusion}$ (kJ/mol)</th>
<th>$T_g$ (°C)</th>
<th>$T_{cl}$ Onset (°C)</th>
<th>Max. Wt. Loss Temp. (°C) onset</th>
<th>Max. DTGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Meq$_2$Ga</td>
<td>282</td>
<td>44.5</td>
<td>136</td>
<td>none</td>
<td>381</td>
<td>451</td>
</tr>
<tr>
<td>2Meq$_2$GaOAc</td>
<td>277</td>
<td>n.d.</td>
<td>101</td>
<td>none</td>
<td>325</td>
<td>391</td>
</tr>
<tr>
<td>2Meq$_2$GaOTF</td>
<td>238</td>
<td>26.6</td>
<td>89</td>
<td>165</td>
<td>311</td>
<td>343</td>
</tr>
<tr>
<td>2Meq$_2$GaODMP</td>
<td>270</td>
<td>33.4</td>
<td>103</td>
<td>none</td>
<td>316</td>
<td>364</td>
</tr>
<tr>
<td>2Meq$_2$GaOH</td>
<td>354</td>
<td>26.8</td>
<td>177</td>
<td>265</td>
<td>388</td>
<td>431</td>
</tr>
</tbody>
</table>

* n.d = not determined due to overlapping peaks.

The $T_m$ of the 2Meq$_2$GaOR chelates increased in the order 2Meq$_2$GaOTF < 2Meq$_2$GaODMP < 2Meq$_2$GaOAc < 2Meq$_2$GaOH. The different melting points of the chelates are indicative of the different intermolecular interactions between molecules of these compounds in the solid state. Therefore as expected 2Meq$_2$GaOTF exhibits the lowest $T_m$ due to the repulsion between molecules caused by the trifluoromethyl group. The bulky dimethylpropionate group in 2Meq$_2$GaODMP exhibited a lower $T_m$ compared to 2Meq$_2$GaOAc. And the high $T_m$ of 2Meq$_2$GaOH is possibly because of the hydrogen bonding between molecules.

In the second heating cycle of the 2Meq$_2$GaOH and 2Meq$_2$GaOTF, recrystallization was observed after the $T_g$ and before melting, but in 2Meq$_2$GaOAc and 2Meq$_2$GaODMP such recrystallization was not observed. In order to evaluate if this is due to any degradation of the materials, a sample was removed and cooled after its melting and a $^1$H NMR spectrum was obtained, which was consistent with the purified material.
2.3 Synthetic Procedures

Gallium (III) bis(2-methyl-8-quinolinolato) acetato (2Meq$_2$GaOAc): 1.60 g (6.25 mmol) of Ga(NO$_3$)$_3$$\times$6H$_2$O and 2.5 g of NH$_4$OAc where placed in a 150 mL Erlenmeyer flask and dissolved in ~50 mL of de-ionized water. In a separate 150 mL flask 2.0 g (12.6 mmol) of 2Meq ligand was added and dissolved in 50 mL of 1M acetic acid. The Ga(NO$_3$)$_3$$\times$6H$_2$O was then added drop wise to the mixture and a bright yellow precipitate resulted.
formed immediately. The thick yellow mixture was then stirred rapidly for 30 minutes and the crude product was filtered, air dried and dried under vacuum at a ~ 120 °C for 2 hours to give 1.68 g. (60%). The crude material was recrystallized in methanol to give bright yellow micro crystals of melting temperature 271-272°C, and purified by high vacuum gradient-temperature sublimation over a period of 3 days (~ 10⁻⁶ Torr, up to 275°C).

¹H NMR (CDCl₃, 20°C): δH3(J₃,a)=7.42(d,7.9); δH4(J₄,3)=8.24(d,8.4); δH5(J₅,6)=7.15 (d,8.3); δH6(J₆,7,J₆,₅)=7.44(t,8.1); δH7(J₇,8)=7.13(7.8); δCH₃₂Meq=s,3.07; δCH₃OAc=1.9. Anal. Calcd for C₂₂H₁₉N₂O₄Ga (445.13): C, 59.36%; H, 4.3%; N, 6.29%. Found: C, 59.38%; H, 4.2%; N, 6.32%.

Gallium (III) bis(2-methyl-8-quinolinolato) trifluoroacetato (2Meq₂GaOTF): Prepared according to a similar procedure as described for 2Meq₂GaOAc, using 1.28 g of Ga(NO₃)₃·xH₂O (5.0 mmol), 2.0 mL (26.9 mmol) of trifluoroacetic acid, 1.59 g (10 mmol) of 2Meq ligand, and 1.0 g (7.63 mmol) of NH₄OTF. The bright yellow precipitate was recrystallized from methanol to give bright yellow micro crystals of melting temperature 229-230°C and purified by high vacuum gradient-temperature sublimation over a period of 3 days (10⁻⁶, Torr, °C).

¹H NMR (CDCl₃, 20°C): δH3(J₃,a)=7.48(d,8.2); δH4(J₄,3)=8.28(d,8.4); δH5(J₅,₆,J₅,₇)=7.21(dd,7.4,0.8); δH6(J₆,7,J₆,₅)=7.44(t,7.7); δH7(J₇,₈,J₇,₅)=7.17(dd,7.6,0.8); δCH₃₂Meq=s,3.05. Anal. Calcd. for C₂₂H₁₆N₂O₄GaF₃ (499.1): C, 52.94%; H, 3.23%; N, 5.61%. Found: C, 52.82%; H, 3.38%; N, 5.64%.
Gallium (III) bis(2-methyl-8-quinolinolato) dimethylpropionato (2Meq₂GaODMP):  
Synthesized as published\(^2\). Obtained from Sapochak L.S., and purified by high vacuum gradient sublimation over a period of 3 days (10\(^{-6}\) Torr, up to 220°C).

\(^1\)H NMR (CDCl₃, 20°C): \(\delta H3(J_{3,4})=7.44(d,8.1); \delta H4(J_{4,3})=8.23(d,8.4); \delta H5(J_{5,6,7})=7.21(d,7.9); \delta H6(J_{6,7,6,5})=7.43(t,7.9); \delta H7(J_{7,6,5})=7.1(d,7.7); \delta CH3_{2Meq}=s,3.03; \delta C(CH3)3=s,1.02.\)  
Anal. Calcd. for C\(_{22}H_{21}N_2O_4Ga (487.21): C, 61.63%; H, 5.17%; N, 5.75%.  
Found: C, 61.94%; H, 4.94%; N, 5.92%.

Gallium (III) tris(2-methyl-8-quinolinolato) (2Meq₃Ga):  
3.0 g (18.85 mmol) of 2Meq was dissolved in 25 mL of ethanol in a 250 mL Erlenmeyer flask and was added dropwise to a solution of Ga(NO₃)₃·6H₂O (1.6 g, 6.26 mmol) dissolved in 25mL water and 0.6 ml of nitric acid. The solution was stirred for 30 minutes and 2N NH₄OH was added dropwise to induce precipitation at pH ~ 7-8 and stirred an additional 15 minutes. The bright yellow product was filtered, air dried and dried under a vacuum at ~ 120 °C for 2 hours to give 2.57 g (75.3%) of product. The crude material was recrystallized from methanol to give bright yellow and brown/green prism-like crystals (61.5%), 282-285°C. Material was further purified by high vacuum gradient-temperature sublimation over a period of 3 days (~ 10\(^{-6}\) Torr, up to 300°C).

\(^1\)H NMR (CDCl₃, 20°C): fac: \(\delta H3(J_{3,4})=7.08(d,8.4); \delta H4(J_{4,3})=8.02(d,8.4); \delta H5(J_{5,6,7})=7.00(d,7.1); \delta H6(J_{6,7,6,5})=7.44(t,8.5); \delta H7(J_{7,6,5})=7.07(dd,7.7,1.0); \delta CH3_{2Meq}=s,2.58: \)  
mer: \(\delta H3(J_{3,4})=7.29(d,8.6); \delta H4(J_{4,3})=8.24(d,8.4); \delta H5(J_{5,6,7})=7.03(d,6.7); \delta H6(J_{6,7,6,5})=7.38(t,7.9); \delta H7(J_{7,6,5})=7(dd,7.2,1.0); \delta CH3_{2Meq}=s,2.71, 3.15.\)  
Anal. Calcd. for C\(_{30}H_{24}N_3O_3Ga (544.09): C, 66.23%; H, 4.45%; N, 7.72%. Found: C, 65.60%; H, 4.68%; N, 7.76%.

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Gallium (III) bis(2-methyl-8-quinolinolato) trichloroacetato (2Meq2GaOTCl):

Ga(NO$_3$)$_3$·6H$_2$O (0.72 g, 2.81 mmol) was dissolved in a 150 mL Erlenmeyer flask using ~20 mL of de-ionized water. In a separate 150 mL flask 2Meq (0.52 g, 3.27 mmol) and trichloroacetic acid (3.0 g, 18.36 mmol) where dissolved in ~ 150 mL of de-ionized water. The gallium nitrate solution was added dropwise over a period of 5 minutes and the mixture was stirred rapidly for 30 minutes. 2N NH$_4$OH solution was added dropwise to induce precipitation at a pH ~4-5. The crude yellow precipitate was filtered and washed 3 times with ~ 100 mL portions of deionized water. The crude product was air dried to give 0.76 g. (49%) Attempts to recrystallize in methanol and toluene decomposed the product.

$^1$H NMR (CDCl$_3$, 20°C): δH3(J3.4)=7.47(d,8.4); δH4(J4.3)=8.29(d,8.4); δH5(J5.6,4)=7.21(d,8.2); δH6(J6.7,J6.5)=7.47(t,7.9); δH7(J7.6)=7.16(d,7.7); δCH32Meq=s,3.10.

Gallium (III) bis(2-methyl-8-quinolinolato) hydroxide (2Meq2GaOH):

Prepared according to a similar procedure as described for 2Meq2GaOTCl, but after precipitation at pH ~5-6, continued to add the base till pH was 8-9. The solution was stirred continuously for 1 hour. After 5-10 minutes of stirring the solut yellow precipitate turned white. After 1 hour the white solution was filtered and washed with deionized water until the filtrate was neutral to pH paper. The crude product was air dried under a vacuum at ~ 120 °C for 2 hours to give 0.76 g. (58%) The crude material was recrystallized in benzene and purified by high vacuum gradient-temperature sublimation over a period of 3 days (10$^7$ Torr, °C).

$^1$H NMR (CDCl$_3$, 20°C): δH3(J3.4)=7.49(d,8.4); δH4(J4.3)=8.32(d,8.4); δH5(J5.6,4)=7.22(d,8.0); δH6(J6.7,J6.5)=7.48(t,7.9); δH7(J7.6)=7.16(d,7.6); δCH32Meq=s,3.10.
Reference


CHAPTER 3

EVALUATION OF \textit{mer}/\textit{fac} ISOMERIZATION OF GALLIUM TRIS(2-METHYL-8-QUINOLINOLATO) CHELATE

3.1 Introduction

As discussed in Chapter 1, metal tris (8-quinolinolato) chelates can exist as two geometric isomers, \textit{mer} and \textit{fac}. The \textit{mer} isomer lacks symmetry and the formation of optical isomers are also possible. Schmidbauer previously reported the characterization of nMeq₃M (n = 2, 3, 4, 5, 6, 7; M = Al⁺³, Ga⁺³) chelates by variable temperature $^1$H NMR spectroscopy in CDCl₃. \(^1\) All chelates, with the exception of 2Meq₃Ga were reported to exhibit broadened aromatic resonances, but no significant changes in the methyl resonances when the temperature was raised to 50°C. The authors proposed that the M-N bond is labile enough so that at elevated temperatures this bond can break producing a "ligand equilibrating" process as depicted in Figure 3.1, which was responsible for the broadening. The $^1$H NMR spectra of all nMeq₃M chelates, with the exception of 2Meq₃Ga showed peaks for the \textit{mer} isomer only. 2Meq₂Ga exhibited aromatic and methyl resonances for both the \textit{mer} and \textit{fac} isomers.

Schmidbauer proposed that 2Meq₂Ga existed as both isomers because of the steric hindrance produced by C2-methylation, so that during the ligand equilibrating process a
because single x-ray crystallography of mer-2Meq₃Ga reported by Sapochak et.al, showed that the Ga-N bonds were significantly lengthened and the Ga-O bonds significantly shortened compared to the unsubstituted analogues, Alq₃ and Gaq₃. (2)

A more detailed evaluation of the mer/fac isomerization of 2Meq₃Ga is reported here. ¹H and ¹³C NMR spectroscopies and thermal analysis were used to evaluate isomeric interconversion after different purification procedures and different heat treatments. Results from these investigations suggest that 2Meq₃Ga also exhibits mer/fac isomerization in the solid state and/or gas phase.

Figure 3.1. Ligand equilibrating process showing the interconversion of the optical (i and ii) and geometric isomers (i and iv) of meta tris(8quinolinolato) chelates.

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3.2 Experimental

$^1$H and $^{13}$C NMR studies were conducted in CDCl$_3$ at room temperature. Samples were analyzed by $^1$H NMR from different purification steps, and are denoted as: (1) crude, precipitated chelate without any purification; (2) RC, recrystallized from MeOH; (3) purified, RC sample further purified slowly over a 3-day period by high vacuum temperature gradient sublimation; and (4) film, purified sample sublimed quickly at $-10^{-3}$ Torr and 220°C.

Thermal analysis (STA – simultaneous thermal analysis) was conducted on the purified sample according to instrumental conditions described in Chapter 2, but at variable heating rates (20K/min, 5K/min, and 1K/min). Both crimped and uncrimped aluminum pans were utilized for the experiments, where the sample was heated just past $T_m$ and then quenched with liquid nitrogen. The TGA curve from the STA experiments was evaluated to calculate any weight loss because of sublimation, which has been observed previously for other metal tris(8-quinolinolato) chelates. The sample was removed and analyzed by $^1$H and $^{13}$C NMR in CDCl$_3$.

In order to determine whether these samples might change by isomeric interconversion during room temperature NMR analysis a test experiment was conducted. The purified sample was dissolved in CDCl$_3$ and the $^1$H NMR was analyzed (probe temperature, 20°C and scan time, 8 min): (1) immediately; (2) after 1.5 hours; and (3) then after heating the solution at 50°C for 15 minutes. No significant changes were observed in the resulting spectra.

The methyl peak resonances and H4 aromatic resonances for the mer and fac isomers were assigned according to previous reports, and the integrals were used to
evaluate the $\text{fac/mer}$ isomeric ratio in the different samples. These proton resonances were chosen because they were well separated from other resonances. For the case of the aromatic protons, there was a single resonance for H4 at 8.02 ppm assigned to the $\text{fac}$ isomer, but for $\text{mer}$, the resonance at 8.24 ppm only corresponds to two of the H4 protons, and this was taken into account in the calculation. Values were determined from the raw integrals by measuring with a ruler.

3.3 Results and Discussion

3.3.1 Effect of Purification Method on $\text{fac/mer}$ ratio

3.3.1(a) $^1$H NMR Results

Table 3.1 shows the results for the $\text{fac/mer}$ ratios calculated from the $^1$H NMR spectra of 2Meq$_3$Ga at different purification levels. Calculations from both the methyl and aromatic resonances showed an increase in the amount of $\text{fac}$ isomer as the material was purified. Although the magnitudes are different when calculating from different regions of the spectra the trend was the same. All spectra are listed in Appendix 1.

Table 3.1: Amount of $\text{fac/mer}$ after different purification procedures.

<table>
<thead>
<tr>
<th>2Meq$_3$Ga</th>
<th>$\text{fac/mer}$ ($\text{Me}$)*</th>
<th>Increase in $\text{fac isomer}$ relative to crude</th>
<th>$\text{fac/mer}$ ($\text{H4}$)*</th>
<th>Increase in $\text{fac isomer}$ relative to crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude</td>
<td>0.3</td>
<td>1.0</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>RC</td>
<td>1.3</td>
<td>4.3</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Purified</td>
<td>2.5</td>
<td>8.3</td>
<td>2.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Film</td>
<td>4.1</td>
<td>13.7</td>
<td>3.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>

*Resonances used for calculation
Note that the largest amount of fac isomer was identified in the film sample. This result suggests that upon vapor deposition of 2Meq₃Ga, isomeric interconversion must occur. Whether the interconversion occurs in both the solid state and/or gas phase was further evaluated by thermal analysis experiments (section 3.3.2).

¹H NMR of the sublimed 2Meq₃Ga showed peaks at approximately 7.7 and 6.8 ppm, not assigned to that compound, similar to that seen in 2Meq₃Ga after heating in an uncrimped pan (Appendix I). This may be due to the presence of the intermediate state as depicted in the ligand equilibrating process. ¹H NMR analysis of Lithium tetra(2-methyl-8-quinolinolato) boron complex has shown the H₄ of the 2Meq ligand to resonate at ~ 7.8 ppm. In this complex the 2Meq ligand is not bound by the nitrogen atom, similar to the intermediate state.

3.3.1(b) ¹³C NMR Characterization

The resonance for the aromatic carbon bound to the phenolic oxygen, C8 is observed at ~155 ppm for the 2Meq ligand, and Alq₃ exhibits two peaks at 158.6 ppm and 159.0 ppm. This is because Alq₃ exists primarily as the meridional isomer. Although the three ligands are inequivalent, similar to the ¹H NMR data, two of the ligands resonate at nearly the same frequency and therefore only two peaks were observed. The ¹³C NMR spectra of 2Meq₃Ga: (1) purified; (2) sublimed; and (3) samples from thermal heating (discussed in the next section) were obtained. All spectra exhibited the same number of peaks and similar relative intensities. Unlike the ¹H NMR experiments (8 minutes), ¹³C experiments were run for 8 hours. Therefore, a possible explanation for the similarity of the ¹³C spectra for all 2Meq₃Ga samples is that during the experiment the
samples equilibrate to the same mixture of isomeric species. This suggests that \( \text{2Meq}_3\text{Ga} \) undergoes isomeric interconversion in solution facilely, even at room temperature and that no matter what the initial \( \text{fac/mer} \) ratio of the sample is before the experiment, equilibrium to an approximately 50:50 mixture of the two isomers results.

In addition, compared to \( \text{Alq}_3 \), six peaks were observed in the region between 150-158 ppm for all samples of \( \text{2Meq}_3\text{Ga} \) (Figure 3.2) assigned to C8. Figure 3.2 illustrates the partial \( ^{13}\text{C} \) spectra of 150 - 158 ppm, increasing to the right, for a sublimed \( \text{2Meq}_3\text{Ga} \) sample showing multiple resonances in C-O region and the same region for \( \text{Alq}_3 \). These additional \( ^{13}\text{C} \) C-O resonances may be due to the intermediate species (Figure 3.1), which further supports the ligand equilibrating process proposed by Schmidbaur. \(^{(1)}\)

(a) (b)

Figure 3.2. Partial \( ^{13}\text{C} \) spectra for: a) film \( \text{2Meq}_3\text{Ga} \) sample showing multiple resonances in C-O region; and b) same region for \( \text{Alq}_3 \).

3.3.2 Thermal Analysis / \( ^1\text{H} \) NMR Results

The STA/\( ^1\text{H} \) NMR results are shown in Table 3.2. When the sample pan was crimped no weight loss was observed in the STA curves and the \( \text{fac/mer} \) ratios calculated
from $^1$H NMR analysis of the samples after the heating experiment were similar, but lower than the purified sample before the heating experiment. However, uncrimped pans showed an increasing weight loss as the heating rate was increased accompanied by a larger presence of the $fac$ isomer. Furthermore, increasing weight loss also correlated with a significant reduction of the higher temperature endotherm and more prominent lower temperature transitions as shown in Figure 3.3.

Table 3.2: Results of thermal analysis and $^1$H NMR experiments.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Sample pan</th>
<th>% weight loss</th>
<th>$fac/mer$ ratio$^*$</th>
<th>Observed Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>20K/min</td>
<td>Uncrimped</td>
<td>2.5</td>
<td>0.77</td>
<td>273, 287</td>
</tr>
<tr>
<td>5k/min</td>
<td>Uncrimped</td>
<td>7.5</td>
<td>1.73</td>
<td>273, 278, 287</td>
</tr>
<tr>
<td>1K/min</td>
<td>Uncrimped</td>
<td>10</td>
<td>2.10</td>
<td>273, 278, 285</td>
</tr>
<tr>
<td>20K/min</td>
<td>Crimped</td>
<td>none</td>
<td>1.1</td>
<td>271, 275, 288</td>
</tr>
<tr>
<td>1K/min</td>
<td>Crimped</td>
<td>none</td>
<td>1.2</td>
<td>273, 276, 277, 278, 285</td>
</tr>
</tbody>
</table>

"S" denotes a shoulder; "*" denotes from methyl resonances.

Figure 3.3. DSC curves for 2Meq$_3$Ga showing the reduction of the high temperature endotherm and more resolved low temperature transitions with slower heating rate.
When looking carefully at the DSC curves, several endothermic transitions were observed. These transitions were more resolved for the slower heating rates for both crimped and uncrimped pan experiments (Figure 3.4). No attempt was made to assign this series of complicated transitions. However, these transitions are most likely due to both isomeric interconversion and polymorphism of the sample. The polymorphic nature of mer-$\text{Alq}_3$ has recently been reported. Further studies are required to isolate these polymorphs, separating them by their melting points.

Figure 3.4. DSC curves comparing: a) 20K/min; b) 1K/min heating rates for sample run in crimped and uncrimped pans. A closer look at the weaker transitions observed at lower temperatures are shown: c) 20k/min; and d) 1K/min.
$^1$H NMR analysis of purified 2Meq$_3$Ga after the heating experiments showed changes in the $\text{fac/mer}$ ratios. The aromatic region after heating at 1K/min in crimped and uncrimped pans are shown in Figure 3.5. In the uncrimped pan additional peaks were observed, which may be from the intermediate species (Figure 3.1). The calculated $\text{fac/mer}$ ratio for the uncrimped pan was twice as large as that for the crimped pan (Table 3.2).

Note that as the amount of $\text{fac}$ isomer increased, the aromatic region in the NMR spectrum becomes more resolved. This is due to the fact that the $\text{fac}$ isomer is symmetrical and gives rise to a single resonance for each proton. However, the $\text{mer}$ isomer has no symmetry and thus when present at higher concentrations causes the aromatic resonances to broaden.

These results suggest that 2Meq$_3$Ga also undergoes isomeric interconversion in the solid/gas phase states. The difference between the $\text{fac/mer}$ ratios for the uncrimped and crimped pan experiments may be explained as follows. When the pan is crimped, sublimation of the sample still occurs, but the vapor is prevented from escaping. This maintains the equilibrium between the different isomeric forms leading to a $\text{fac/mer}$ ratio close to 1 for both heating rates. This is consistent with the solution studies. However, when the pan is uncrimped, the vapor is allowed to escape, disrupting this equilibrium. Since analysis of the film sample formed from sublimation of the purified material exhibited the largest presence of the $\text{fac}$ isomer, we propose that the $\text{fac}$ isomer may sublime out of the pan. This would result in the formation of more $\text{fac}$ isomer in the pan in order to regain equilibrium.
Figure 3.5. Aromatic region of the $^1$H NMR spectra of 2Me$_3$Ga heated at 1K/min in: a) crimped pan; and b) uncrimped pan.

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Reference


3. The Aldrich Library of 1H NMR Spectra; Charles, J.P.; Edition1; Aldrich Chemical Company, Co.


CHAPTER 4

PHOTOPHYSICAL CHARACTERIZATION

4.1 Introduction

Luminescence is the emission of photons from electronically excited states. In photoluminescence (PL) the electronically excited state is achieved by light (photon) absorption. In contrast, electroluminescence (EL), the basic phenomena behind OLED's, takes place through electronically excited states achieved by electrical excitation. Although it is believed that the excited state achieved by both methods is similar, a study of the PL of the metal chelate systems will help further understand factors that affect EL. PL studies in the solid state would provide the most insight into the EL process. However, in the absence of such facilities, solution PL studies in solvents of different polarity are described below. PL efficiency ($\phi_{PL}$) refers to the efficiency of the emission process compared to the other non-radiative modes of decay of the excited state. (e.g. energy loss by vibration and heat). A loss of energy is often observed between the absorption and emission of light, referred to as the Stokes' shift (Frank-Condon shift). In solutions of different polarity, this may be caused by several different solvent interactions, and could also give information about specific interactions like hydrogen bonding, which may affect the solid state interactions of these molecules.
The optical transition most responsible for the photoluminescence in metal quinolate chelates is centered on the organic 8-quinolinolato ligand. This transition is a \(\pi-\pi^*\) charge-transfer from the phenoxide ring (location of HOMO) to the pyridyl ring (location of LUMO). Previously, Padmaperuma presented a detailed photophysical study of \(\text{nMeAlq}_3\) and \(\text{nMeGaq}_3\) (\(n=3,4,5\)), where energy shifts and PL efficiencies were correlated with the position of methyl substitution.\(^1,2\) All of the gallium chelates were red shifted compared to the aluminum analogues and exhibited four times lower PL efficiencies.

The C2-methylated derivatives were not included in those studies because \(\text{Al}^{3+}\) does not form a stable chelate with the sterically hindered ligand. Although the C2-methylated chelate of \(\text{Ga}^{3+}\) can be isolated, Sapochak reported that the material was unstable.\(^3\) However, the instability is not due to lack of chelation, as in the case of \(\text{Al}^{3+}\), but to the facile conversion between the \textit{mer} and \textit{fac} isomers as determined by \(^1\text{H} \text{NMR}\) studies in CDCl\(_3\).

On the other hand, pentacoordinate gallium chelates ligated to two 2Meq and a mondentate carboxylate (2Meq_2GaOR) were shown to be very stable and exhibited larger PL efficiencies than both Alq_3 and Gaq_3. Significant red shifts of absorption and emission energies were observed for all C2-methylated Ga\(^{3+}\) chelates relative to Gaq_3. In addition, these energies were identical for all 2Meq_2GaOR chelates in CH_3Cl and the Frank-Condon shifts were more similar to Gaq_3 than 2Meq_3Ga, which exhibited a much larger shift. This was attributed to the significantly larger differences between the ground and excited state geometries in 2Meq_3Ga caused by the steric congestion.
A more detailed photophysical study of 2Meq$_2$GaOR chelates, 2Meq$_3$Ga, Gaq$_3$ and Alq$_3$ in different solvents is presented here. In particular, the effects of C2-methylation of the ligand in tris-chelates and changes in the monodentate ligand (OR) in pentacoordinate chelates are discussed.

4.2 Experimental

PL studies were performed on an Aminco SLM 48000 Spectrofluorometer. Samples were run as dilute solutions in dichloromethane (CH$_2$Cl$_2$), dimethylformamide (DMF) and methanol (MeOH). The concentrations of the sample solutions were adjusted, so that the optical densities at 365 nm (excitation wavelength) were all close to 0.20 using a VARIAN CARY 3BIO UV-VIS Spectrophotometer. The emission maxima, full width at half maxima (FWHM), and the area under the emission spectra were calculated using the graphing software, Origin. Samples were run on the same day and all instrument parameters were kept constant.

The PL efficiency (PL quantum yield) values were calculated by the equation given below. (1)

$$\phi_{PL(x)} = \phi_{PL(Alq)} \left( \frac{A_x(390\text{nm})}{A_r(390\text{nm})} \right) \left( \frac{D_r}{D_x} \right)$$

Alq$_3$ was used as a reference and quantum efficiencies are reported relative to Alq$_3$ ($\phi_{PL} = 0.116$, DMF) (13) the optical density at 365 nm is used as $A_r$, area under the emission spectrum is used as $D_r$. Using the above relationship, if absorbance at 365 nm ($A_x$) and area under the emission spectrum ($D_x$) is known for an unknown sample, $Q_x$ can be calculated.
4.3 Results and Discussion

4.3.1 Absorption Studies

The absorption peaks for all metal chelates for different solvents is shown in Table 4.1. The $\lambda_{\text{max}}$ of absorption in CH$_2$Cl$_2$ is consistent with reports in CHCl$_3$ for all chelates with the exception of 2Meq$_3$Ga. Previous studies showed that C2-methylation of the ligand resulted in a large blue shift for 2Meq$_3$Ga and the pentacoordinate carboxylate chelates, where the shift was much larger for the tris-chelate. However, in the studies presented here, the $\lambda_{\text{max}}$ in CH$_2$Cl$_2$ is identical for all 2Meq chelates.

Table 4.1: Absorption peaks (nm) in different solvents.

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>CH$_2$Cl$_2$</th>
<th>MeOH</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>305*, 318, 334, 388*</td>
<td>304*, 315, 332, 375*</td>
<td>308*, 318, 333, 388*</td>
</tr>
<tr>
<td>Gaq$_3$</td>
<td>305*, 320, 334, 392*</td>
<td>304*, 316, 334, 379*</td>
<td>307*, 321, 333, 392*</td>
</tr>
<tr>
<td>2Meq$_3$Ga</td>
<td>303*, 316, 366*</td>
<td>300*, 312*, 355</td>
<td>323*, 331*, 373</td>
</tr>
<tr>
<td>2Meq$_2$GaOAc</td>
<td>302*, 316, 365*</td>
<td>303*, 315, 359*</td>
<td>305*, 317, 336*, 372*</td>
</tr>
<tr>
<td>2Meq$_2$GaODMP</td>
<td>299*, 316, 365*</td>
<td>298*, 312, 359*</td>
<td>305*, 320, 338*, 372*</td>
</tr>
<tr>
<td>2Meq$_2$GaOTF</td>
<td>299*, 314, 365*</td>
<td>301*, 315, 360*</td>
<td>305*, 320, 338*, 372*</td>
</tr>
<tr>
<td>2Meq$_2$GaOTCl</td>
<td>299*, 314, 365*</td>
<td>298*, 312, 359*</td>
<td>305*, 320, 338*, 372*</td>
</tr>
<tr>
<td>2Meq$_2$GaOH</td>
<td>302*, 316, 365*</td>
<td>298*, 312 359*</td>
<td>305*, 320, 338*, 372*</td>
</tr>
</tbody>
</table>

* Denotes $\lambda_{\text{max}}$ s= shoulder.

This discrepancy may be due to a different ratio $\text{fac/mer}$ isomers in 2Meq$_3$Ga, since in previous studies the sample was not purified by high vacuum temperature gradient sublimation before analysis, and as shown in Chapter 3, the method of purification has a large effect on the amounts of each isomer present. In addition, the higher energy peaks exhibit a substantially higher intensity for 2Meq$_3$Ga compared to all the other metal chelates, including the pentacoordinate systems (Figure 4.1). Therefore,
these differences are not simply due to the electronic effects of C2-methylation, but to the presence of the two geometric isomers.

Figure 4.1. Absorption spectra of (a) Alq₃, (b) Gaq₃, (c) 2Meq₃Ga and (d) 2Meq₃GaOAc in CH₂Cl₂, showing the significantly different character of the spectrum for 2Meq₃Ga.

In CH₂Cl₂, as observed in previous studies, a red shift of 329 cm⁻¹ (a shift to lower energy) is seen for the lowest energy transition in Gaq₃ compared to Alq₃. Comparing Gaq₃ and 2Meq₃Ga, a blue shift of 1810 cm⁻¹ (a shift to higher energy) is seen in 2Meq₃Ga caused by C2-methylation of q (Figure 4.1). Previous studies of nMeAlq₃ and nMeGaq₃ have shown that methyl substitution of the pyridyl ring shifts the LUMO to higher energy, resulting in a blue shift in their longest wavelength absorption peak. For example, 4Meq₃Ga showed a blue shift of 395 cm⁻¹ while 3Meq₃Ga did not shift compared to Gaq₃. Similar shifts were seen between nMeq₃Al (n=3,4) and Alq₃. But, as shown in this section, C2-methylation showed the largest blue shift. A change in the carboxylato ligand had no effect on the absorption peaks and the λₘₐₓ for all the chelates are identical (Table 4.1 and Figure 4.2).
Figure 4.2. Absorption spectra of all 2Meq2GaOR chelates in CH₂Cl₂, overlayed showing no energy shifts.

Solvent effects on Mqₙ (M=Al, Zn, Li) have previously been reported by Sapochak.⁴ Alq₃, Gaq₃ and 2Meq₃Ga showed a blue shift of ~ 800 cm⁻¹ of the lowest energy peak in MeOH compared to CH₂Cl₂. This is due to the excess stabilization of the ground state molecules by hydrogen bonding, relative to the excited state. But 2Meq₂GaOAc showed a smaller blue shift of 458 cm⁻¹. While Alq₃ and Gaq₃ show no change in the lowest energy peak in DMF compared to CH₂Cl₂, 2Meq₃Ga and 2Meq₂GaOAc show a red shift of 515 cm⁻¹. This is indicative that 2Meq₃Ga and 2Meq₂GaOAc have more polar excited states, which are stabilized by DMF. The lack of change in Alq₃ in CH₂Cl₂ and DMF has been previously attributed to the similarity in the polarity of the ground and excited states.⁵
4.3.2 Photoluminescence Studies

Table 4.2 shows the PL emission energies, full-width-at-half-maximum (FWHM) of the emission spectra, the Frank-Condon shift (F-C shift) ($\Delta$) and relative PL quantum efficiencies ($\phi_{PL}$) of Alq$_3$, Gaq$_3$, 2Meq$_3$Ga and all 2Meq$_2$GaOR chelates in CH$_2$Cl$_2$. Upon substitution of gallium for aluminum, $\lambda_{max}$ of emission was red shifted by 1040 cm$^{-1}$ for Gaq$_3$. On the other hand, similar to absorption studies, all 2Meq-based gallium chelates were blue shifted by $\sim$1550 cm$^{-1}$ from Gaq$_3$. This suggests that the effect of C2-methylation on the photophysical properties is similar regardless of the number of ligands or coordination geometry. All gallium chelates exhibited similar F-C shifts, which were larger compared to Alq$_3$. This may be because the gallium chelates are more vibrationally distorted in their excited state compared to Alq$_3$.

Table 4.2: Photophysical data of all chelates in CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>Absorption $\lambda_{max}$ (nm)</th>
<th>Emission $\lambda_{max}$ (nm)</th>
<th>FWHM (nm)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
<th>Relative $\phi_{PL}$ Alq$_3$=1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>387</td>
<td>514</td>
<td>104</td>
<td>6370</td>
<td>1.00</td>
</tr>
<tr>
<td>Gaq$_3$</td>
<td>392</td>
<td>543</td>
<td>110</td>
<td>7162</td>
<td>0.28</td>
</tr>
<tr>
<td>2Meq$_3$Ga</td>
<td>366</td>
<td>500</td>
<td>102</td>
<td>7300</td>
<td>1.42</td>
</tr>
<tr>
<td>2Meq$_2$GaOAc</td>
<td>365</td>
<td>501</td>
<td>104</td>
<td>7420</td>
<td>1.56</td>
</tr>
<tr>
<td>2Meq$_2$GaOTF</td>
<td>365</td>
<td>495</td>
<td>100</td>
<td>7180</td>
<td>2.04</td>
</tr>
<tr>
<td>2Meq$_2$GaODMP</td>
<td>365</td>
<td>502</td>
<td>104</td>
<td>7460</td>
<td>1.48</td>
</tr>
<tr>
<td>2Meq$_2$GaOH</td>
<td>365</td>
<td>499</td>
<td>102</td>
<td>7340</td>
<td>1.66</td>
</tr>
<tr>
<td>2Meq$_2$GaOTCl</td>
<td>365</td>
<td>495</td>
<td>101</td>
<td>7340</td>
<td>1.88</td>
</tr>
</tbody>
</table>
Figure 4.3. PL spectra of showing relative (\(\phi_{PL}\)) PL efficiencies in CH\(_2\)Cl\(_2\).

The \(\phi_{PL}\) of Gaq\(_3\) is much lower than Alq\(_3\), which has been previously attributed to metal ion substitution.\(^3\) But the \(\phi_{PL}\) of 2Meq\(_3\)Ga is ~ 50% higher than Alq\(_3\). This is also shown for all the 2Meq\(_2\)GaOR chelates, which exhibit similar quantum efficiencies in CH\(_2\)Cl\(_2\). (Figure 4.3 and 4.4). Interestingly, 2Meq\(_3\)GaOTF and 2Meq\(_2\)GaOTCl exhibited the highest relative quantum efficiencies. This might be attributed to the repulsive forces between the halogenated carboxylate ligand, which could reduce any PL quenching due to strong intermolecular interactions of the \(\pi\)-systems. Photophysical data in DMF and MeOH are shown in Table 4.3. In polar DMF, absorption and emission energies were lowered compared to results in CH\(_2\)Cl\(_2\) for all 2Meq-based gallium chelates, but no shifts were observed for Alq\(_3\) and Gaq\(_3\). This is supportive of a more polar excited state for the 2Meq-based chelates. In the polar protic solvent, MeOH, all chelates were shifted to higher energy due to hydrogen bonding of the ground state via the phenolic oxygen of the ligand. This resulted in larger F-C shifts and higher relative PL quantum efficiencies for all chelates.

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Figure 4.4. PL spectra of all 2Meq_GaOR chelates in CH₂Cl₂, showing no emission energy shift.

Table 4.3: Photophysical data of all chelates in different solvents.

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>Solvent</th>
<th>Absorption λ_max (nm)</th>
<th>Emission λ_max (nm)</th>
<th>FWHM (nm)</th>
<th>Δ (cm⁻¹)</th>
<th>Relative ϕ_pl Alq₃=1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃</td>
<td>MeOH</td>
<td>375</td>
<td>521</td>
<td>104</td>
<td>7450</td>
<td>1.00</td>
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<tr>
<td>Ga₃</td>
<td>MeOH</td>
<td>379</td>
<td>548</td>
<td>111</td>
<td>8120</td>
<td>0.33</td>
</tr>
<tr>
<td>2Meq₂Ga</td>
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<td>355</td>
<td>506</td>
<td>102</td>
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<td>359</td>
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<tr>
<td>2Meq₂GaOTF</td>
<td>MeOH</td>
<td>360</td>
<td>508</td>
<td>104</td>
<td>8070</td>
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<td>2Meq₂GaODMP</td>
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<td>506</td>
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<td>8070</td>
<td>2.97</td>
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<tr>
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<td>506</td>
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<tr>
<td>2Meq₂GaOTCl</td>
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<td>507</td>
<td>102</td>
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<td>2.78</td>
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<td>Alq₃</td>
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<td>520</td>
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<td>6530</td>
<td>1.00</td>
</tr>
<tr>
<td>Ga₃</td>
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<td>0.27</td>
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<td>2Meq₂GaOAc</td>
<td>DMF</td>
<td>373</td>
<td>510</td>
<td>111</td>
<td>7180</td>
<td>0.78</td>
</tr>
<tr>
<td>2Meq₂GaOTF</td>
<td>DMF</td>
<td>372</td>
<td>509</td>
<td>108</td>
<td>7220</td>
<td>0.99</td>
</tr>
<tr>
<td>2Meq₂GaDMP</td>
<td>DMF</td>
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<td>509</td>
<td>108</td>
<td>7290</td>
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<tr>
<td>2Meq₂GaOH</td>
<td>DMF</td>
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<td>508</td>
<td>108</td>
<td>7220</td>
<td>1.01</td>
</tr>
<tr>
<td>2Meq₂GaOTCl</td>
<td>DMF</td>
<td>372</td>
<td>509</td>
<td>108</td>
<td>7250</td>
<td>0.99</td>
</tr>
</tbody>
</table>

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Reference


CHAPTER 5

X-RAY ABSORPTION SPECTROSCOPY CHARACTERIZATION

5.1 Introduction

The phenomenon of “synchrotron radiation” which used to be a mere technical nuisance in elementary particle accelerators, have in the past few decades demonstrated its importance in the fields of condensed matter science, biology, and engineering. Synchrotron radiation is the electromagnetic radiation emitted by fast moving electrons along a curved trajectory with a large radius of curvature. The uniqueness of synchrotron radiation derives from the broad range of emitted photon energies, ranging from microwaves to hard x-rays and γ-rays. \(^{(1,2)}\)

The wavelength range of the most important photon energies is \(10^3\) to \(10^{-1}\) Å, which corresponds to the sizes of atoms, molecules, and chemical bond lengths allowing elucidation of chemical structure at the molecular level. Thus, x-ray spectroscopic techniques are fast becoming an essential tool in the structural study of matter. Furthermore, the energy of photons correspond to the binding energy of electrons in atoms, molecules and solids. Bound electrons include valence electrons, electrons involved in chemical bonding and inner shell (core) electrons. Therefore, synchrotron
radiation has the required energy to probe bound electrons in order to study the electronic properties of matter, which is the key to understanding their chemical and physical properties.\(^{(1,2)}\)

The most common x-ray spectroscopic technique is x-ray absorption spectroscopy (XAS) in which atomic core electrons are excited into unoccupied energy states, thus providing a map of the unoccupied states (unoccupied molecular orbitals). Another technique of interest is x-ray emission spectroscopy (XES), which maps the valence or occupied states through detection of light emission when a valence electron relaxes to a core "hole" created by energy absorption. More recently, near edge x-ray absorption fine structure (NEXAFS) spectroscopy, a surface science technique was developed in the 1980's for elucidating the structure of molecules bonded to surfaces, in particular the low-Z molecules.\(^{(1)}\) The term "low-Z" molecules refer to organic molecules containing important atoms such as carbon, oxygen, nitrogen, hydrogen and fluorine.\(^{(1)}\)

In designing efficient emitter materials for electroluminescence (EL) applications, the optimization of several material properties is required. As discussed in Chapter 1, EL efficiency depends on photoluminescence (PL) efficiency in addition to charge injection and charge transport efficiencies through the thin film layers of the emitter material. All these material properties are strongly dependent on both the electronic and molecular structure of the material. Previously, Curioni, et. al. studied vapor deposited thin films of the most well characterized EL material, \(^{(3)}\) Alq\(_3\) using NEXAFS and XES spectroscopies. He probed the C 1s, N 1s, and O 1s edges of Alq\(_3\) and proposed assignments of the resulting spectra based on a theoretical treatment of the molecule. More recently, Padmaperuma reported a NEXAFS study of a series of aluminum and
gallium tris-(8-quinolinolato) chelates and the corresponding methyl substituted derivatives. (4) No significant differences were observed in the C 1s and N 1s NEXAFS spectra between Al^{3+} and Ga^{3+} chelates, suggesting that the electronic structure of metal tris chelates of q were not affected by metal ion substitution. However, x-ray photoelectron spectroscopic (XPS) studies of Alq3, Gaq3, and Inq3 showed that the Ga^{3+} ion was the most covalently bonded to the oxygen atom of the ligand. (5) NEXAFS studies of the O-edge of Gaq3, which can provide more detailed information about this difference in bonding of the metal ions with the ligand has not been reported. An investigation of the O 1s edge is important because Gaq3 based OLED's have been shown to exhibit comparable EL efficiencies to Alq3 even though the PL efficiency was significantly lower. (4,6,7,8) The reason for the enhanced EL efficiency has not been elucidated and may be related to the difference in bonding with the ligand.

On the other hand, changes in the C 1s NEXAFS spectra were observed upon methyl substitution of the ligand for both Al^{3+} and Ga^{3+} tris-chelates. (4) Consistent with theoretical calculations, substitution of the electron deficient pyridyl ring of the q ligand raises the energy of the LUMO. (9) Experimentally, a corresponding shift to higher energy of the lowest energy C 1s peaks in the NEXAFS spectra were observed for 3- and 4-methyl substituted metal tris-chelates relative to the C5-methylated and unsubstituted derivatives. Similar energy shifts would be expected for the C2-methylated derivative of Alq3 (2Meq3Al), (10) but this metal chelate cannot be synthesized because of steric hindrance. However, the Ga^{3+} tris-chelate of 2Meq, 2Meq3Ga can be synthesized because the larger gallium ion can better accommodate the bulky ligand resulting from methyl substitution next to the nitrogen of the pyridyl ring. Previously, X-ray crystal structure
data showed that the Ga-N bond lengths are significantly increased and the corresponding Ga-O bond lengths are significantly decreased in 2Meq3Ga compared to both Alq3 and Gaq3. Therefore, it is expected that these geometric changes should also affect the electronic structure of the molecule. In this thesis, the O 1s NEXAFS study of Gaq3 is reported here for the first time, as well as the C 1s, N 1s, and O 1s NEXAFS studies of 2Meq3Ga and the pentacoordinate 2Meq2Ga-OR chelates. Results and discussion of these studies will be presented for groups of compounds. First, the NEXAFS results of Alq3, Gaq3, and 2Meq3Ga will be compared in order to elucidate the effect of metal ion substitution and 2-methyl substitution of q on the electronic structure of the tris-chelates. Second, NEXAFS results for 2Meq3Ga and 2Meq2GaOAc will be compared to identify the effects due to geometry changes (hexacoordinate to pentacoordinate) and the presence of the monodentate carboxylato ligand. Finally, the 2Meq2Ga-OR chelates will be presented and the effect of changing the nature of the monodentate ligand on the pentacoordinate chelates will be discussed.

5.2 Experimental Method

X-ray absorption spectroscopy experiments were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). Previous experiments were performed at beamline (BL) 6.3.2, but recent experiments have been performed on a newer BL 6.3.1. This BL uses the same energy beam as 6.3.2, but has a different and new chamber. Samples to be analyzed are sublimed onto copper (99.9999% Cu metal assay purchased from Alfa Aesar) slides of ~ 1 cm². Copper is the best-known substrate in the industry as it is less prone to oxidation unlike substrates like aluminum.
The cut Cu pieces are first polished by sand paper to obtain an even surface. The slides are then cleaned according to the following procedure: 1) ultrasound treatment in a particle free solution of Alconox (detergent); 2) boiling in 1,1,1-trichloroethane, acetone (reagent grade) and methanol (reagent grade) respectively; and 3) drying under pure argon gas. The slides are then stored in argon filled vial and used as soon as possible. After the samples are sublimed onto the substrates, they are stored in argon filled petri dishes and shipped via air courier to the ALS.

The sample slides are mounted onto the BL chamber by pasting them on carbon tape, which is pasted on a glass microscope slide. Approximately, 5 – 6 samples can be mounted on each slide and it is placed at a 90° angle to the incoming beamline. A grating of 600 l/mm was used for the carbon and nitrogen K-edge experiments and a grating of 1200 l/mm was used for the oxygen K-edge. A filter was not used in any of the experiments in order to avoid contamination and since there was no significant change in the resolution upon using a filter.

The x-ray absorption experiments were performed via the total electron yield method. The energy range used in each experiment depended on the atom of interest, for example in order to promote a core electron from an atom of carbon in an organic material energy of 270 – 330 eV is required. Since nitrogen and oxygen are more electronegative elements than carbon they will require a higher energy, thus nitrogen requires 390 – 415 eV and oxygen requires 525 – 565 eV. When a core electron is excited into an unoccupied state, it gives rise to an excited molecule, which does not bare a charge, but a “core hole” is created. This excited state can decay by, recombination of the hole and the excited electron, production of photoelectron and/or Auger emission. The
major pathway of decay is Auger emission and detectors measure the electrons that escape. The current required to balance the electrons that escape the sample, is called the drain current. Changes in the drain current define the changes in the intensity of the spectrum. The NEXAFS spectra are obtained as a function of change in drain current vs. photon energy of the x-ray beam. Therefore, an electrical connection is needed between the sample and the detector, which is why the cu slides are pasted on conducting carbon tape.

Even though BL 6.3.1 was built more recently, and contains less carbonic contaminants, the resolution of the carbon edge of the metal-chelates was poorer than that of BL 6.3.2. Data from experiments from both beam lines are presented. The data was calibrated to the energy of BL 6.3.2, which is a calibration beamline.

5.3 Background: NEXAFS Studies of Alq3

As determined previously by semi-empirical calculations, both the occupied and unoccupied states of mer-Alq3 near the HOMO-LUMO gap group into sets that have the same orbital character with slightly different energies on each of the three ligands making up the metal tris-chelate. Therefore, the LUMO and HOMO of the molecule are localized on a single ligand. The HOMO set is mainly localized on the electron rich phenoxide ring and the LUMO set is mainly localized on the electron deficient pyridyl ring. (Figure 5.1)

Curioni compared the NEXAFS spectrum of Alq3 with the calculated photoabsorption spectra and assigned the spectral peaks as transitions from the 1s orbital to various available unoccupied states corresponding to four different LUMO "sets"
generated by the theoretical treatment of the molecule. The lowest energy unoccupied orbital set, and the one believed to be most involved in the PL process, contains the majority of the electron density distributed around the pyridyl ring nitrogen and carbon atoms and very little on the oxygen of the phenoxide ring. The higher energy unoccupied orbital sets include: LUMO+1 containing a symmetric distribution of electron density mainly on the carbon atoms of both rings, excluding C4 and C5; LUMO+2 state containing electron density mainly on the phenoxide ring oxygen and carbons but with some density on the pyridyl nitrogen; and LUMO+3 state containing an almost symmetric distribution of electron density over both rings and all atoms.

The C 1s-edge NEXAFS spectra of metal tris (8-quinolinolato) chelates are complicated because there are so many different carbons. Alq3 exhibited three major peaks in the pre-edge spectrum, where only the lowest energy peak assigned to the C 1s to LUMO was well defined in the NEXAFS spectrum. This peak was proposed to be dominated by transitions from C1s to the LUMO of the carbon atoms at the C4-position.
of the pyridyl ring. Two higher energy broad peaks were also observed with the lower
energy one assigned to mixtures of contributions from the C 1s to LUMO, LUMO +1, and
LUMO +2 sets, where the maximum relative intensity was due to the C 1s to LUMO
+2 from carbons atoms at the C5-position of the phenoxide ring.

Curioni observed that the N 1s and O 1s spectra had much narrower peaks than
the C 1s transitions as the three N and O atoms are almost chemically equivalent. The N
1s spectra of Alq₃ consisted of three transitions, the first intense transition was due to N
1s to LUMO, the second and third less intense peaks were assigned as transitions from N
1s to LUMO + 2 and LUMO + 3 respectively. The N 1s to LUMO + 1 was not observed
since the LUMO + 1 orbital is mainly localized on carbon atoms. In the case of the O 1s
spectra, two peaks were observed and assigned to O 1s to LUMO and LUMO + 2,
respectively. Similar to the N 1s spectrum, the transition to LUMO + 1 was not observed.

5.4 NEXAFS Spectroscopic Results and Discussion
5.4.1. C 1s NEXAFS Results
5.4.1(a) Comparison of Alq₃, Gaq₃, 2Meq₃Ga

A comparison of the C 1s spectra of Alq₃, Gaq₃ and 2Meq₃Ga is shown in Figure
5.2(a), where the three major peaks observed in the pre edge spectra are labeled P(1),
P(2) and P(3), in order of increasing energy. For the C2-methylated derivative, 2Meq₃Ga
a shift to higher energy for the P(1) (~0.12 eV) from both Alq₃ and Gaq₃ was observed
(Figure 5.2b). Previous studies of both methylated Alq₃ and Gaq₃ derivatives showed
that substitution of the pyridyl ring at the C4 and C3-positions of the ligand resulted in
\( \sim 0.25 \text{ eV} \) and \( <0.1 \text{ eV} \) shifts to higher energy of \( P(1) \), respectively. Similar shifts have also been observed for 4Meq\(_2\)Zn and 4Meq\(_2\)Li when compared to their unsubstituted analogues, Znq\(_2\), Liq.\(^{11,12}\) These results are consistent with Curioni’s assignment of the \( P(1) \) peak being due primarily from a single transition, C 1s of C4 to the LUMO. Therefore, in comparing Alq\(_3\), Gaq\(_3\), and 2Meq\(_2\)Ga, the energy of the \( P(1) \) peak is not affected by metal ion substitution but is shifted to higher energy by C2-methyl substitution. The second lowest energy peak, \( P(2) \) observed in the C 1s NEXAFS spectra for Alq\(_3\), Gaq\(_3\), and 2Meq\(_2\)Ga was also seen to change upon C2-methylation of the ligand, but not for metal ion substitution. No significant differences were observed for peak \( P(3) \). Figure 5.2b shows a magnification of the spectra.

![Figure 5.2](image)

**Figure 5.2.** C 1s NEXAFS spectra for Alq\(_3\), Gaq\(_3\) and 2Meq\(_2\)Ga: a) full range; and b) magnification of \( P(1) \) and \( P(2) \) peaks.

As discussed in Section 5.2.1, for Alq\(_3\), \( P(2) \) arises from more than one transition and appears as a broad peak. For 2Meq\(_2\)Ga, a narrowing of \( P(2) \) on the lower energy side was observed. There are two possible interpretations for this peak narrowing effect. One
interpretation is that the transition of C 1s to LUMO +1, which contains an equal
distribution of electron density on carbon atoms: C2, C3, C6, C9, and C10, but none on
C4 or C5 may have shifted to higher energy upon C2-methylation. Previously, results for
4Meq3M and 5Meq3M, where M = Al^3 and Ga^3, showed a higher energy shoulder
appear on the P(2) peak compared to the unsubstituted analogues. Those shoulders may
be due to an increase in energy of the C1s to LUMO transition for C4-methylation and C
1s to LUMO+2 transition for C5-methylation, both consistent with the concentration of
electron densities at the different methyl-substituted positions. A second plausible
explanation is that the fac isomer is dominant in solid state films of 2Meq3Ga resulting in
a different C1s NEXAFS signature. Unlike the mer isomer, the three 2Meq ligands of the
fac isomer are equivalent, thus reducing the number of possible transitions due to carbons
in different environments. Although both explanations are viable, the second
interpretation is strengthened by ^1H NMR spectroscopic and thermal analysis results
(Chapter 3), which support the higher abundance of the fac isomer.

5.4.1(b) Comparison of 2Meq3Ga and 2Meq2GaOAc

The C 1s spectra of 2Meq2GaOAc and 2Meq3Ga are shown in Figure 5.3. The
energies and shapes of both the P(1) and P(2) peaks do not change upon substitution of
one of the 2Meq ligands with the monodentate acetato ligand resulting in a
pentacoordinate geometry about the Ga^3 ion. However, a small shift in energy of P(3)
and appearance of a new peak is observed for 2Meq2GaOAc, as depicted in Figure 5.3b.
The most likely assignment of this peak is due to the C 1s transition to \( \pi^* \) of the acetato
C=O, at ~ 288 eV, consistent with previous assignments for carbonyl compounds. The transition is weak because there is only one carbon of this type in the compound.

![Figure 5.3. C ls spectra of 2Meq2GaOAc and 2Meq3Ga: a) full range; and b) magnification of peak P(3) from BL 6.3.2.](image)

This comparison of the C ls NEXAFS spectra of 2Meq3Ga and 2Meq2GaOAc indicates that the unoccupied states of 2Meq are unaffected by the coordination about the metal ion and presence of the acetato group. Furthermore, it can be concluded that there is most likely no electronic communication through the metal ion between the 2Meq and acetato ligand.

5.4.1(c) Comparison of 2Meq3GaOR Chelates

The C ls spectra of 2Meq2GaOAc, 2Meq2GaOTF and 2Meq2GaODMP are shown in Figure 5.4. The energies and shapes of P(1), P(2) and P(3) do not change upon changing the carboxylato ligand. This supports the assignment proposed in the preceding section for the C ls to π* transition of C=O at ~288 eV for all 2Meq2GaOR chelates. The

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The effect of fluorination of the acetato group showed little effect on this transition, but this is consistent with other fluorinated carbonyl compounds studied by NEXAFS. For example, it has been shown that the C 1s resonance energy shifts from 286.0 eV to 290.9 eV moving from H₂C=O to F₂C=O. This is because the fluorine atoms are directly bonded to the C=O moiety. The only differences observed in the NEXAFS spectra for this group of compounds were in the higher energy σ transition region (far edge), which showed two prominent transitions for 2Meq₂GaOTF only. This has been previously observed in organo fluorine compounds and may be due to the C 1s transitions from the trifluoromethyl group.

![C 1s NEXAFS spectra for 2Meq₂GaOAc, 2Meq₂GaOTF and 2Meq₂GaODMP.](image)

The most important result that can be concluded from comparing the C 1s NEXAFS spectra of the 2Meq₂GaOR chelates is that there were no changes observed for the transitions associated with the 2Meq ligand, supporting the supposition that the
presence of the carboxylato ligand does not change the nature of the unoccupied states of
the 2Meq2GaOR chelates.

5.4.2 O 1s NEXAFS Results

5.4.2(a) Comparison of Alq3, Gaq3, and 2Meq3Ga

The O 1s spectra of Alq3, Gaq3 and 2Meq3Ga are shown in Figure 5.5. Two
major transitions were observed for all metal tris chelates in the pre edge region,
consistent with reports by Curioni for Alq3. \(^{(2)}\) These transitions are labeled P(1) and P(2)
in order of increasing energy in the figure. The P(1) and P(2) energies are similar for Alq3
and Gaq3, but are shifted to higher energy for 2Meq3Ga by \(-0.2\) eV and \(-0.4\) eV,
respectively.

Both Gaq3 and 2Meq3Ga show a broadening of the low energy side of the edge
(threshold) of the spectra compared to Alq3 (Figure 5.5a) One possible explanation is that
the Ga\(^{3+}\) ion has a larger number of low energy accessible Rydberg states compared to
Al\(^{3+}\), due to the higher number of available d-orbitals. This would expectedly increase the
probability of more transitions resulting in peak broadening.

As discussed in section 5.3 (Background) Curioni observed that the narrow O 1s
transitions in the Alq3 NEXAFS spectrum were due to the oxygen atoms being in
approximately equivalent environments. Even though Alq3 has two geometric isomer
forms, mer and fac, the contribution from the fac isomer is believed to be very small. \(^{(14)}\)
In the case of 2Meq3Ga, which also exists as two isomers, the contribution of the facial
isomer in a thin film is much higher than that for Alq3, as discussed in Chapter 3. Since
the facial isomer is the higher energy form, the broadening of P(1) in the O1s NEXAFS
spectrum may be due to both the meridional and facial isomers, with the higher energy side of the peak due to the latter.

Figure 5.5. O 1s spectra of Alq$_3$, Gaq$_3$ and 2Meq$_3$Ga; (a) full range and (b) lowest energy transitions.

5.4.2(b) Comparison of 2Meq$_3$Ga and 2Meq$_2$GaOAc

When comparing 2Meq$_3$Ga and 2Meq$_2$GaOAc (Figure 5.6), no observable energy differences were evident for P(1) and P(2). However, the relative intensities of the peaks were different between the two metal chelates. The higher intensity P(1) of 2Meq$_2$GaOAc could arise because of contributions from transitions to $\pi^*$ from the O 1s of the C-O and C=O of the acetato ligand. On the other hand, the higher intensity of P(2) for 2Meq$_3$Ga compared to 2Meq$_2$GaOAc, most likely results, from transitions originating from the O 1s of the C-O of the three 2Meq ligands as opposed to two in 2Meq$_2$GaOAc.
5.4.2(c) Comparison of 2Meq$_2$GaOR chelates

The O 1s NEXAFS spectra of 2Meq$_2$GaOAc, 2Meq$_2$GaOTF and 2Meq$_2$GaODMP are shown in Figure 5.7. Intensity differences are similar in P(1) confirming the previous assignment in section 5.4.2.b, of the O 1s transitions from the acetato ligand appearing at this energy.
5.4.3. N 1s NEXAFS Results

5.4.3(a) Comparison of Alq₃, Gaq₃, 2Meq₃Ga

The N 1s spectra of Alq₃, Gaq₃ and 2Meq₃Ga (Figure 5.9) are similar except for a shift to higher energy (0.2 eV) and broadening of P(3) transition in 2Meq₃Ga. (Figure 5.9b) Once again this broadening can be explained by the change in environment around the nitrogen atoms of 2Meq₃Ga because of the presence of both the fac and mer isomers.

Previous studied of the N edge of Alq₃, 3Meq₃Al and 4Meq₃Al showed a shift to lower energy in P(3) upon methylation of the pyridyl ring. The nMeq₃Ga chelates showed a similar trend. Unlike the carbon edge spectra, the methyl groups are not directly associated with the nitrogen atom, thus it is more difficult to evaluate these shifts. One possibility, is that the core hole created on the nitrogen atom may be stabilized by the electron donating methyl group (weakly) more efficiently when the methyl group is on the pyridyl ring.

When comparing Alq₃, Gaq₃ and 2Meq₃Ga (Figure 5.8) we see that P(3) of both Gaq₃ and 2Meq₃Ga are shifted to higher energy, while 2Meq₃Ga is much broader than the former. The shifts are due to metal ion substitution in Alq₃. The broadening of P(3) in 2Meq₃Ga could be due to more high energy transitions than in Gaq₃.

As discussed in Chapter 3, the Ga-N bond lengths are significantly lengthened for 2Meq₃Ga compared to both Alq₃ and Gaq₃. Therefore, it may be that steric factors created by methylation at C2 may have increased the energy of that respective LUMO state and/or the core hole created on the N-atom is less stabilized. Furthermore, it was also shown and discussed in Chapter 3 that in the solid state (film) the fac:mer ratio for
$2\text{Me}q_3\text{Ga}$ is $\sim 4:1$, therefore the larger presence of the $\text{fac}$ isomer may be the reason for the shift.

Figure 5.8. N 1s spectra of $\text{Alq}_3$, $\text{Gaq}_3$ and $2\text{Meq}_3\text{Ga}$. (a) Full range and (b) P(3) transition.

5.4.3(b) Comparison of $2\text{Meq}_3\text{Ga}$ and $2\text{Meq}_2\text{GaOAc}$

Figure 5.9. N 1s spectra of $2\text{Meq}_3\text{Ga}$ and $2\text{Meq}_2\text{GaOAc}$; (a) Full Range and (b) P(3) transition.
The pentacoordinate gallium chelates are less sterically hindered than 2Meq_3Ga resulting in a shorter Ga-N bond length. (7) This results in a high energy shift of ~0.2 eV of P(3) for 2Meq_3Ga compared to 2Meq_2GaOAc. No change was observed for the other peaks in the N-edge spectra (Figure 5.9).

5.4.3 (c) Comparison of 2Meq_3GaOR Chelates

The N ls NEXAFS spectra for all pentacoordinate chelates were identical as shown in Figure 5.10.

Figure 5.10. Identical N ls NEXAFS spectra of 2Meq_2GaOR chelates.
Reference


CHAPTER 6

CONCLUSIONS

One of the most important suppositions in this research project was that the LUMO states of the 2Meq2GaOR chelates were similar, hence leading to similar charge injection in OLED's consisting of these materials. This supposition was brought forth by studies done in Chapter 4, where identical absorption and emission energies were observed in different solvents. The first detailed NEXAFS spectroscopy study of the 2Meq2GaOR chelates reported in Chapter 5, verified that the LUMO states of these materials are indeed identical. This satisfies the basic criteria for similar energy level alignment at the interface with the cathodes.

But in an OLED these metal chelates are sandwiched between the HTL and the metal cathode. Charge injection is a phenomena that takes place at the interface between the cathode and the ETL (2Meq2GaOR chelates) and the polarity of the chelates may cause band bending and affect the energy level alignment at the interface, hence affect charge injection. Further studies on the LUMO states at the interface should be performed. One way this can be done is by growing thin films of these chelates at varying thickness on a thin film of the cathode material and probing their LUMO states by NEXAFS spectroscopy.
In Chapter 4 we presented the effect of 2-methyl substitution on the LUMO states of the tris-quinolinolato chelates by NEXAFS spectroscopy. We also presented for the first time the detection of the *facial* and *mer* isomer of 2Meq₃Ga on a thin film using NEXAFS spectroscopy. It has been previously stated that Alq₃ and nMeq₃Al primarily exist as the meridional isomer in thin film. But 2Meq₃Ga is known to exist in higher, detectable proportions.

This led to the first detailed study into the interconversion of the two isomers of 2Meq₃Ga in the gas phase and solid state, in Chapter 3. It was concluded that the *mer*-2Meq₃Ga interconverted into *fac*-2Meq₃Ga during melting/sublimation and in the gas phase. Previous theoretical studies on *fac*-Alq₃ have suggested that it may act as an electron trap during device operations, but no supportive experimental studies have been done. Based on the experiments done in Chapter 3, it may be possible to control the *fac*/mer ratio of 2Meq₃Ga in a thin film by controlling the temperature of the substrate onto which samples are sublimed. By studying the device performance of 2Meq₃Ga with varying *fac*/mer isomer ratios, the effect of the *fac* isomer on charge transport can be further studied. Currently, experiments are in progress to isolate and study the two isomers using x-ray crystallography. Attempts will be made to isolate separate crystals and polymorphs of 2Meq₃Ga and study their packing in solid state.

Thermal analysis of 2Meq₂GaOAc, 2Meq₂GaODMP and 2Meq₂GaOTF was indicative of different intermolecular interactions between molecules of these chelates. These interactions will affect the charge transport properties of these chelates in devices. X-ray crystallography studies of these chelates are also currently in progress.
Finally, these materials need to be incorporated into OLED’s and their device performance studied, in order to understand the affects of the above mentioned factors on EL efficiency.
APPENDIX I

\(^1\text{H} \text{ NMR DATA}\)
Figure A-1. $^1$H NMR spectrum of 2Meq (ppm)

Figure A-1.1. Aromatic region (ppm)
Figure A-2. $^1$H NMR spectrum of 2Meq$_2$CrOAc (ppm)

Figure A-2.1. Aromatic region (ppm)

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Figure A-3. $^1$H NMR spectrum of 2Me$_2$GaODMP (ppm)

Figure A-3.1. Aromatic region (ppm)
Figure A-4. $^1$H NMR spectrum of 2Meq$_2$GaOTF (ppm)

Figure A-4.1. Aromatic region (ppm)
Figure A-5. $^1$H NMR spectrum of 2Me$_2$GaOTCl (ppm)

Figure A-5.1. Aromatic region (ppm)
APPENDIX II

$^{13}$C NMR DATA
Figure B-1. $^{13}$C NMR spectrum of $\text{Me}_2\text{GaOAc}$ (ppm)

Figure B-2. $^{13}$C NMR spectrum of $\text{Me}_2\text{GaODMP}$ (ppm)
Figure B-3. $^{13}\text{C}$ NMR spectrum of 2Me$\text{eq}_2\text{GaOTF}$ (ppm)

Figure B-4. $^{13}\text{C}$ NMR spectrum of 2Me$\text{eq}_2\text{GaOTCl}$ (ppm)

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APPENDIX III

FT-IR DATA
Figure C-1. FT-IR spectrum of 2Meq₂GaODMP as (a) KBr pellet and (b) thin film on salt plate

Figure C-2. FT-IR spectrum of 2Meq₂GaOTCl as a KBr pellet

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APPENDIX IV

THERMAL ANALYSIS, $^1H$ AND $^{13}C$ NMR DATA

OF

TRIS(2-METHYL-8-QUINOLINOLATO) GALLIUM (III) CHELATE
Figure D.2. $^1$H NMR of 2MeC$_3$Ga recrystallized from methanol.
$^{1}H$ NMR of 2MeCpGa heated to 350°C at 20K/min – Crimped pan
Figure D.10. $^{13}C$ NMR of 2Me$_3$Ga heated to 350°C at 5K/min – Uncrimped pan
Figure D-12. STA scan of 2Meq\textsubscript{3}Ga heated to 350 at 20K/min – Uncrimped pan
Figure D-13. STA scan of 2MgGa heated to 350 at 5K/min - Uncrimped Pan
Figure D-14. STA scan of 2Meq$_3$Ga heated to 350 at 1K/min – Uncrimped pan
Figure D-16: STA scan of 2Me3Ga heated to 300 at 1K/min – Crimped pan
APPENDIX V

PHOTOPHYSICAL DATA
Figure E-1. Absorption spectra of Alq₃, Gaq₃, 2Meq₂Ga and 2Meq₂GaOAc in DMF

Figure E-2. Absorption spectra of all 2Meq₂GaOR in DMF
Figure E-3. Absorption spectra of Alq, Gaq, 2MeqGa and 2MeqGa in MeOH

Figure E-4. Absorption spectra of all 2Meq2GaOR in MeOH

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Figure E-5. Emission spectra of Alq₃, Gaq₃, 2Meq₃Ga and 2Meq₂GaOAc in DMF

Figure E-6. Emission spectra of all 2Meq₂GaOR in DMF

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Figure E-7. Emission spectra of Alq₃, Gaq₃, 2Meq₂Ga and 2Meq₂GaOAc in MeOH

Figure E-8. Emission spectra of all 2Meq₂GaOR in MeOH

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Thesis Title: Characterization of 2-methyl-8-quinolinolato gallium(III) chelates

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