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Electronic Structure

Revisiting the Electronic Ground State of Copper Corroles**

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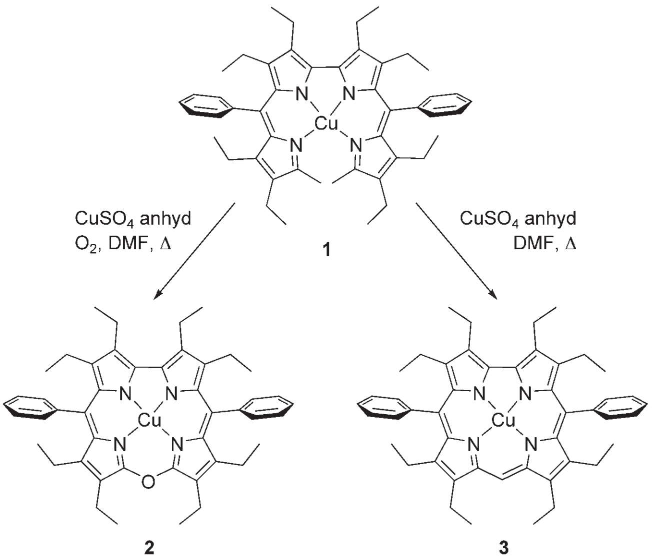
The oxidation state of the metal centers in corrole complexes is currently a topic of lively debate.[1–4] High-valent metal ions have been reported to be present in copper, iron, chromium, cobalt, and manganese corroles. Speculation that the corrole ligand in these complexes has a non-innocent character has stimulated renewed interest in this field. Metal porphyrins are usually employed as reference compounds for the discussion of metal corroles, despite the fact that the sizes of the N_4 cavities of corrole and porphyrin ligands—and, thus, the strength of the metal–ligand interactions—differ significantly. A better reference ligand would be an aromatic porphyrinoid with the contracted N_4 core of corrole and the double negative charge of porphyrin. We have now identified 10-oxacorrole as an ideally suited reference system. Herein, we present a comparative study of isostructural copper complexes with 10-oxacorrole and corrole ligands, in which the metal ions have different formal, yet identical physical oxidation states.[5]

Copper corroles are simple porphyrinoid metal complexes with a diamagnetic ground state. The central copper ion in these complexes has been assigned an oxidation state of +3,[1] on the basis of X-ray diffraction (XRD; short Cu–N distances), and UV/Vis (porphyrinoid spectral type) and ^{1}H NMR (low-field shift of the aromatic signals at low temperature) spectroscopy. These findings were subsequently confirmed by several authors for a number of related copper corroles.[2] DFT calculations, electrochemical studies, and Raman spectroscopy have provided additional support for the interpretation of copper corroles as typical low-spin copper(III) complexes with a low-lying triplet excited state.[3]

During our studies on the oxidative macrocyclization of open-chain tetrapyrrolic 2,2′-bidipyrrins, we observed that, upon treatment with anhydrous copper(II) sulfate, **1** is transformed selectively into product **2** or **3**, depending on the reaction conditions (Scheme 1). Heating **1**[6] with 10 equiv of copper(II) sulfate in dry oxygen-free dimethylformamide (DMF) gives **3** as the only nonpolymeric product, in 65% yield. However, if oxygen is passed through the reaction, under otherwise similar conditions, **2** is formed in 6% yield. Both new products crystallize isotypically as dark violet cubes, but can be easily distinguished by the green (**2**) or red (**3**) color of their solutions. The remarkable loss of two or one methyl groups that occurs during the formation of **2** or **3**, respectively, is not yet fully understood. However, similar reactions have been observed previously[7] and are well-established in syntheses of porphyrins from open-chain biladiene precursors.[8]



Scheme 1. Syntheses of the copper 10-oxacorrole **2** and the copper corrole **3** from the 2,2′-bidipyrrin complex **1**.

The porphyrinoid, macrocyclic nature of **2** and **3** is apparent in their optical spectra (see Supporting Information), which contain strong Soret absorption bands near 400 nm, as well as weaker bands between 500 and 650 nm. A comparison of these spectra with literature data[1,9] and with the results of a mass spectrometric study confirms that the products of the oxidative macrocyclizations are indeed the 10-oxacorrole and corrole complexes **2** and **3**. In addition, the electron paramagnetic resonance (EPR) spectrum of **2** is consistent with that expected for a porphyrinoid copper(II) system,[10] while **3** is EPR silent. The signal of the *meso* protons in the ^{1}H NMR spectrum of **3** is strongly temperature-

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dependent; this behavior is indicative of the presence of a thermally accessible excited triplet state, as is characteristic for copper corroles. Analysis of the temperature-dependent NMR spectra[1] indicates that the triplet state of **3** lies (24.1 ± 2.5) kJ mol^{-1} above the singlet ground state. This value is in good agreement with literature data for related compounds.[1–3] On the basis of these combined results, **3** can be regarded as a typical copper corrole.

Whereas the spectroscopic data for **2** and **3** are perfectly in line with the copper oxidation states assigned in the literature, Cu^{II} in 10-oxacorroles and Cu^{III} in corroles, the molecular structures determined by single-crystal XRD cast substantial doubt on this interpretation (Figures 1 and 2). Both compounds crystallize isostructurally in the space group $P2_1/c$ with $Z = 4$ and with nearly identical unit-cell parameters.[11] The metrics of the CuN$_4$ fragments in both compounds are also very similar, which is clearly inconsistent with the assignment of different oxidation states for the copper ions in **2** and **3**. The Cu–N distances are in fact slightly shorter, on average, for the putative Cu^{II} ion in **2** (1.884(2)–1.896(2) Å) than for the alleged Cu^{III} ion in **3** (1.883(5)–1.907(5) Å). Furthermore, the enhanced saddling distortion of the corrole backbone in **3**, measured as the angle between the mean planes of opposite C$_4$N rings (10.2(4) and 17.2(4)° for **3** versus 2.78(19) and 11.68(18)° for **2**), cannot be explained on the basis of the literature assignments. Rather, this structural characteristic of **3** points to additional attractive interactions between the copper ion and the π system of the ligand.

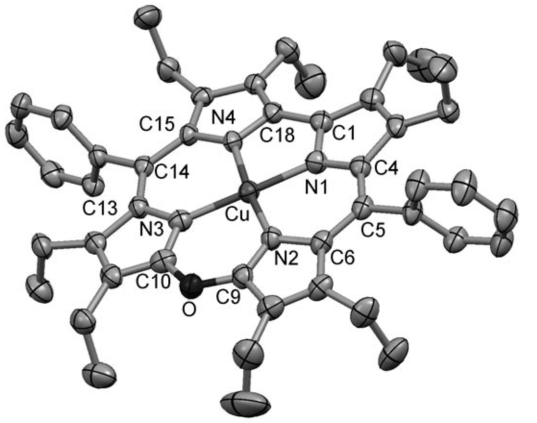

Figure 1. Molecular structure of **2**. Bond lengths [Å] and angles [°]: Cu–N1 1.884(2), Cu–N2 1.895(3), Cu–N3 1.896(2), Cu–N4 1.885(3), C1–C18 1.479(5), C4–C5 1.414(4), C5–C6 1.407(4), C9–O 1.356(4), O–C10 1.360(4), C13–C14 1.411(4), C14–C15 1.420(4); N1-Cu-N2 91.23(11), N1-Cu-N4 83.07(11), N2-Cu-N3 94.19(11), N3-Cu-N4 91.59(11), N1-Cu-N3 173.14(11), N2-Cu-N4 174.15(11), C4-C5-C6 125.5(3), C9-O-C10 125.2(3), C13-C14-C15 126.1(3), N1-C1-C18-N4 8.3(4). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

In fact, the saddled structure of **3** is not an exception, but rather a general feature of all copper corroles for which structures have been determined.[1,2] All interpretations and most calculations, however, have been based on the assumption that copper corroles are essentially planar species. In view of the crystallographic evidence that copper corroles are nonplanar, and in view of the fact that the Cu–N bond lengths do not necessarily reflect the oxidation state of the central copper ion, we studied the singlet and triplet states of **3** by quantum chemical means.[12]

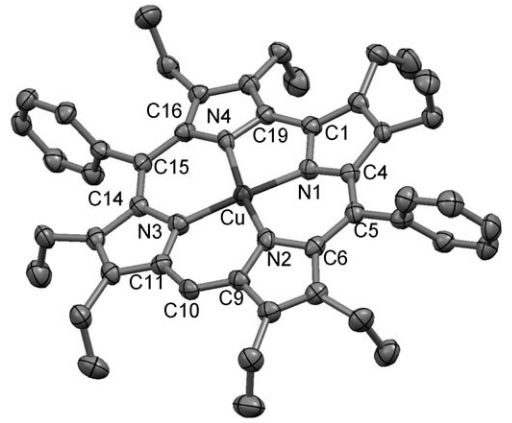

Figure 2. Molecular structure of **3**. Bond lengths [Å] and angles [°]: Cu–N1 1.904(5), Cu–N2 1.892(5), Cu–N3 1.907(5), Cu–N4 1.883(5), C1–C19 1.447(9), C4–C5 1.390(10), C5–C6 1.430(10), C9–C10 1.398(10), C10–C11 1.388(9), C14–C15 1.420(10), C15–C16 1.410(10); N1-Cu-N2 90.4(2), N1-Cu-N4 82.7(2), N2-Cu-N3 98.2(2), N3-Cu-N4 90.8(2), N1-Cu-N3 165.9(2), N2-Cu-N4 167.2(2), C4-C5-C6 123.3(6), C9-C10-C11 126.7(7), C14-C15-C16 124.8(6), N1-C1-C19-N4 18.7(8). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

DFT calculations on the realistic model **3′** (derived from **3** by replacing the ethyl by methyl substituents) were performed, and geometry optimizations for two singlet (closed-shell and broken-symmetry wave functions) and one triplet state were carried out. The results reveal a substantial preference for saddling distortions in the singlet states, the copper(III) corrole and the antiferromagnetically coupled copper(II) corrole (Table 1). A nearly planar minimum structure, however, is calculated for the triplet state, the ferromagnetically coupled copper(II) corrole. These results are illustrated as spin-density plots in Figure 3. The calculated geometries of the triplet state and the open-shell singlet system lead to symmetry correlations between the interacting ligand π and copper σ orbitals that are in agreement with Kahn's concept of orthogonal magnetic orbitals.[13] The description of a planar triplet state and a nonplanar singlet state is not new, but has been used before, in line with our arguments, to explain different electronic ground states of copper porphyrin radical cations.[14]

Table 1: Comparison of DFT and XRD results for **3**.

	Singlet Cu^{III}[a]	Singlet (BS) Cu^{II}[a]	Triplet Cu^{II}[a]	XRD
saddling [°][b]	29.2	25.4	1.0	13.7
Cu–N [Å][c]	1.919	1.932	1.931	1.898
ΔG^{298} [kJ mol^{-1}]	20	0	8	–

[a] Data from DFT calculations on **3′**. [b] The average angle between the mean planes of opposite C$_4$N rings. [c] The mean distance; see ref. [17].

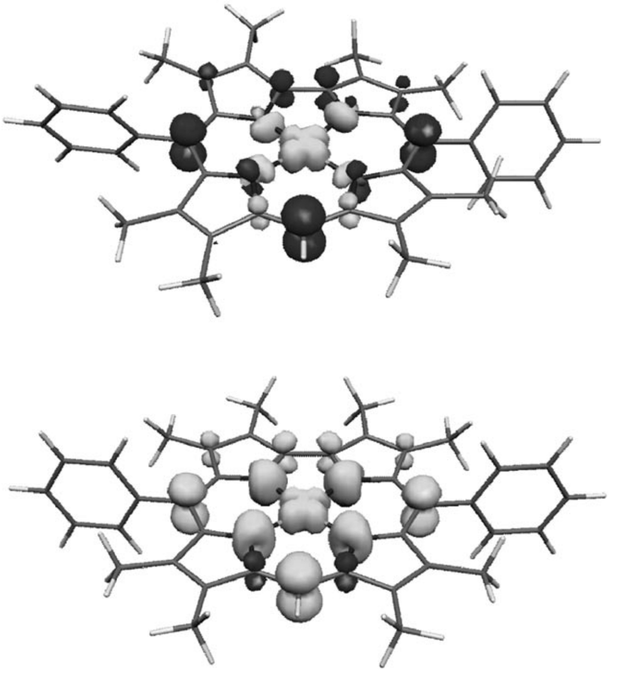

Figure 3. Spin-density plots for **3′** in the saddled broken-symmetry singlet state (top) and the planar triplet state (bottom), illustrating the antiferromagnetic or ferromagnetic exchange interactions, respectively, between the Cu^{II} ion and the ligand radicals (isopycnic surfaces drawn at 0.005 au using the program Molekel;[15] α-spin density in light gray, β-spin density in dark gray).

The saddling distortion of the corrole ligand in the singlet states allows attractive σ–π interactions between the copper $3d_{x^2-y^2}$ σ orbital and a corrole b_1-type π orbital,[16] as discussed earlier by Ghosh and co-workers.[3b] In the limiting cases, these interactions can be described as either an additional dative two-electron bond to a Lewis acidic Cu^{III} ion, or as a strong antiferromagnetic exchange coupling of an electron in a singly occupied π orbital with the unpaired d electron of a Cu^{II} ion. Our calculations suggest that a continuous transition between these two descriptions occurs, depending on the degree of molecular distortion.

In conclusion, a detailed comparison of the copper corrole **3** with the isostructural 10-oxacorrole complex **2** demonstrates that the interpretation of copper corroles as typical copper(III) species is not fully satisfying. In fact, the comparative DFT/XRD study of **3** suggests that the copper ion in these complexes is better described as Cu^{II}. More generally, we have demonstrated that 10-oxacorrole is a dramatically better reference system for corroles and provides a powerful new tool for the investigation of the electronic structures of porphyrinoid transition-metal complexes.

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[11] Crystal data for **2**: $C_{46}H_{50}CuN_4O$, $M_r = 738.44$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 20.086(2)$, $b = 7.9156(5)$, $c = 25.756(3)$ Å, $\beta = 111.222(14)°$, $V = 3817.3(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.285$ g cm^{-3}, $R_1 = 0.0483$, $wR_2 = 0.1152$ (for 7510 reflections with $I_o > 2\sigma(I_o)$). Crystal data for **3**: $C_{47}H_{51}CuN_4$, $M_r = 735.46$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 19.7401(15)$, $b = 7.9414(6)$, $c = 25.980(2)$ Å, $\beta = 111.021(9)°$, $V = 3801.7(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.285$ g cm^{-3}, $R_1 = 0.0776$, $wR_2 = 0.1815$ (for 7211 reflections with $I_o > 2\sigma(I_o)$). Data were collected at 193 K (STOE IPDS diffractometer with Mo$_{K\alpha}$ radiation, $\lambda =$

0.71073 Å). The structures were solved by the Patterson method (**2**) or by direct methods (**3**) and refined by full-matrix least-squares procedures (SHELX97). CCDC-619506 (**2**) and CCDC-619507 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] The commonly used C_{2v} notation for metallocorroles is used herein; see ref. [3a]. Since only planar metallocorroles can display b_1-symmetric π orbitals, we use the term "b_1-type" for the corresponding orbitals of nonplanar corroles.

[17] An overestimation of M−N bond lengths by 0.02–0.03 Å is typical for common functionals: W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed., Wiley-VCH, Weinheim, **2001**.