Triarylboron-Functionalized Cu(II) Carboxylate Paddlewheel Complexes

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Ⓢ *Supporting Information*

ABSTRACT: The assembly of two copper(II)−carboxylate dimer complexes appended with four peripheral triarylborane functionalities has been achieved. Complex stabilities in the presence of fluoride are examined.

Recently, triarylboron functionalized metal complexes have contributed significantly to the development of organic light emitting diodes (OLEDs)[1] as emitters for electron transport materials,[2] and as colorimetric or fluorescent sensors for selective detection of anions such as fluoride and cyanide.[3] Appended to the periphery of ligand sets such as 2,2′-bipyridine,[4] 2-phenyl-pyridine,[5] or 2-(2-pyridyl)thiophene,[6] the triarylboron moiety often provides enhanced photoluminescence and electron transport properties relative to those of the parent boron-free compounds due to the introduction of the low-lying empty p_{π} orbital of the boron center. These ligand sets, however, are charge neutral and thus not ideal candidates for the functionalization of surfaces or nanoparticles. On the other hand, carboxylate-terminated ligands have been shown to be extremely effective in this regard.[7,8] In our pursuit of such conjugated boron-functionalized materials we have synthesized a versatile ligand motif, which in addition to surface modification (to be reported in due course), can act as a bridging ligand in the assembly of metal−carboxylate dimeric complexes. Some recent reports on this class of dinuclear species have investigated molecular magnetics,[9] catalysis,[10] and of course repeating nodes in metal−organic frameworks (MOFs).[11] Here, we report the synthesis of two new discrete triarylboron-containing copper-(II)−carboxylate dimer complexes as model compounds toward the development of their metal−carboxylate MOF counterparts. Synthesis of the ligand can be achieved in two steps from commercially available starting materials, followed by the self-assembly step of the metal-containing products, making this a versatile approach to luminescent paddlewheel-shaped complexes.

Ligand **2** was successfully synthesized by two sequential lithium−halogen exchange reactions. The reaction protocol proceeds by treating 4,4′-dibromobiphenyl with one equivalent of butyllithium at −78 °C in tetrahydrofuran (THF), followed by quenching of the aryl-lithiate with dimesitylboronfluoride to afford **1**.[12] Subsequent lithiation of **1** (Scheme 1) under the same conditions followed by bubbling of the reaction solution with CO_2 results in the formation of carboxylate **2**-Li, which, after acidification, is isolated as the carboxylic acid **2** in 72% yield. The reaction of its sodium salt (**2**-Na) with Cu-

Scheme 1. Synthetic Pathways to 2, 3, and 4
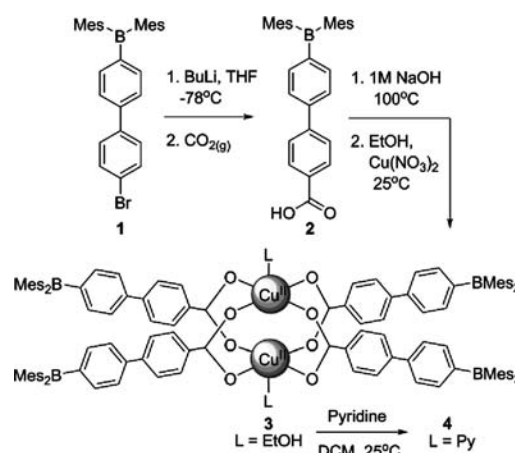
$(NO_3)_2 \cdot 2.5H_2O$ (2:1 ratio) in ethanol (EtOH) at room temperature resulted in the immediate precipitation of the copper(II) dimer **3** as a blue solid in 69% yield. Finally, copper complex **3** was converted to **4** by the addition of two equivalents of pyridine in CH_2Cl_2. The blue-green compound **4** was isolated by precipitation of the crude solid with EtOH at room temperature in 94% yield. All compounds synthesized are air-stable and fully characterized by NMR, elemental analysis, UV−vis, and fluorescence spectroscopy.

The structures of ligand **2** and Cu dimers **3** and **4** were determined using single crystal X-ray diffraction analysis. The crystal morphology of all three compounds resembled very thin needles and diffracted only weakly (see Supporting Information (SI)), which led to the poor quality of refinements and structural data. Nonetheless, the key structural features of these compounds were established unequivocally. Ligand **2** crystallizes in the monoclinic space group $P2_1/c$. As one would expect for carboxylic acids, ligand **2** forms a head-to-head hydrogen-bonded pair with an average H-bond distance of ~2.62 Å (O···O), as shown in Figure 1.

Complex **3** also belongs to the monoclinic $P2_1/c$ space group. The structure of **3** possesses a crystallographically imposed inversion center of symmetry (Figure 2). The Cu···Cu separation distance, 2.61 Å, is similar to those of previously known Cu(II) carboxylate dimers.[9a,13] The Cu(II) centers adopt a square-pyramidal geometry with an average Cu−O (carboxylate) bond length of 1.95 Å, while the axial Cu−O
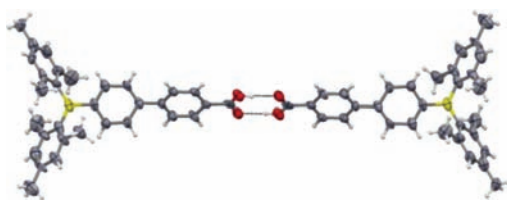
Figure 1. The crystal structure of **2**, illustrating the head-to-head hydrogen-bonding geometry with 35% thermal ellipsoids. Boron, yellow; oxygen, red.
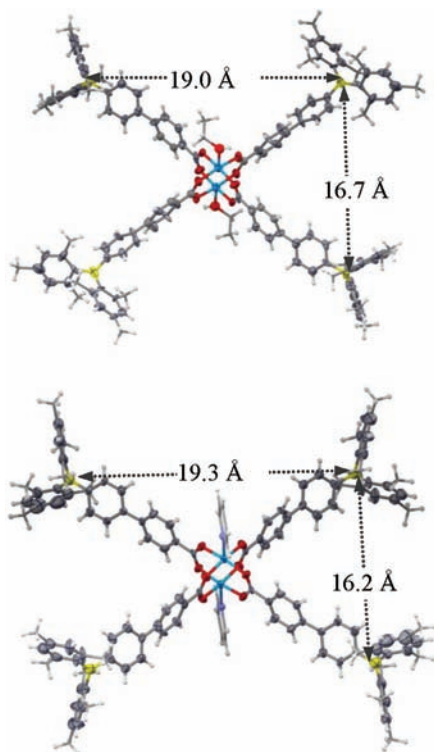

Figure 2. Crystal structures of **3** (top) and **4** (bottom) with 35% thermal ellipsoids. The carbon atoms in the disordered ethanol/pyridine ligands and all methyl groups are shown as stick models for clarity. Boron, yellow; oxygen, red; nitrogen, blue; copper, sky blue.

(ethanol) bond distances are much longer (2.17 Å). The four boron centers have a rectangular arrangement with B···B separation distances of 16.7 Å and 19.0 Å, respectively, along the edge of the rectangle. The diagonal B···B separation distance is 25.3 Å. Copper complex **4** crystallized in the triclinic $P\bar{1}$ space group with a Cu···Cu distance of 2.65 Å. Again, the paddlewheel geometry is obtained with pyridine at the axial positions, resulting in a square-pyramidal geometry about each Cu center with an average Cu−O (carboxylate) bond length of 1.96 Å. In this case, the average axial Cu−N (pyridine) distance is measured to be 2.16 Å. The four boron centers, again, have a rectangular arrangement with B···B separation distances of 16.2 Å and 19.3 Å, respectively, along the edge of the rectangle. Here, the diagonal B···B separation distance is approximately 25.2 Å

In THF, the free ligand **2** shows two strong absorption peaks (Figure S1, λ_{max} = 328 and 292 nm) likely caused by π−p$_\pi$ and π−π* transitions, respectively. The absorption spectra of complexes **3** and **4** exhibit very little deviation from that of **2**, with the exception of a very weak d−d transition at approximately 675 nm, common for blue copper(II)-dimer

complexes.[14] This indicates that the higher energy transitions are dominantly ligand-based. Emission spectra of all three compounds are similar, exhibiting purple luminescence with broad emission profiles, characteristic of triarylboron-containing species,[2] with maxima between 400 and 410 nm. Metal complexes **3** and **4** show little or no shift in the emission spectra. Again, this indicates that emission is a ligand-based process with little contribution from the metal centers. However, quantum efficiencies of the metal complexes (**3**, Φ = 0.05; **4**, Φ = 0.06) are much lower compared to ligand **2** (Φ = 0.18), which is likely due to either an increase in vibrational modes for energy dissipation in the larger complexes relative to the smaller **2**, energy transfer to the lower energy d−d excited state, or a combination of both. Solid-state emission spectra for **2** and its methyl-ester (Figure S5) were also recorded, which are similar to the solution spectra. Complexes **3** and **4** were not observably emissive in the solid state. Cyclic voltammetry was also performed on complex **4** (which lacks protic solvent co-ligands) to examine the reduction potential of the boryl ligand. Two reduction peaks similar to the methyl ester of ligand **2** were observed for the complex, attributable to the reduction of the carbonyl and the boron center, respectively (Figure S22). In addition, the complex shows an irreversible oxidation peak at ∼0.24 V (relative to that of FeCp$_2$$^{+/0}$, similar to the electrochemical profile of anhydrous copper(II) acetate (see the SI).

The Lewis acidity of triarylboranes makes them susceptible to complexation by small anions,[3] and thus examining the stability of the Cu^{II} moiety in the presence of fluoride anions was of interest. Ligand **2** was not subjected to fluoride binding experiments (as a standard) due to interference from the carboxylate proton. Since the high energy transitions of complexes **3** and **4** seem to be ligand centered, we employed the methylester of **2** and titrated it with tetra-*n*-butylammonium fluoride (TBAF, monitored by both absorption and fluorescence spectroscopy, see the ESI) in order to better model the interaction of the fluoride anion with the boron center of the ligands. The UV−vis absorption profile of the titration experiment is comparable to that of trimesitylborane;[15] the transition at 333 nm quenches upon the addition of multiple equivalents of fluoride. The same is true when **3** and **4** are subjected to excess TBAF (Figure 3). Initially, we were concerned about the stability of **3** and **4** in the presence of fluoride. Inspection of the d−d transitions (675 nm) of the
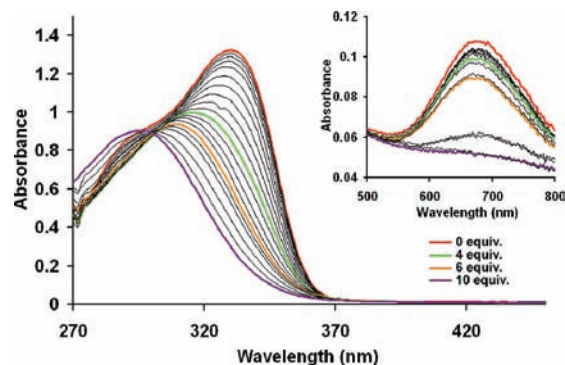

Figure 3. UV−vis absorption titration of copper dimer **3** (1×10^{-5} M) with TBAF (0−10 equiv) in THF at 298 K. (Inset: UV−vis absorption titration of copper dimer **3** (1×10^{-4} M) with TBAF (0−10 equiv) in THF at 298 K focusing on the d−d transition of copper dimer **3**). Titration experiments with **4** show similar trends.

Cu—Cu dimer upon titration with TBAF (Figure 3, inset), however, revealed that the complexes remained intact after four equivalents of fluoride were added (the stoichiometry of F^- required for saturation of the four boron sites) but were fully quenched above six equivalents of TBAF. Fluorescence experiments where copper complexes **3** and **4** were titrated with TBAF confirmed this observation, as the ligand-centered emission for both complexes exhibits almost complete quenching at approximately four equivalents of TBAF.

In summary, we have described the synthesis of a new triarylboron-appended carboxylic acid, which acts as a suitable ligand in the facile assembly of copper(II)—carboxylate dimer complexes. Spectroscopic characterization revealed that the luminescent properties of these complexes are predominantly ligand-centered. This observation was confirmed by fluoride binding experiments, where boron-centered emission was quenched at elevated concentrations of the fluoride anion. In addition, dissociation of the ligand from the complexes was not observed below four equivalents of fluoride anion, suggesting that all four boron sites become occupied by fluoride before dissociation occurs. These studies also suggest that the Lewis acidity of triarylboron ligand systems in the presence of carboxylate—metal dimers is such that the boron sites will associate small guests well before complex degradation occurs, making this class of metal—organic nodes an interesting candidate for guest binding in an extended network. As such, we have started to expand these metal—triarylborane systems into three dimensions by employing a C_3 symmetric tris-carboxylate analogue of **2** toward the self-assembly of new borane-containing MOFs, in addition to studying the use of **2** and other related molecules in surface functionalization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

All experimental details for **2—4** and **2**-OMe; absorption and emission titration data for **2**-OMe, **3**, and **4**; cyclic voltammetry for **4**; and single crystal X-ray diffraction data for **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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