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X-ray Structure and Variable Temperature NMR Spectra of [*meso*-Triarylcorrolato]copper(III)

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The diamagnetic square planar d^8 complexes [*meso*-arylcorrolato]copper(III) become paramagnetic upon warming, indicative of the equilibrium between the [corrolato]copper(III) and the $[\text{corrolato}]^{+\bullet}$ copper(II) forms of the complex. [*meso*-Triphenylcorrolato]copper(III) was structurally characterized and found to be saddled.

Corroles are tetrapyrrolic macrocycles containing three methine bridges and one direct pyrrole−pyrrole linkage.[1] The smaller trianionic corrolato ligand has a greater ability to stabilize higher central metal oxidation states than the larger dianionic porphyrinato ligand.[2−9] This, combined with the discovery of the catalytic activity of *meso*-triarylcorrolato complexes of metals in high oxidation states, generated considerable interest in metallocorrole chemistry.[2−10] Recently, however, doubts were raised with respect to the earlier assignments of the oxidation state of the corrolato iron complexes.[10] In general, the noninnocent role of the corrolato ligand is debated.[5,6,10,11] A number of complementary methods for the synthesis of *meso*-triarylcorroles are available.[8,9,12]

The oxidation state of the central metal in copper β-octaalkylcorrolato complexes was shown to be +III.[3] A recent report by Ghosh and co-workers supports this assignment for the copper complexes of *meso*-triarylcorroles.[8] In comparison, the stable oxidation state of the copper complexes of porphyrins is +II. Calculations predicted the conformation of [*meso*-tris(pentafluorophenyl)corrolato]copper(III) (**$\mathbf{T^F}$PCCu**) to be largely planar while the β-octabromo derivative was predicted to be saddled. These findings correlated well with trends delineated by resonance Raman spectroscopy.[8]

Our investigations of the synthesis of copper triarylcorrolato complexes parallel the literature findings.[13] We present here data on [*meso*-triarylcorrolato]copper(III) complexes which complement and refine Ghosh's findings: the structural characterization of the surprisingly nonplanar [*meso*-triphenylcorrolato]copper(III) (**TPCCu**) and a variable temperature ^{1}H NMR investigation of [*meso*-tritolylcorrolato]copper(III) (**TTCCu**).

meso-Triarylcorroles **TPCCu** and **TTCCu** were prepared from the free base corroles and copper(II) acetate in pyridine in the presence of air.[8] The complexes display at 25 °C in $CDCl_3$ a diamagnetic ^{1}H NMR spectrum (Figure 1). Thus, the complexes are diamagnetic as expected for a d^8 square planar low-spin Cu(III) complex.

Although the peaks are resolved and found in the general region expected for metallocorroles, the signals assigned to the β-protons are shifted and broadened as compared to the β-signals in the corresponding Ag(III) or Al(III) complexes.[9,14] This may be due to a small paramagnetic contribution to the overall spin state of the molecule.[15]

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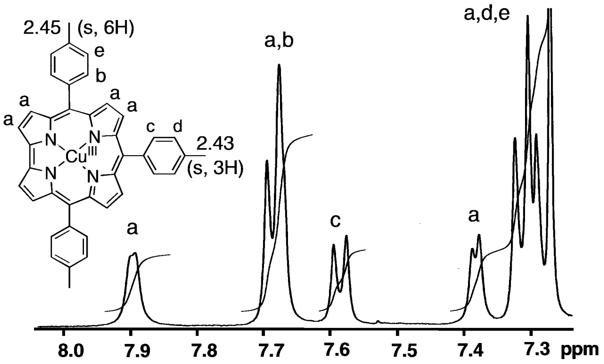


Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$, δ) of **TTCCu** at 25 °C.

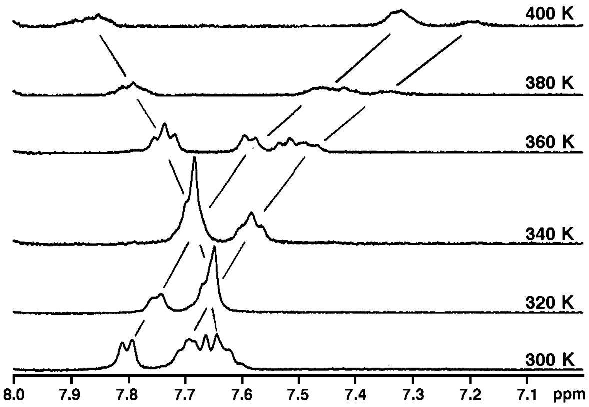
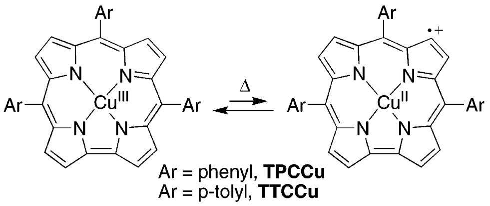


Figure 2. ^{1}H NMR (400 MHz, DMF-d_7, δ) of **TPCCu** at the temperatures indicated.

Scheme 1. Redox Equilibrium Observed for Cu(III) Corrolato Complexes



Using DFT calculations, Ghosh et al. calculated the ground-state copper complex of corroles to be a diamagnetic Cu(III) state, with Cu(II) ligand π-cation radical states higher in energy. A $^3A_2$ state of 0.161 eV (~15 kJ mol^{-1}) and a $^3B_1$ state of 0.354 eV (~34 kJ mol^{-1}) higher relative to the $^1A_1$ ground state were predicted.[5] The equilibrium between these two states (Scheme 1) is solvent- and temperature-dependent. The room temperature NMR spectrum of **TPCCu** in DMF-d_7 (Figure 2, bottom trace) is much less resolved as compared to its spectrum in $CDCl_3$ (Figure 1). Heating of the sample in the NMR magnet causes line shifts and line broadening. Thus, as expected for the narrow singlet−triplet state energy gap, heating shifts the equilibrium toward the paramagnetic species. The observed shifts are reversed upon cooling the sample back to 300 K.

NMR peak positions are particularly sensitive to the presence of paramagnetic species, but the observed shifts do not allow a direct measurement of the extent to which the singlet−triplet equilibrium is shifted. The Evans method for the determination of the magnetic moment of the paramagnetic species by NMR could not be applied, however, because the low solubility of the complexes in suitable high-boiling solvents provided only insignificant solvent signal shifts.[16]

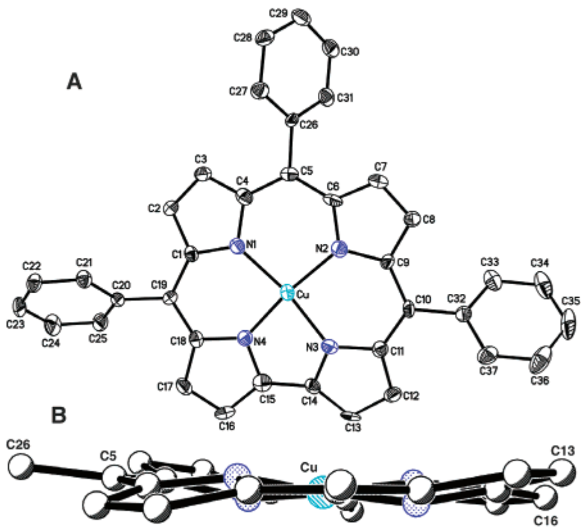


Figure 3. Molecular structure of [5,10,15-triphenylcorrolato]Cu(III) (**TPCCu**). A: top view, ORTEP representation with atom labeling, thermal ellipsoids at 50% probability (H atoms omitted for clarity). B: Side view along C20−C19 axis (H atoms and all atoms of the *meso*-phenyl groups except for *ipso* carbons removed for clarity). Select bond distances (Å): Cu−N(1) 1.891(4), Cu−N(2) 1.892(4), Cu−N(4) 1.893(4), Cu−N(3) 1.894(4). Select bond angles (deg): N(1)−Cu−N(2) 96.66(18), N(1)−Cu−N(4) 91.30(17), N(2)−Cu−N(4) 166.13(18), N(1)−Cu−N(3) 169.00(17), N(2)−Cu−N(3) 91.50(18), N(4)−Cu−N(3) 82.23(18).

TPCCu dissolved in pyridine-d_5 is paramagnetic, as judged by the inability of recording any NMR signals in the range −2 to 12 ppm. The UV−vis spectrum of **TPCCu** in pyridine does not indicate the presence of a π-radical cation ligand.[3] Thus we interpret the paramagnetism to be the result of axial ligation inducing a d^8 high-spin state. This effect of pyridine on the isoelectronic [porphyrinato]nickel(II) complexes is well-known.[17]

Interestingly, while our results parallel the finding for the copper complex of β-octaalkylcorrole,[3] the copper complexes of two *meso*-phenyl core-substituted corroles (with N_3O and N_2S_2 donor sets) were assigned +II oxidation states.[18] This further highlights the importance of the electrostatic component in the stabilization of high oxidation states.

Proof for the constitution of the Cu(III) complex **TPCCu** was provided by single-crystal X-ray crystallography.[19] No indication for the presence of a proton bound to the central nitrogens or an additional ion can be found, further supporting the +III oxidation state of the central metal (Figure 3A).

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(19) $C_{37}H_{23}N_4Cu$, fw 587.13 g mol^{-1}, $T = 150(2)$ K, $\lambda = 0.71073$ Å, triclinic system, $P\bar{1}$ with $a = 9.7915(7)$ Å, $b = 11.7732(8)$ Å, $c = 12.4638(9)$ Å, $\alpha = 111.986(1)°$, $\beta = 93.565(1)°$, $\gamma = 98.982(1)°$, $V = 1304.5(2)$ Å^3, $Z = 2$, $\mu = 0.874$ mm^{-1}. Refinement: full-matrix least-squares on F^2, data/restraints/parameters 4428/0/379, GOF = 1.058, $R = 0.0605$, and $R_w = 0.1188$ [$I > 2\sigma(I)$], largest diff. peak/hole 1.234 and −0.640 e Å^{-3}.

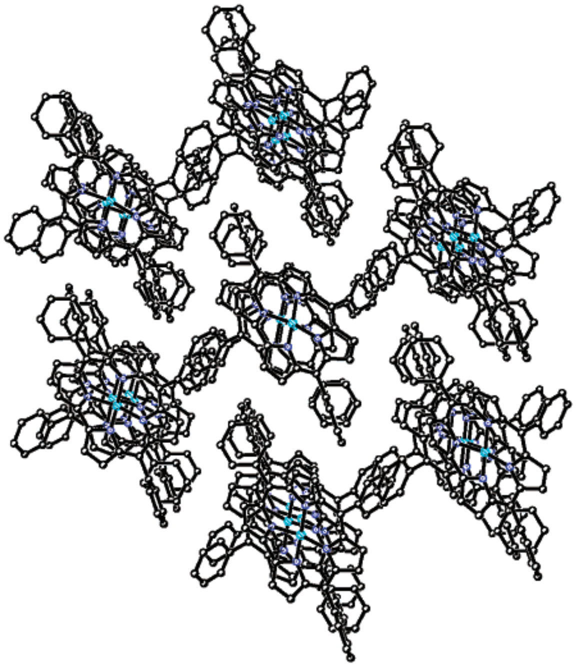

Figure 4. Crystal packing diagram of **TPCCu**, shown along the crystallographic *a* axis.

The corrolato macrocycle assumes a saddled conformation, i.e., the pyrrolic subunits are alternately tilted up and below the mean plane (rms of $C_{23}N_4$ plane: 0.183 Å) (Figure 3B).

The marked nonplanarity of **TPCCu** is unexpected. Ghosh's calculations predicted a planar macrocycle, and Vogel's octaethylcorrolato copper complex was also only slightly distorted from planarity. The nitrogens form a twisted square metal coordination sphere (rms of N_4 plane: 1.65 Å) around the central metal. All four Cu−N bond distances are near-identical, ranging from 1.891(4) to 1.894(4) Å, and lie within the range characteristic for Cu(III)−N bonds.[20] In comparison, the Cu−N bond lengths in [octaethylcorrolato]-copper(III) are shorter and range from 1.867(5) to 1.896(5) Å (median bond lengths 1.879(6) Å). The average Cu−N distance in [*meso*-tetraphenylporphyrinato]copper(II) is 1.981 Å.[21] The calculated bond lengths for **T^{F}PCCu** of 1.882 and 1.912 Å (average 1.897 Å) fairly accurately predicted the experimental value. Ghosh's calculations also predicted that an increased saddling of the macrocycle causes a bond-lengthening of the Cu−N bonds. Therefore, the longer bond lengths found for **TPCCu** as compared to the octaalkyl species can be attributed to its nonplanarity. Thus, the Cu−N bond lengths are a reflection of the metric parameters of the ligand rather than any measure of the oxidation state or ion size of the central metal. We recently reported the structure of the [*meso*-tritolylcorrolato]Ag(III) complex, which features a very similar but slightly more pronounced saddled conformation (rms of $C_{23}N_4$ plane: 0.186 Å) together with significantly longer metal−N bond distances (between 1.966(2) and 1.944(2) Å).[9]

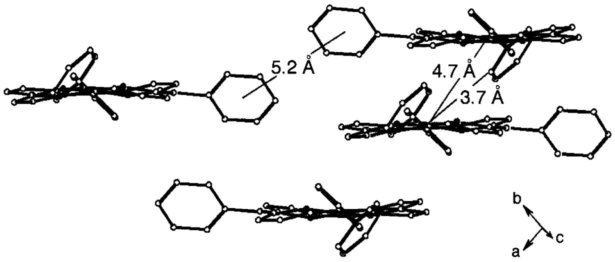

Figure 5. Detail of the crystal packing of **TPCCu**.

The corrolato complexes pack in the solvent-free crystal with an intricate network of $\pi-\pi$ and π-edge interactions. The median corrole−corrole distance is 4.7 Å and the closest π-edge to π interaction distance is 3.7 Å (*m*-C to phenyl-centroid) (Figures 4 and 5). The macrocycles stack in offset columns, resulting in a zigzag pattern of copper atoms (Cu−Cu distance 4.6 Å). Two consecutive macrocycles in a column form a racemic pair related by 180°, generating an *a*,*b*-type layering with adjacent columns separated by 5.2 Å (phenyl centroid−phenyl centroid), thus linking the columns into $\pi-\pi$-associated sheets.

In conclusion, *meso*-triarylcorroles are, at room temperature, diamagnetic d^8 [corrolato]Cu(III) complexes. Upon heating, these complexes are in equilibrium with the corresponding paramagnetic Cu(II) ligand π-cation radical species. Despite calculations predicting the conformation of the corrolato complexes to be largely planar, the conformation of **TPCCu** was shown to be saddled. These Cu(III) complexes underline once again the special ability of corroles to stabilize higher oxidation states as compared to the corresponding porphyrinato complexes, albeit the ligand appears to be "noninnocent".

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Supporting Information Available: X-ray crystallographic file (CIF) for **TPCCu**. This material is available free of charge via the Internet at http://pubs.acs.org.

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