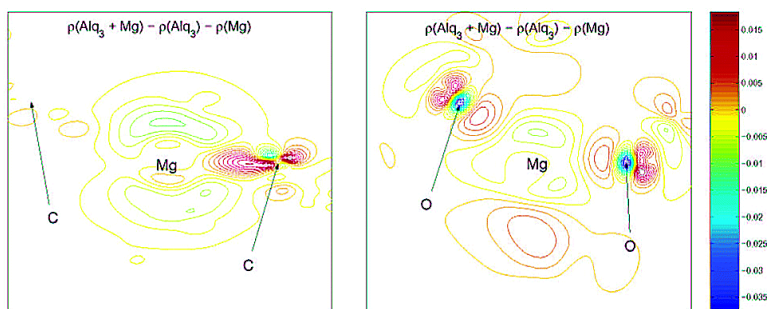


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Chemistry between Magnesium and Multiple Molecules in Tris(8-hydroxyquinoline) Aluminum Films

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Tris(8-hydroxyquinoline)aluminum (Alq₃) is widely used in modern organic light emitting diodes (OLEDs) because of its excellent stability and electroluminescent properties.¹ The efficiency of electroluminescent devices is highly dependent on the injection behavior of the metallic contacts.² Thus, many research efforts, both experimental^{3–6} and theoretical,^{7,8} have been devoted to understanding the interface chemistry between Alq₃ thin films and the metals that are deposited on it as cathodes. Spectroscopic data show that formation of metal–Alq₃ complexes takes place at the interface in the early stage of metal deposition. This is signaled in the UPS spectra by the appearance of new states in the gap above the HOMO level of the Alq₃ and in XPS spectra by metal core level shifts toward higher binding energy. Such spectroscopic evidence has been reported for Li and K,⁵ Ca,⁴ Mg, and Al.^{3,6} Overall, it indicates metal oxidation and subsequent donation of electronic charge to the Alq₃. A simple interpretation of this process is the formation of an ion-pair that stabilizes the metal–Alq₃ complex. This picture has been supported by self-consistent density functional theory (DFT) calculations for Li^{5,7} and K⁵ and, to some degree, also for Al and Ca.⁷ In these calculations, the Alq₃ thin film is modeled by a single Alq₃ molecule in a vacuum. Curioni and Andreoni,⁷ in particular, reported an accurate analysis of chemical interactions, which shows that the metal atoms interact mostly with the oxygen atoms of the Alq₃ leading to ion-pair formation in the case of Li ions; a less effective coupling takes place between the oxygen lone pair and the metal orbitals for Al and Ca. They predicted that Mg should exhibit behavior similar to Ca, although the ion-pair complex would be thermodynamically less stable in this case because Mg has a higher ionization potential (IP) than Ca.

The simple charge-transfer picture, involving only metal and oxygen atoms of the quinolate ligand, is, however, inconsistent with recent XPS data^{3,6} for Mg and Al on Alq₃. Indeed, while the chemical shift of the N(1s) core level is to lower binding energies (BE), as predicted by the ion-pair model, the O(1s) and Al(2p) levels shift to higher BE by 1.4 and 0.4 eV, respectively, contrary to the prediction of the ion-pair model. Moreover, the measured N(1s) core level shift is as large (~1.8 eV) as that recorded for K⁵, although the IP of K is almost one-half of that of Mg. Shen et al.^{3,6} propose that Mg (and Al) forms an organometallic complex with Alq₃ similar to its behavior with anthracene.⁹ To elucidate the situation, we report here a DFT investigation of the interaction between a single Mg atom and Alq₃ both in the gas and in a condensed crystalline phase. In the gas phase, we consider

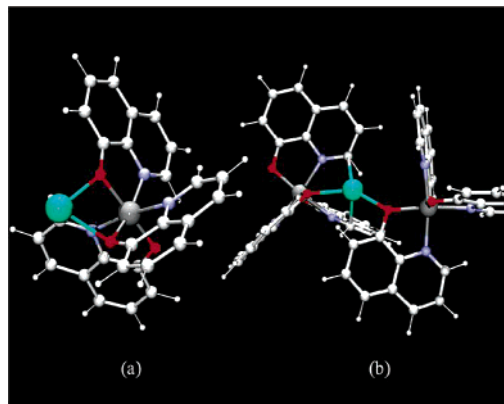


Figure 1. Mg–Alq₃ (meridional) complex: (a) gas phase, (b) solid (crystalline) phase. Atoms are represented by balls: Mg is green, C is gray, N is blue, Al is dark gray, and H is white.

separately the facial and meridional isomers of the Alq₃ molecule. In the condensed phase calculations, we use its known crystalline structure based on the meridional conformation.¹⁰ Although the disordered nature of the thin films is neglected in our calculations, the crystalline local environment should be a substantially better model for the local environment in a thin film than an isolated Alq₃ molecule in a vacuum.

Our approach is based on first-principles molecular dynamics¹¹ to simultaneously relax electronic and ionic degrees of freedom. We describe the electronic ground-state structure within the DFT using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof¹² (PBE) for the exchange and correlation energy. The interaction of the valence electrons with the nuclei and the core electrons is modeled by pseudopotentials (PPs).¹³ The valence electronic orbitals are expanded in plane-waves, and we use the Γ point only to sample the Brillouin zone. The details of our implementation have been described.¹⁴

First, we studied the structural properties of the two Alq₃ isomers in a vacuum. The results are in very good agreement with experiments¹⁰ and previous theoretical work.¹⁵ We have then studied the reaction of a single Mg atom with an Alq₃ molecule by performing several local optimization runs starting from different initial positions of the Mg atom. The results of these calculations confirmed predictions by Curioni and Andreoni:⁸ the metal atom is attracted by the oxygens of the ligands forming a weak charge-transfer complex (Figure 1a). The corresponding binding energies are 5 and 11 kcal/mol for the meridional and the facial isomer, respectively. To model a Mg atom in a thin film environment, we inserted a Mg atom in the monoclinic cell corresponding to the experimentally synthesized Alq₃ crystal:¹⁰ this contains four meridional Alq₃ molecules. The structure obtained for the isolated

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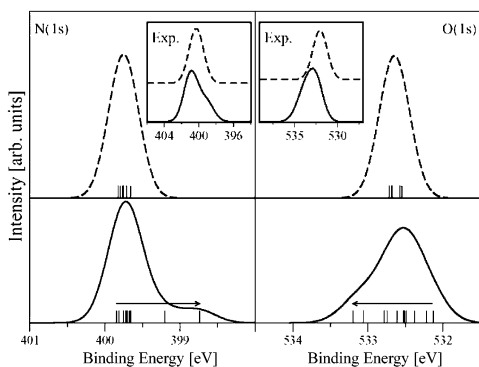


Figure 2. Calculated O(1s) and N(1s) core level shifts in pure Alq₃ (dashed line, upper diagram) and Mg–Alq₃ (continuous line, lower diagram). The calculated BEs (vertical bars) are convoluted with a Gaussian function to obtain the spectra. XPS data from ref 3 are reported in the inset (dashed line, spectra of a pure Alq₃ film; continuous line, spectra after deposition of 4 Å of Mg). In this figure, the absolute energy scale (which is arbitrary in our calculation) has been chosen to closely correspond to experiment.

meridional Alq₃–Mg complex is still a local minimum structure. However, in the present case, a few picoseconds of isothermal first-principles molecular dynamics evolution at 600 °C was sufficient to spontaneously find another, more stable, structure. The resulting structure, after local optimization, is shown in Figure 1b. Interestingly, this structure corresponds to an organometallic complex having characteristics similar to those proposed on the basis of experimental data^{3,6} to explain the observed core level shifts. The binding energy of the organometallic complex is 11.3 kcal/mol, more than twice the BE of the corresponding charge-transfer complex Mg–Alq₃ in the meridional configuration. The organometallic complex is stabilized by covalent interactions between the Mg atom and two C and two O atoms belonging to two adjacent Alq₃ molecules. The Mg–C (2.4–2.8 Å) and Mg–O (2.3 Å) bond lengths are in good agreement with typical bond lengths determined by X-ray diffraction in Mg complexes with organic compounds.⁹ Moreover, the calculated density of states values obtained from Kohn–Sham eigenvalues are also in good agreement with UPS data,⁶ showing the appearance of a new level in the gap at ~1.6 eV above the HOMO of the molecule.

We used a well-established methodology to compute core level shifts in the context of plane-wave pseudopotential DFT calculations.¹⁶ Only the relative core level shifts, that is, the BE differences with respect to a reference configuration, are accessible to these calculations. Experimentally, the absolute BE of all of the Alq₃ levels shifts rigidly upon metal deposition following interface formation.^{3,17} This effect is outside the reach of our calculation. The calculated chemical shifts for the N(1s) and O(1s) core levels in the fully relaxed structures of our model crystalline systems are reported in Figure 2.

Four Alq₃ molecules belong to the unit crystalline cell: two of them interact directly with Mg, while other molecules, more distant, are essentially unaffected by the formation of the Alq₃–Mg complex. Taking the unreacted molecules as reference, in analogy to what is done in experiments, we obtain an O(1s) curve symmetrically broadened in the reacted system. The core level shift due to the reaction is 1.1 eV, in good agreement with the measured³ 1.4 eV, toward higher BEs. The shape of the N(1s) is also similar

to experiment. The shoulder is shifted toward lower BEs by 1.1 eV, again in excellent agreement with the measured value of 1.2¹⁷–1.8³ eV. The corresponding peak intensities are, of course, different from experiment because of the different concentration of Mg atoms in our model system and in the real thin film. Had we considered the weak charge-transfer complex occurring when Mg interacts with an isolated Alq₃ molecule (either meridional or facial), the agreement between theory and experiment would have been poorer, with calculated BE shifts of 0.5 eV or smaller, albeit in the right direction. We conclude that the large core level shifts observed signal the formation of an organometallic complex substantially as proposed,^{3,6} but which involves Mg interacting with two adjacent molecules in the thin film; simple Mg reaction with an isolated Alq₃ molecule is not supported by our calculations. The large BE shifts and their signs can be explained as follows. The formation of covalent bonds between O and Mg results in a reduction of the electronic charge screening a O(1s) core hole (this is apparent in the O–Mg–O charge density difference plot). On the other hand, an increase of screening charge for a N(1s) core hole is a consequence of the rebonding that affects a C atom adjacent to N. This C atom, bonding to Mg, becomes four-coordinated with the attached H moving out of the plane of the pyridine ring. The π bond between C and N is therefore disrupted, yielding an excess of screening charge for a N(1s) core hole.

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