Bis[(μ-chloro)copper(II)] Amethyrin: A Bimetallic Copper(II) Complex of an Expanded Porphyrin

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One of the primary objectives driving the preparation of expanded porphyrins is the synthesis of macrocycles that might allow the rich metalation chemistry of the porphyrins to be extended or refined. Part and parcel of this objective is a desire to prepare porphyrin-like, polypyrrolic systems that may act as ligands for the coordination of *two* metal centers within *one* macrocyclic core. Nonetheless, in spite of this desire, such binucleating systems remain rare at present,[1−4] with the number of structurally characterized systems being smaller still.[2,4]

The current shortage of well-characterized bimetallic expanded-porphyrin complexes presumably reflects a lack of suitable binucleating porphyrin-like ligands. In an effort to address this issue, we recently prepared a new class of hexapyrrolic expanded porphyrin (e.g., **1**) to which the trivial name "amethyrin" was

1

2

3

assigned.[2] Using this expanded porphyrin, we were able in initial work to prepare and characterize structurally an in-plane-coordinated bis[(μ-chloro)zinc(II)] complex.[2] Interestingly, this complex was found to have but four of the possible six macrocyclic pyrroles involved in metal coordination. This earlier study thus left open the obvious question as to whether ligands such as **1** could be made to function as true hexadentate
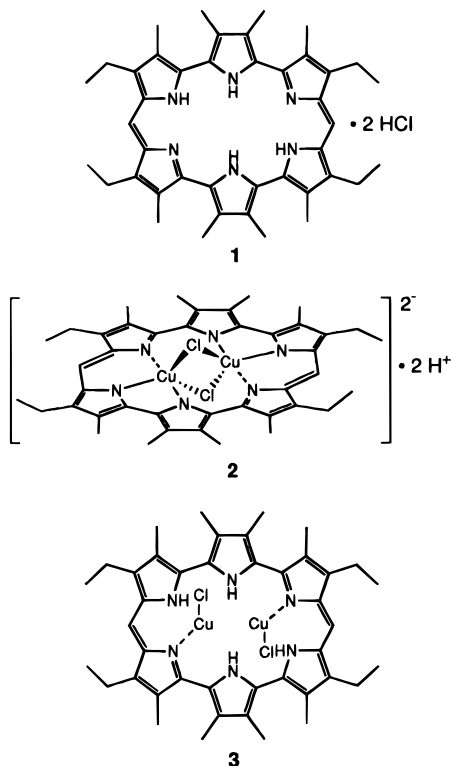
binucleating ligands. We have now found that they can: we have prepared and report here a bis[(μ-chloro)copper(II)] amethyrin adduct (**2**) in which *all six* of the nitrogen atoms originally present in **1** act as in-plane donor ligands for the metal centers. To the best of our knowledge, this is the first time an expanded porphyrin has been used to hold two metal centers together in close side-by-side proximity.

The bis[(μ-chloro)copper(II)] amethyrin complex **2** was prepared by treating the bis-HCl amethyrin salt **1** with CuCl to afford a somewhat air-sensitive complex, tentatively formulated as the bis[chlorocopper(I)] amethyrin species **3**. When a suspension of this latter material is stirred in methanol left open to the air, oxidation to the corresponding bis[(μ-chloro)copper-(II)] species (complex **2**) occurs over the course of a few hours in high yield.[5]

High resolution mass spectroscopic data provided initial support for the dinuclear nature of both **2** and **3**. Specifically, strong peaks corresponding to the proposed formulations were observed in the FAB spectra of these two materials. From ¹H NMR analyses, complex **3** was further assigned as being diamagnetic, as indicated by the well-resolved spectrum obtained for this complex. This assignment, coupled with the high degree of symmetry inferred from the simple, first-order nature of the ¹H NMR spectrum, provides critical support for the formulation of complex **3** as a bis[chlorocopper(I)] amethyrin complex. In contrast, complex **2** showed only very broad signals in its ¹H NMR spectrum. This is as expected for a complex such as **2**, which is presumed to contain paramagnetic metal centers.

Further confirmation that complex **2** is a bis-copper adduct was obtained from a single-crystal X-ray diffraction analysis. The resulting structure (Figure 1) revealed the presence of two copper atoms centrally bound within the core of a slightly bowl-shaped macrocycle and confirmed that complex **2** contains two bridging chloride anions. Interestingly, in the present bis-copper instance, all six of the pyrrolic nitrogen atoms are donating to the copper atoms. Thus, each metal center is ligated by three of the internal nitrogen atoms of the amethyrin ligand. This macrocyclic coordination in conjunction with the two bridging chloride anions gives rise to a pseudo-trigonal-bipyramidal coordination geometry about each of the copper atoms. It also results in a dramatic distortion of the macrocycle in **2** relative to what is seen in the X-ray structure of **1**.[2]

The interatomic Cu−Cu distance in complex **2** is 2.761(1) Å. This is an unusually short Cu−Cu distance. In fact, a Cambridge Crystallographic Database search revealed only two examples of structurally characterized Cu(II)−Cu(II) dimers that contain Cu−Cu bond lengths shorter than this.[6] This rather short distance is presumably the result of the core of the ligand forcing the close proximity of the copper atoms. The short metal−metal bond also results, presumably, in significantly more acute Cu−Cl−Cu bond angles than are typically observed for bis-[(μ-chloro)copper(II)] complexes.

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(4) Accordion porphyrins: Acholla, F. V.; Takusagawa, F.; Mertes, K. B. *J. Am. Chem. Soc.* **1985,** *107*, 6902.

(5) Characterization data for **2**: UV−vis (CH₂Cl₂) λ_max (nm) 505, 810, 884, 1024; HRMS (FAB+) *m/e* calcd for C₄₂H₄₆N₆Cu₂ (M⁺) 760.2354, found 760.2354.

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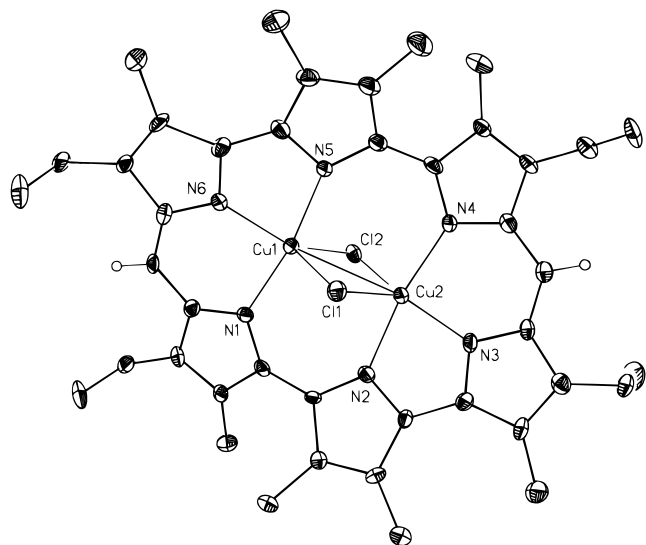
Figure 1. View of bis[(μ-chloro)copper(II)] amethyrin (**2**) approximately perpendicular to the hexaaza plane. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale; most are omitted for clarity. The Cu–Cu separation is 2.761(1) Å. The Cu–Cl bonds are asymmetric with Cu1–Cl bonds of 2.476(2) Å to Cl1 and 2.366(2) Å to Cl2, while the Cu2–Cl bonds are 2.458(2) Å to Cl1 and 2.387(2) Å to Cl2. The axial Cu–N bonds are slightly longer than the equatorial Cu–N bonds. The axial bond lengths average 2.012(3) Å, while the equatorial bond lengths average 1.920(4) Å.

Complex **2** exists in the solid state in a slightly bowl-shaped conformation. This conformation gives rise to slightly longer Cu–Cl bond lengths on one side of the complex relative to the other. Additionally, the four Cu–Cl bond lengths are all nonequivalent. Again, a Cambridge Crystallographic Database search revealed that this type of system with all four Cu–Cl bonds being nonequivalent is rather rare in Cu(II) dimer systems.[7]

Assignment of the copper oxidation states in complex **2** was made on the basis of electron paramagnetic resonance[8] (EPR) spectroscopy. A frozen 2:1 dichloromethane/toluene (v/v) solution spectrum of **2** taken at 77 K gives a classic EPR pattern[9,10] for a triplet state ($S = 1$), with both $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ (half-field) transitions being resolved. The spectrum indicates the presence of a Cu(II) dimer but does not distinguish between ferromagnetic exchange with an $S = 1$ ground state and antiferromagnetic exchange that is weak enough that the $S = 1$ excited state is appreciably populated at 77 K. The fine-structure splitting of the $g_\perp = 2.21$ doublet (see Figure 3 in the Supporting Information) gives the zero-field splitting of the triplet state, $D = 0.094$ cm^{-1} (940 G). Using the point-dipole approximation and the measured D, the Cu–Cu separation was calculated to be 2.81 Å (r (Å) = (0.433$g_\perp^2$/[D (cm^{-1})])$^{1/3}$), which matches closely the interatomic separation ($r = 2.764$ Å) determined by X-ray diffraction analyses.

The magnetic susceptibility[11] of complex **2** was measured in the temperature range 30–300 K. The complex shows a room-temperature magnetic moment per copper ($\mu_{eff} = 1.57\ \mu_B$)

slightly below that of an uncoupled Cu(II) ion. When the temperature is lowered to 30 K, the μ_{eff} per Cu(II) decreases to 1.33 μ_B, indicating antiferromagnetic exchange. The molar paramagnetic susceptibility data were fit to an expression based on the general isotropic exchange Hamiltonian, $\mathcal{H} = -2JS_1 \cdot S_2$, with J = magnetic exchange coupling constant and $S_1 = S_2 = \frac{1}{2}$:[12]

$$\chi_m = (N\beta^2 g^2 / kT)[2e^{2x}/(1 + 3e^{2x})] \tag{1}$$

Here, N, g, β, k, and T have their usual meanings and $x = J/kT$. Optimization of the data fit[13] gave $J = -5(2)$ cm^{-1} and $g = 2.29$ with a correlation coefficient of 0.9969 (see Figure 4 in the Supporting Information). The two Cu(II) ions in **2** are thus considered weakly antiferromagnetically coupled.

The lack of any other anions or cations in the crystal lattice of complex **2** is indicative of a neutral complex. However, if the fully deprotonated ligand accounts for a 4− charge, and the two copper(II) centers make up a total 4+ charge, then the additional total 2− charge of the two bridging chlorides is not accounted for. To explain this, we considered the two following scenarios. First, the macrocycle, during metalation, could have oxidized to a dianionic 22-π-electron ligand system. This possibility was ruled out, however, by subjecting **2** to strongly basic conditions such as, e.g., washing a dichloromethane solution of **2** with 1 N aqueous NaOH. Such treatments result in demetalation and regenerate in good yield the original free-base 24-π-electron ligand (as judged from ^{1}H NMR, UV–vis, and mass spectroscopy, as well as single-crystal X-ray diffraction analysis).

The second possible explanation for the apparent charge discrepancy is one in which the complex observed is *not* neutral, as the crystal structure might lead one to infer. Rather, the complex isolated is dianionic, with two presumed proton countercations being present on or near the macrocycle to neutralize the 2− charge. However, these presumed protons could not be found crystallographically. Nevertheless, the EPR data, in conjunction with the above-described observation that the macrocycle appears (as suggested by structure **2**) to remain in a 24-π-electron oxidation state, best support this latter hypothesis.

In conclusion, system **2** serves as a cogent illustration that an expanded porphyrin approach, if suitably elaborated, can serve as a means for generating binuclear metal complexes. In the present instance, such an elaboration leads to the generation of a Cu(II)–Cu(II) dimer in which the two copper centers are in remarkably close proximity. Such a finding, in turn, is relevant to the problem of preparing accurate models for the putative dinuclear copper centers in the Cu$_A$ site of cytochrome c oxidase and N$_2$O reductase,[14] wherein mixed-valence Cu dimers with remarkably short Cu···Cu distances are thought to exist.[15]

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and torsion angles for **2**, figures giving additional ORTEP views and a unit cell packing diagram for **2**, an X-band EPR spectrum of **2**, and a plot of χ_m^{corr} vs T for solid **2** (23 pages). Ordering information is given on any current masthead page.

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