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Synthesis of Ln(III) Chloride Tetraphenylporphyrin Complexes

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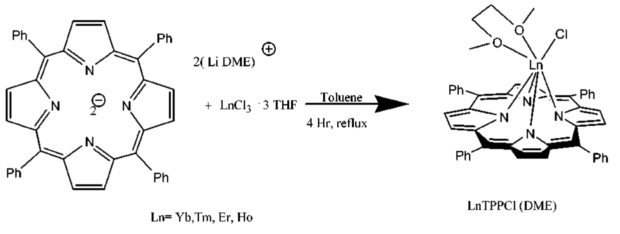
The isolation and identification of the first examples of anhydrous lanthanide chloride tetraphenylporphyrin complexes have been described. The purple complexes were generated by the reaction of dilithiotetraphenylporphyrin bis(dimethoxyethane) with lanthanide trichloride tris(tetrahydrofuran) salts to yield the products in up to 85% yield. The crystal structures for the holmium and ytterbium complexes are also presented.

Recently, we have been interested in the use of lanthanide tetraphenylporphyrin (LnTPP) complexes as the luminescent centers in near-infrared (NIR) polymer electroluminescent devices (PLED).[1] These devices possess an active layer that is a blend of a LnTPP complex and a poly-*p*-phenylene (PPP). Excited states on the PPP, generated by electron–hole recombination, are transferred to an acetylacetonoate (acac) tetraphenylporphyrin complex of ytterbium or erbium, which then emit at 980 or 1550 nm, respectively. Performance of the devices should be governed by the Förster energy transfer equation, which indicates that the efficiency of energy transfer is directly proportional to the spectral overlap of the donor molecule's (PPP) fluorescence and the molar absorbtivity of the acceptor molecule (LnTPP) at those wavelengths.[2] Prior to this work many groups reported on NIR emitting PLEDs that incorporated lanthanide trisdiketone phenathroline complexes. Although these complexes are easy to synthesize, they have relatively low molar absorbtivities at typical polymer emission wavelengths and therefore are expected to act as poor Förster energy acceptors when coupled with light-emitting polymers.[3] In contrast, LnTPP complexes absorb strongly at the desired energy but they have been more difficult to synthesize and lack the structural diversity of the diketones. Herein we report a simple, high-yielding, general synthesis for anhydrous LnTPP complexes.

Porphyrin complexes of the early transition metals have been studied extensively.[4] There are far fewer studies of porphyrin complexes of the lanthanide metals, with the majority of work focusing on the diamagnetic members.[5] The first reported synthesis of a LnTPP complex entailed distillation of acetylacetone from a Ln(acac)$_3$ in the presence of the TPPH$_2$ giving LnTPP(acac).[6] While the preparation reported a high crude yield as determined by UV–visible data, isolated yields are low (10–30%) due to the need for extensive column chromatography to isolate the product. More recently LnTPP complexes have been synthesized by amine elimination reactions between lanthanide trisamide complexes and TPPH$_2$.[7]

We have focused our efforts on the salt metathesis reaction of LnCl$_3$•3(THF) with dilithiotetraphenylporphyrin bis-dimethoxyethane (eq 1).[8] Reaction of the two components in refluxing toluene gives complete conversion to the lanthanide tetraphenylporphyrin chloride dimethoxyethane complex (LnTPPCl(DME)). Progress of the reaction is



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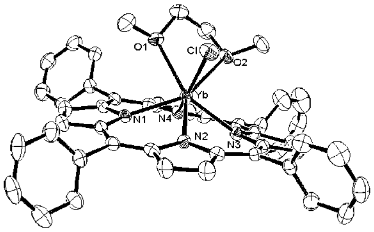

Figure 1. ORTEP drawing of YbClTPP·DME with thermal ellipsoids at 50% probability. Distances (Å): Yb−Cl 2.605, Yb−O1 2.438, Yb−O2 2.395, Yb−N1 2.334, Yb−N2 2.314, Yb−N3 2.310, Yb −N4 2.339.

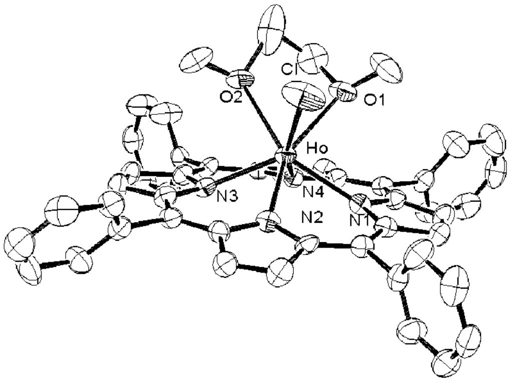

Figure 2. ORTEP drawing of HoClTPP·DME with thermal ellipsoids at 50% probability. Distances (Å): Ho−Cl 2.603, Ho−O1 2.473, Ho−O2 2.459, Ho−N1 2.335, Ho−N2 2.358, Ho−N3 2.359, Ho−N4 2.376.

conveniently monitored by following the appearance of the Soret band of the metalloporphyrin at 422 nm and by the increase of the Q-band absorbance at 551 nm.[9] The resulting mixture is cloudy with lithium chloride, which is separated from the solution by hot filtration. The solution is then reduced to $^{1}/_{3}$ its original volume and cooled to 0 °C, whereupon the LnTPPCl(DME) precipitates in approximately 75−85% yield. This synthetic approach has been applied to ytterbium, thulium, erbium, and holmium, though we expect that it will be applicable to the larger lanthanide metals (though it is possible that the larger size of the early Ln metals may result in the formation of dimers or complexes with higher coordination numbers). The formation of lithium chloride *ate* complexes, which has been observed for other lanthanide salt metathesis reactions, is presumably suppressed due to the low polarity of toluene.[10] Attempts to repeat this reaction in ethereal solvents produced less than satisfactory results (low yields with the material contaminated with lithium chloride). Once the complexes have been isolated, there is no change in their spectral properties on standing for several days under an inert atmosphere or when exposed to alcohols. Exposure to 1 M HCl in diethyl ether produces the 416 nm Soret band of the free tetraphenylporphyrin, suggesting that the complex has been demetalated. The stability of these complexes to ambient conditions is not known, but exposure to water should result in the displacement of the DME and the subsequent coordination of two or more water molecules to the metal center of the LnTPP.[7]

Thermal ellipsoid plots of the solid-state structures of the ytterbium and holmium complexes, in conjunction with selected atom labels and bond distances, are presented in Figures 1 and 2, respectively. The ytterbium ion sits 1.105(1) Å above the centroid of the least squares mean plane defined by the four pyrrole nitrogens and has an average Yb−N bond distance of 2.324(2) Å. The angle between the line perpendicular to the N4 mean plane passing through the N4 mean plane centroid and the line passing through the metal and the centroid is 0.8°, placing the ytterbium directly above the center of the porphyrin cavity. To accommodate the relatively large metal, the ring loses planarity and adopts a saddle shape. Defining mean planes using the pyrrole rings leads to dihedral angles of 21.36(16)° and 16.71(18)° for the N1−N4 and N2−N3 planes. In contrast, the N1−N2 and N3−N4 dihedral angles are 4.0(2)° and 6.5(2)°. The seven-coordinate Ho atom lies 1.154(3) Å above the centroid of the pyrrole nitrogen mean plane and has an average Ho−N distance of 2.357(1) Å, as is consistent with its slightly larger ionic radius. The angle between the line perpendicular to the N4 mean plane passing through the N4 mean plane centroid and the line going through the metal and the centroid is 0.7°, placing the holmium above the center of the ring. The porphyrin ring adopts a domed conformation with the mean planes defined by the pyrrole rings having dihedral angles of N1−N2 13.02(21)°, N2−N3 14.95(13)°, N3−N4 8.97(17)°, and N4−N1 15.09(16)°.

Dilithioporphyrins have been used as the starting material for various other metal porphyrin complexes.[11] Most notably dilithiooctaethylporphyrin reacts with 1 equiv of scandium trichloride to produce the scandium chloride octaethylporphyrin complex in a good yield.[12] The complex lacks any coordinating solvents such as that observed in our system. This is in all likelihood due to the much smaller size of scandium relative to lanthanide metals. In addition, the metal is much closer to the plane of the porphyrin ring, being only displaced from the centroid of the 4 N mean plane by 0.68 Å.[13] It can therefore be expected that the porphyrin ring also provides some amount of steric hindrance to the coordination environment around the metal center. More recently, a seven-coordinate ytterbium tetra(*p*-tolyl)porphyrin complex has been generated which has a metal to porphyrin centroid displacement of 1.090°.[7a]

The remaining chloride on the complexes can be easily replaced by a second salt metathesis reaction. Addition of potassium acetylacetonoate to the Yb complex in dimethoxyethane at room temperature leads to the YbTPP acac complex in 91% isolated yield, giving an overall yield of 72% based on $LnCl_3 \cdot 3(THF)$.[14] This yield is a substantial improvement

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(9) UV−visible spectra were taken under an inert, anhydrous atmosphere.

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on the current method used to synthesize the LnTPP acac compounds.[6] We are currently exploring this methodology for the synthesis of a variety of LnTPP(X) complexes, where the anionic ligand X is chosen to optimize the performance of NIR PLEDs.

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(14) Identity of the compound was established via ^{1}H NMR and was in agreement the published spectrum.[6]