Inorg. Chem. **2006**, *45*, 2367–2369

Inorganic Chemistry
Communication

Aluminum Tetraphenylporphyrin and Aluminum Phthalocyanine Neutral Radicals

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Received October 17, 2005

Treatment of tetraphenylporphyrinato(aluminum) chloride, Al(TPP)Cl, with Na/Hg in THF yields the stable radical Al(TPP)(THF)$_2$. Similarly, treatment of aluminum phthalocyanine chloride, Al(Pc)Cl, with Na/Hg in THF yields the stable radical Al(Pc)(THF)$_2$. Solution-phase magnetic susceptibility measurements show that both are monomeric radicals in solution, and ESR spectroscopy and density functional theory (DFT) calculations indicate that in both molecules the unpaired electron is delocalized throughout the ring system. While DFT calculations indicate that both molecules should undergo a Jahn–Teller distortion, only the porphyrin complex exhibits the predicted C–C bond length alternation in its X-ray crystal structure. That distortion of the ring system has precedent only in the similar reduced porphyrin complex Si(TPP)(THF)$_2$.

As part of our investigations of isostructural dopants for molecular semiconductors, we have synthesized a variety of reduced, neutrally charged molecules.[1−3] Porphyrin and phthalocyanine complexes are convenient systems for the implementation of isostructural doping because the oxidation state of the porphyrin or phthalocyanine ring system can be changed while maintaining charge neutrality of the molecule as a whole by changing the identity of the metal center in the complex. For example, we recently reported the synthesis of the unusual reduced porphyrin complex tetraphenylporphyrinato(silicon)bis(tetrahydrofuran) [Si(TPP)(THF)$_2$] in which the porphyrin ring system has the oxidation state 4−.[3] To generate a neutral, oxidized complex where the oxidation state of the ring system is 1−, one would use lithium as the complexed metal: the porphyrin radical Li(TPP) has been reported,[4] and the phthalocyanine radical Li(Pc) has been thoroughly investigated as a molecular conductor.[5−10] A neutral, reduced porphyrin or phthalocyanine with a ring oxidation state of 3− should be accessible as an aluminum complex. We recently reported the first isolation of such an aluminum phthalocyanine, the aluminum octa(pentoxy)phthalocyanine radical,[11] but we were unable to obtain crystals suitable for single-crystal X-ray diffraction. The aluminum tetraphenylporphyrin radical, Al(TPP), has been generated by photolysis of Al(TPP)(Et) and trapped by 2,4,6-tri-*tert*-butylnitrosobenzene in solution,[12] but the porphyrin radical has never been isolated. Herein we report the synthesis and characterization of the radicals Al(TPP)(THF)$_2$, Al(Pc)(THF)$_2$, and Al(Pc)(anisole)$_2$. The X-ray crystal structures of Al(TPP)(THF)$_2$ and Al(Pc)(anisole)$_2$ are, to the best of our knowledge, the first crystallographic characterization of a porphyrin or phthalocyanine complex with a ring system in the 3− oxidation state.

The precursor Al(TPP)Cl[13] has low solubility in THF, but treatment with 1.2 equiv of Na/Hg in THF at 22 °C results in its slow dissolution with reaction to form a dark-green solution. After 12 h, the mixture was filtered and heptane added to the filtrate to precipitate green, highly air-sensitive Al(TPP)(THF)$_2$ in 79% yield. Single crystals of Al(TPP)(THF)$_2$·2THF suitable for X-ray diffraction were grown by performing the reduction in an unstirred solution.

The structure of Al(TPP)(THF)$_2$ is shown in Figure 1. In contrast to Si(TPP)(THF)$_2$, which is highly ruffled because of the small covalent radius of Si,[3] the porphine core of Al-

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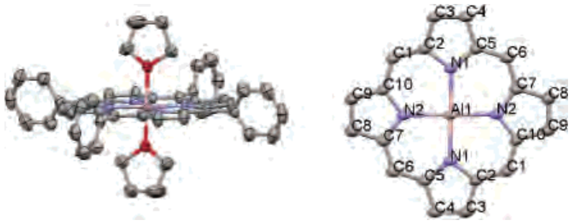

Figure 1. X-ray crystal structure of Al(TPP)$(THF)_2$ (left) and a numbered diagram of the porphine core (right).

Table 1. Carbon−Carbon Bond Lengths in Al(TPP)$(THF)_2$

bond	distance (Å)	bond	distance (Å)
C10−C1	1.406(3)	C5−C6	1.379(3)
C1−C2	1.375(3)	C6−C7	1.403(3)
C2−C3	1.431(3)	C7−C8	1.410(3)
C3−C4	1.340(4)	C8−C9	1.367(3)
C4−C5	1.440(3)	C9−C10	1.407(4)

(TPP)$(THF)_2$ is essentially planar. The Al−N bond distances of 1.991(2) and 1.994(2) Å are at the lower limit of M−N distances that occur in planar porphyrins; at shorter M−N distances, a porphyrin complex is forced to adopt a ruffled structure.[14] As in Si(TPP)$(THF)_2$, Al(TPP)$(THF)_2$ exhibits bond-length alternation around the 20-carbon periphery of the porphine ring system (see Table 1). The average difference in bond length between the longer and shorter bonds for $C_\beta-C_\beta$ is 0.028 Å, for $C_\alpha-C_\beta$ 0.027 Å, and for $C_{meso}-C_\alpha$ 0.029 Å (C1 is an example of a C_{meso}, C2 is a C_α, and C3 is a C_β). Those values represent approximately half of the bond-length alternation of the equivalent bonds in Si(TPP)$(THF)_2$, which are 0.053, 0.055, and 0.070 Å, respectively.[3] The porphine core of the precursor Al(TPP)Cl presumably has the D_{4h} symmetry characteristic of normal-valent porphyrin complexes (complexes in which the oxidation state of the porphyrin ring system is 2−). When it is reduced by one electron to Al(TPP)$(THF)_2$, the electron is added to one of the degenerate e_g lowest unoccupied molecular orbitals,[15] leading to a Jahn−Teller distortion. The observed distortion is exactly what would be expected based on the topology of the e_g molecular orbitals.[16] The single electron in the (former) e_g molecular orbital of Al(TPP)$(THF)_2$ leads to approximately half of the driving force for distortion as the two electrons in the (former) e_g molecular orbital of Si(TPP)$(THF)_2$, and hence approximately half of the distortion. The type of distortion observed in Al(TPP)$(THF)_2$ and Si(TPP)$(THF)_2$ is without precedent in crystallographically characterized porphyrin complexes.

The geometry of a model compound, tetramethylporphyrinato(aluminum)$(OMe_2)_2$ [Al(TMP)$(OMe_2)_2$], was optimized in a DFT calculation (*Gaussian 03*,[17] UB3LYP/6-31G*). The optimized structure is moderately ruffled, with C_{meso} displacements from the N_4 plane of 0.54 Å, in contrast to the planar porphine core of Al(TPP)$(THF)_2$ in the crystal structure. In addition, the calculated peripheral C−C bond lengths are systematically longer than those in the crystal structure, by 0.013 Å on average. However, the calculation very accurately predicts the peripheral C−C bond-length alternation, with differences between the longer and shorter bonds as follows: $C_\beta-C_\beta$ 0.026 Å, $C_\alpha-C_\beta$ 0.028 Å, and $C_{meso}-C_\alpha$ 0.035 Å.

The calculated electronic structure of Al(TMP)$(OMe)_2$ shows that the unpaired electron spin density is delocalized throughout the ring system, and we expect the same to be true of Al(TPP)$(THF)_2$. The ESR spectrum of a dilute solution of Al(TPP)$(THF)_2$ in benzene shows one broad, strong absorption at $g = 2.0188$ with a peak-to-peak width of 3.0 G. Individual hyperfine couplings to the many nuclei could not be resolved. Evans method measurements[1,18] of the magnetic susceptibility of Al(TPP)$(THF)_2$ in pyridine-d_5 indicate a magnetic moment of 1.82−1.86 μ_B. The reason for the deviation from the single-electron spin-only value of 1.73 μ_B is unknown, but the measured value clearly indicates that Al(TPP)$(py)_2$ is a monomeric radical in solution.

Cyclic voltammetry of Al(TPP)$(THF)_2$ in THF shows one reversible wave, the 0/1+ couple, at −1.39 V vs ferrocene$^{0/+}$. That potential can be compared to that of the 0/1− couple of Al(TPP)Cl, which corresponds to the same set of 2−/3− oxidation states of the porphyrin ring. In CH_2Cl_2, a solvent with a dielectric constant similar to that of THF, the 0/1− couple of Al(TPP)Cl is at −1.56 V vs ferrocene (converted from a saturated calomel reference electrode[19]).[20] Al(TPP)$(THF)_2$ has a significantly more positive redox potential because the entity at the center of the porphyrin is Al$(THF)_2^{3+}$, while in Al(TPP)Cl, the entity is $AlCl^{2+}$. The greater positive charge of Al$(THF)_2^{3+}$ leads to a more easily reduced porphyrin ring system. One goal in the creation of Al(TPP)$(THF)_2$ was to make a neutral porphyrin complex that is a good reducing agent, and its 0/1+ redox potential of −1.39 V indicates that it is a reasonably strong reducing agent, slightly stronger than cobaltocene.[19]

Al(TPP)$(THF)_2$ is very oxygen-sensitive, and for that reason we have been able to obtain UV−vis spectra of the unoxidized compound only at relatively high concentration, where we can observe two low-absorptivity peaks at 702 and 830 nm. Any spectra obtained at concentrations low enough to observe the higher absorptivity peaks resulted in oxidation of the sample.

Our previous success in isolating the aluminum octa(pentoxy)phthalocyanine radical[11] led us to attempt to synthesize the parent aluminum phthalocyanine radical, Al(Pc). We originally worked with the octa(pentoxy)phthalocyanine derivatives because of their improved solubility in organic solvents, but we have found that Al(Pc) has some solubility when axial donor ligands are bound to the aluminum (see below). There were indications from our previous study that Al(Pc) might be a particularly good solid-state electrical

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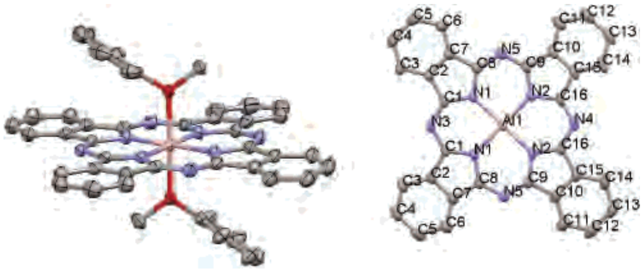

Figure 2. X-ray crystal structure of Al(Pc)(anisole)$_2$. Selected bond distances (Å): Al$-$N1, 1.9324(13); Al$-$N2, 1.9378(13); N1$-$C8, 1.384(2); C8$-$N5, 1.326(2); N5$-$C9, 1.328(2); C9$-$N2, 1.382(2); Al$-$O(anisole), 2.051(2); Al$-$O(anisole), 2.081(2).

conductor, so we synthesized Al(Pc) with labile anisole ligands and attempted, unsuccessfully, to isolate unligated Al(Pc).

Reduction of Al(Pc)Cl[21] with 1.1 equiv of Na/Hg in THF at 22 °C for 12 h results in a very dark-blue solution. Most of the THF was removed under vacuum, toluene was added, and the solution was filtered. Heptane was added to the filtrate to precipitate blue-purple, air-sensitive Al(Pc)(THF)$_2$ in 75% yield. A similar reduction performed in anisole (with the filtration performed directly on the anisole reaction mixture) yields Al(Pc)(anisole)$_2$. Crystals suitable for X-ray diffraction were grown by performing the reduction in an unstirred anisole solution.

Figure 2 shows the solid-state structure of Al(Pc)(anisole)$_2$. A comparison with the only other high-quality crystal structure of an aluminum phthalocyanine, [NBu$_4$][Al(Pc)(NO$_2$)$_2$],[22] shows that the Al$-$N bonds of Al(Pc)(anisole)$_2$ are slightly shorter [average 1.935(1) vs 1.957 Å] while the inner C$-$N bonds are slightly longer [1.384(2) vs 1.370 Å]. The differences can be rationalized by the fact that in a normal-valent phthalocyanine such as [NBu$_4$][Al(Pc)(NO$_2$)$_2$] there are two covalent and two dative Al$-$N bonds, while Al(Pc)(anisole)$_2$ is best described as having three covalent and one dative Al$-$N bonds. Similarly, an examination of the resonance structures of Al(Pc) reveals that the formal bond order of the C$-$N bonds has decreased compared to normal-valent phthalocyanine complexes.

In the crystal structure of Al(Pc)(anisole)$_2$ there is no bond-length alternation of the type observed in the porphyrin crystal structure. However, the calculated (UB3LYP/6-31G*) structure of Al(Pc)(OMe$_2$)$_2$ does have bond-length alternation, with, for example, a difference of 0.037 Å between the longer and shorter N$_{meso}-$C bonds. It is possible that the calculated structure is incorrect, or it is also possible that there is bond-length alternation in the structure of Al(Pc)(anisole)$_2$ but it is dynamic in the crystals. The thermal ellipsoids of the crystal structure give no clear indication of such a dynamic in the solid state.

The ESR spectrum of Al(Pc)(anisole)$_2$ in benzene is similar to that of Al(TPP)(THF)$_2$, with one strong signal at $g = 2.0021$ and a peak-to-peak width of 8.2 G. An Evans method measurement of the magnetic susceptibility of Al(Pc)(THF)$_2$ in pyridine-d_5 yielded a magnetic moment of 1.69 μ_B, indicating that Al(Pc) exists as monomeric radicals in a pyridine solution.

Cyclic voltammetry of Al(Pc)(THF)$_2$ in THF (with a secondary internal standard of decamethylferrocene) shows that its 0/1+ redox potential is -0.85 V and that its 0/$-$ potential is -1.54 V, both vs ferrocene$^{0/+}$. While cyclic voltammetry of Al(Pc)Cl has been performed previously in dimethylacetamide,[23] we examined its behavior in THF for a better comparison with Al(Pc)(THF)$_2$. In THF, the 0/1$-$ potential of Al(Pc)Cl is -1.15 V and its 1$-$/2$-$ potential is -1.55 V (again vs ferrocene). The first reduction potential of -1.15 V is significantly negative of the -0.85 V of Al(Pc)(THF)$_2$ for the same reason given for the porphyrin complex and its chloride. The Al(Pc)Cl$^{2-/-}$ potential of -1.55 V is the same as that of Al(Pc)(THF)$_2{}^{-/0}$, which may imply that the chloride anion is dissociating from Al(Pc)Cl^{2-} or Al(Pc)Cl$^-$, which would give a species identical to the one in the electrochemistry of Al(Pc)(THF)$_2$. The cyclic voltammograms are available in the Supporting Information.

Al(Pc)(THF)$_2$, like the porphyrin complex, is very oxygen-sensitive. The UV$-$vis spectrum inevitably showed some oxidation, but it was possible to assign an absorption at 649 nm to the radical.

Neither Al(TPP) nor Al(Pc) exhibits any detectable ^{1}H NMR signal in solution. However, both react cleanly with oxidizing agents such as I$_2$ or benzoyl peroxide to give the iodide or benzoate, respectively, with those ligands bound to aluminum. The oxidized species have normal ^{1}H NMR spectra.

While both Al(TPP) and Al(Pc) are good reducing agents, neither is a strong enough reductant to spontaneously transfer an electron to its normal-valent analogue [for example, Zn(TPP) and Zn(Pc), respectively]. One strategy for the creation of more reducing isostructural molecules is to use a tetravalent central atom, as in the recently reported Si(TPP)[3] and the similar, and possibly unruffled, Ge(TPP). Work on both of those systems is underway.

Acknowledgment. We thank Brian Barnes and Lev Gelb for assistance with DFT calculations and the NSF (Grant CHE-0133068) and Research Corp. (Grant RI0697) for financial support.

Supporting Information Available: Synthetic details, NMR and visible spectra, cyclic voltammograms, calculated bond lengths, and crystallographic details, including CIF files. This material is available free of charge via the Internet at http://pub.acs.org.

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