X-ray Crystal Structure of Gallium Tris-(8-hydroxyquinoline): Intermolecular $\pi-\pi$ Stacking Interactions in the Solid State

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Received October 1, 1998
Revised Manuscript Received December 17, 1998

Efficient electroluminescence (EL) from an organic light-emitting device (OLED) was first reported by Tang and Van Slyke using tris(8-hydroxyquinoline)aluminum (Alq_3).[1] Since this report, the interest in Alq_3 and other metal−chelate systems to produce EL in different spectral regions for display applications has considerably increased.[2−5] Although Alq_3 and Gaq_3 have low fluorescence quantum yield, they have excellent properties as EL materials, namely, good charge transport, highly stable film formation, and good heat resistance. Forrest and co-workers have shown that Gaq_3 has a thin film PL quantum efficiency of only 25% of that for Alq_3. However, the power efficiency of its light-emitting devices is higher than that of Alq_3 by 50%,[6] suggesting that the Gaq_3 is a superior emitter material for display application. The relatively high EL efficiency of Gaq_3 was attributed to the higher charge transport capability. Although considerable progress has been made in OLED materials with different molecular structures,[7] there remains a lack of systematic study relating the solid-state structure to the fundamental EL properties of the organic materials. It is important to design EL materials with high fluorescence efficiency and good carrier transport capability. The molecular design strategy for high fluorescence efficiency is well-understood. Less clear, however, is the dependence of the carrier transport characteristics on the molecular structure. It is well-known that the physical and chemical properties of a molecular solid depend directly on the relative orientations and spacing of the constituent molecules. It is interesting to investigate the solid-state structures of OLED materials. Here, we report the preparation and X-ray structural analysis of Gaq_3. The intermolecular $\pi-\pi$ stacking and hydrogen-bonding interactions were revealed in the solid of Gaq_3.

Gaq_3 was synthesized by dissolving $GaCl_3$ and 8-hydroxyqunoline in a 1:3 mole ratio in water. Excess potassium acetate was added to the solution. The reaction mixture was heated under reflux for 5 h and a light yellow Gaq_3 precipitate was obtained. The product was purified by vacuum sublimation. Single crystals, suitable for X-ray diffraction analysis, were grown by vapor diffusion of diethyl ether into a solution of Gaq_3 in chloroform.

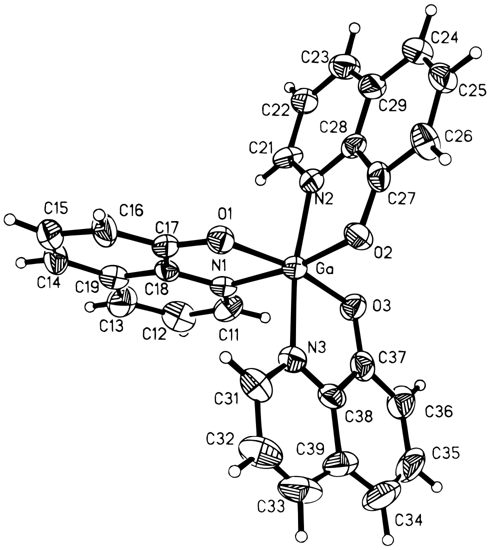
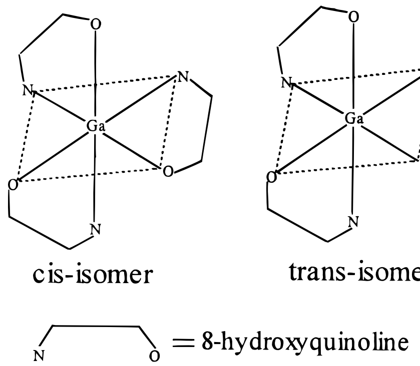


Figure 1. Labeled view of Gaq_3.

During the course of the crystal preparation it was found that almost all of the yellow needle solids grown from chloroform were amorphous. Few rectangle crystals can be selected from these amorphous solids. These rectangle crystals were suitable for X-ray crystallography.[8] The reflection intensities were rather low but there was no evidence of crystal decay during the data collection. The poor diffraction power can be attributed to the poor quality of crystals. The attempts to prepare better quality Gaq_3 crystals with other methods proved unsuccessful. Unsymmetrical bidentate ligands, 8-hydroxyquinoline, may give rise to geometrical isomer complexes. When 8-hydroxyqunoline reacts with Ga^{3+}, two geometric isomers of Gaq_3, cis and trans, could be obtained. So the product may be a mixture of cis and trans isomers. However, we could only observe the trans isomer in the crystal (Figure 1). The single-crystal X-ray experiments have been repeated three times for three



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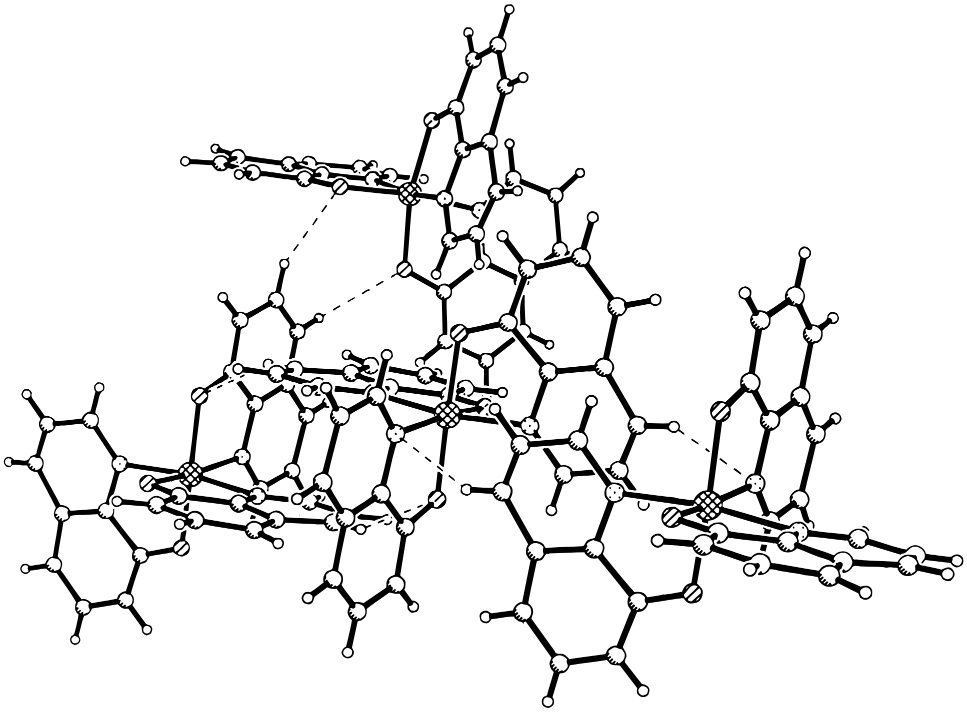

Figure 2. View of the intermolecular hydrogen-bonding interactions.

different pieces of Gaq_3 crystals and the results were identical. Because of the existence of two isomers in the chloroform solution during the assembly of the trans isomer in the solid state, it cannot be avoided that some cis isomers are doped into the trans isomer solids. This leads to defects in the lattice of *trans*-Gaq_3. The molecular structure of Gaq_3 is six-coordinated gallium compounds. The angles around gallium approximate octahedral. They range from 80.6(4)°(O(1)−Ga−N(1)) to 97.3(3)°(O(2)−Ga−O(3)). The average Ga−O and Ga−N bond distances are 1.947 and 2.099 Å, respectively.

Intermolecular $\pi-\pi$ stacking and hydrogen-bonding interactions are the most remarkable structural feature of the Gaq_3 solid. The Gaq_3 molecules are connected by the extensive array of $\pi-\pi$ stacking and hydrogen-bonding interactions. A combination of the intermolecular $\pi-\pi$ stacking and hydrogen-bonding interactions results in an extensive three dimensional framework structure. Three types of C−H···O hydrogen bonds between the 8-hydroxyquinoline oxygen and 8-hydroxyquinoline hydrogen were observed (Figure 2). These are the contacts between C_{14}−H, C_{23}−H hydrogens and the ligand-oxygen atom (O_1) of the adjacent molecules at 2.63 and 2.60 Å, respectively. They are clearly within the sum of the van der Waals radii for hydrogen (1.2 Å) and oxygen (1.5 Å).[9] The hydrogen-bonding distance of $C_{15}-H\cdots O_2$ (2.7505 Å) is so great that it is close to the sum of the van der Waals radii. It is a weak C−H···O hydrogen-bonding interaction.

The crystal structural analysis of Gaq_3 revealed that the $\pi-\pi$ stacking interactions take place in a multiple direction fashion. This is quite different from the planar molecular $\pi-\pi$ stacking feature, which usually takes place in a unique direction. Stacking ligand dimers and stacking ligand trimers are observed in the solid. The stacking ligand trimers are along the *a*-axis in a face-to-face manner but with displacement in a direction parallel to the ligand long axis. Adjacent ligands are offset so that a carbon atom bonded to a nitrogen atom is approximately centered over an aromatic ring in the ligand above or below (Figure 3). There is a $C-H\cdots\pi$ interaction between neighboring ligands. The distances of atoms in one ligand from the mean plane of the adjacent ligand vary between 3.35 and 3.41 Å, which may be compared with 3.35 Å between the layers of graphite[10] and 3.4 Å between stacked nucleotide residues in DNA.[11] Intermolecular $\pi-\pi$ stacking interactions are increasingly found to be common in organic and coordinative networks involving aromatic ring systems and have been deliberately used to control the structures and properties in molecular solid materials. It is well-known that all molecular conductors or semiconductors have a common solid structure feature (i.e., intermolecular $\pi-\pi$ stacking interactions).[12−14] High mobility has been associated with $\pi-\pi$ stacking interactions. The $\pi-\pi$ stacking interactions are also observed in the Gaq_3 solid. We believe that the $\pi-\pi$ stacking interactions in the Gaq_3 solid are the chemi-

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(8) Crystal data of Gaq_3: yellow rectangle crystals, 0.60 × 0.36 × 0.28 mm, monoclinic, $P_{2(1)/n}$, $a = 11.0233(13)$, $b = 13.2751(7)$, $c = 16.920(4)$, $\beta = 98.049(12)°$, $V = 2451.6(6)$ Å^3, $Z = 4$, and $3.92° < 2\theta < 60.00°$. $\lambda(\mathrm{Mo,K}_{\alpha 1}) = 0.71073$ Å. ω scans. $T = 293$ K, 8834 unique reflection of which 7161 had $F > 2\sigma(F)$. Diffraction data were corrected for LP factors and an empirical absorption correction applied by using Simens Texl Version 5.03. Min, max, transmission factors 0.3009−0.2498. The structure was solved by direct methods (Shelxtl-Version 5.03). All atoms were refined anisotropically using a full-matrix least squares program on (F2) to give $R_1 = 0.117$.

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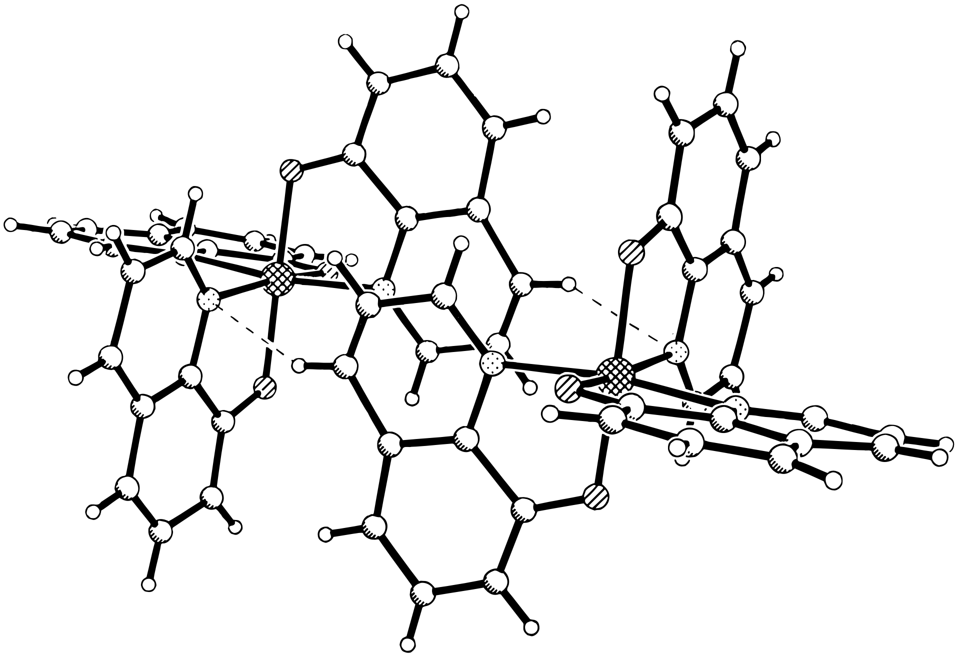

Figure 3. Molecular stacking motif for Gaq_3.

cally decisive factor of its good carrier transport ability. It is worthwhile to note that the interactions in the thin film may be different from the interactions in the crystalline, well-ordered solid state.

In summary, it is considered that the higher mobility for Gaq_3 is attributed to the closely packed face-to-face stacking interactions in the Gaq_3 solid. We expect that our experimental results can enlighten us in designing and synthesizing new OLED materials with high performance.

Acknowledgment. This research was supported by the National Natural Science Foundation of China (No. 597905006).

Supporting Information Available: Crystallographic data for **1** including observed and calculated structure factors, crystal data and structure refinement, atomic parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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