Copper Complexes

Three-Spin System with a Twist: A Bis(semiquinonato)copper Complex with a Nonplanar Configuration at the Copper(II) Center**

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Complexes with a significantly nonplanar environment around tetracoordinate copper(II) centers are comparatively rare and were often investigated in connection with copper enzyme modeling^[1] or with the highly distorted type 1 copper centers in blue copper proteins.^[2] These centers exhibit partial sulfur coordination and act as electron-transfer sites, shuttling between the Cu^{II} and Cu^I states. The Cu^{II,I} couple can also be active in the electron-transfer interaction with one^[3,4] or two^[5,6] non-innocent quinone ligands (Q). While a biochemically relevant valence tautomer equilibrium Cu^{II}(Q²⁻) ≈Cu^I (Q^{-}) has been observed within^[7] and outside^[4] oxidase enzymes, the focus with $Cu(Q)_2$ compounds has been on the study of spin-spin interaction in stable three-spin systems (Q⁻⁻)Cu^{II}(Q⁻⁻).^[5,6] Using sterically protected *o*-benzosemiquinonemonoimines, such as Q_x^{\bullet} , Chaudhuri et al. have described a planar such complex $[(Q_x^{\bullet})Cu^{II}(Q_x^{\bullet})]$ (1), with a $(\uparrow,\uparrow,\downarrow)$ ground state containing two antiferromagnetically coupled radical ligands.^[6]

Herein we describe how a minor modification, the introduction of a potentially coordinating methylthio sub-



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[**] Support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Grant Agency of the Czech Republic (Grant No. 203/03/0821), and the Ministry of Education of the Czech Republic (Grant COSTOCD15.10) is gratefully acknowledged. stituent in the *o*-position of the N-aryl group to form Q_y^- , can considerably change the structure and the properties of this three-spin system.

The new ligand system was synthesized in the reduced form $H_2Q_y^{[8]}$ Its reaction with CuCl produced an air-stable complex $[(Q_y)Cu(Q_y)]$ (2) which could be crystallographically characterized (Figure 1).^[9] A significantly twisted arrange-



Figure 1. Molecular structure of complex **2**. Selected bond lengths [Å] and angles [°]: Cu-O1 1.9173(15), Cu-O2 1.9290(16), Cu-N1 1.9372(19), Cu-N2 1.9368(18), O1-C1 1.296(3), O2-C22 1.292(3), N1-C6 1.355(3), N2-C27 1.352(3), C1-C2 1.430(3), C22-C23 1.430(3), C2-C3 1.380(3), C23-C24 1.373(3), C3-C4 1.433(3), C24-C25 1.433(3), C4-C5 1.371(3), C25-C26 1.368(3), C5-C6 1.419(3), C26-C27 1.421(3), C6-C1 1.453(3), C27-C22 1.455(3); O1-Cu-O2 149.81(8), O1-Cu-N2 97.00(7), O2-Cu-N1 98.30(7), N2-Cu-N1 171.95(8), O1-Cu-N1 84.51(7), O2-Cu-N2 84.40(7).

ment is found about the copper center which has a N1CuO1/ N2CuO2 dihedral angle of 32.20(9)° and is coordinated by two ligands through the N and O donors. However, there is also a weak additional interaction from S1 to the copper atom (Cu–S1 3.198(1) Å; Cu–S2 3.475(1) Å). Very long Cu^{II} – S(thioether) separations have also been reported for certain type 1 copper centers in proteins, especially azurin.^[2] The structural data show unambiguously that the ligands are in the semiquinone state,^[10] which implies the +II oxidation state for the copper center in its highly twisted coordination environment. The sum of bond angles at the copper is 685.8°, about halfway between the values for square planar (720°) and tetrahedral geometry (ca. 657°). Although the Cu–O and Cu-N bonds are comparable, the N1-Cu-N2 angle is closer to linearity at 171.85° than the O1-Cu-O2 angle (149.70°)possibly a result of steric repulsion between the aryl substituents.

Figure 2 shows the dependence of χT on T for the threespin compound $[(Q_y^{-})Cu^{II}(Q_y^{-})]$.^[11a] The room temperature χT value of 0.46 cm³ K mol⁻¹ is much lower than expected (1.125 cm³ K mol⁻¹) for three uncoupled S = 1/2 spins with $g \approx 2$, which indicates predominantly antiferromagnetic exchange interactions in the system. At lower temperatures, the χT value reaches a plateau at $\chi T = 0.365$ cm³ K mol⁻¹, in agreement with an S = 1/2 ground state. At the lowest temperatures the χT value decreases again. This system of three exchange-coupled spins can be described by the

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Figure 2. Magnetic susceptibility-temperature product for **2** as a function of temperature (**1**) at 1 T and fit (—) using the parameters g = 2.00, J = -414 cm⁻¹, and J' = -114 cm⁻¹.

isotropic exchange Hamiltonian [Eq. (1)] where spins S_1 and S_3 refer to the two Q_v ⁻ radicals and spin S_2 is the Cu^{II} center.

$$\mathscr{H} = -J\left(S_1 \cdot S_2 + S_2 \cdot S_3\right) - J'S_1 \cdot S_3 \tag{1}$$

The exchange coupling in such a system leads to three spin states, two with S = 1/2 and one with S = 3/2, the energies of which depend on the sign and magnitude of the two exchange interactions.^[6] The two S = 1/2 states differ in the relative orientation of the magnetic moments of spin S_1 and S_3 which can be described by $S^* = S_1 + S_3$. The spin functions are fully described by the total and intermediate spins as $|S_T S^*\rangle = |\frac{1}{2}0\rangle$, $|\frac{1}{2}1\rangle$, and $|\frac{3}{2}1\rangle$, or in symbolic fashion $(\downarrow,\uparrow,\downarrow) = -J + J'$, $E(\downarrow,\uparrow,\downarrow) = 0$, and $E(\uparrow,\uparrow,\uparrow) = -\frac{3}{2}J$, taking the $(\downarrow,\uparrow,\downarrow)$ state as the energy origin. The χT product as a function of temperature is then given by Equation (2).

$$\chi T = \frac{N_A \,\mu_B^2 \,g_{\frac{1}{2}1}^2 + g_{\frac{2}{2}0}^2 \exp[(J-J')/k \,T] + 10 \exp[3J/2 \,k \,T]}{1 + \exp[(J-J')/k \,T] + 2 \exp[3J/2 \,k \,T]} \tag{2}$$

The S = 1/2 ground state can have either $(\uparrow,\uparrow,\downarrow)$ or $(\downarrow,\uparrow,\downarrow)$ character, depending on whether the antiferromagnetic interaction between the two radicals or between the radical and metal are dominating. Electron paramagnetic resonance (EPR) results indicate that the lowest spin state has predominant radical character (see below), from which it can be concluded that this lowest spin state is best described as $(\downarrow,\uparrow,\downarrow)$. Thus the antiferromagnetic metal-radical interaction must be stronger than that between the two radicals (|J| > |J'|). Since EPR shows no evidence for excited spin states between 110 K and room temperature in the form of extra signals or shifting signals (in the case of fast spin-state interconversion), the excited S = 1/2 state must lie at high energy, meaning that |J| - |J'| is large.

Fitting a susceptibility curve using the Equation (2) is problematic since the parameters are interdependent and there is no unique solution.^[11b] However, the results suggest that the metal-radical interaction is strongly antiferromagnetic with a magnitude of J = -414 cm⁻¹, while the radicalradical interaction is also antiferromagnetic, but probably weaker. For more definitive conclusions to be drawn the excited S = 1/2 $(\uparrow, \uparrow, \downarrow)$ state needs to be determined exactly.

The EPR results for **2** differ significantly from those of **1** (with planar configuration at the metal):^[6] Instead of a signal for copper(II) with $g > 2^{[6]}$ we observe a partially resolved radical-type spectrum at g = 2.0012 in CH₂Cl₂ solution (Figure 3). In the frozen state at 110 K or 4 K the g compo-



Figure 3. EPR spectrum of complex 2 in dichloromethane at 210 K (top) with computer simulation (bottom): $a(^{63,65}Cu) = 0.22$ mT, $a(^{14}N) = 0.70$ mT, $a(^{1}H) = 0.36$ mT (1 H,H³).

nents were found at $g_1 = 2.050$, $g_2 = 1.9937$ ($A_2 = 2.0$ mT), and $g_3 = 1.957$, $g_{av} = 2.0006$. The *g* value and hyperfine data are fully compatible with a copper-coordinated 3,5-di-*tert*-butyl-*o*-semiquinoneimine radical anion,^[3a,4] the slightly lower *g* value signifies the presence of low-lying excited states with non-zero orbital angular momentum.^[12]

The EPR result in particular points to a $(\uparrow,\downarrow,\uparrow)$ ground state for $[(Q_y^{-})Cu^{II}(Q_y^{-})]$ with a dominant antiferromagnetic metal-ligand (and not ligand-ligand^[6]) interaction. Clearly the interligand spin-spin interaction between the two semiquinone ligands is diminished as a consequence of the nonplanar coordination arrangement.

In the absence of detailed structural and magnetic results, the appearance of a radical-type EPR signal could suggest an alternative oxidation state combination of $(Q_y \cdot)Cu^I(Q_y)$ for **2** which would also be in agreement with a nonplanar metal configuration. However, the susceptibility behavior and the bond lengths within the two very similar ligands clearly demonstrate the presence of $[(Q_y \cdot)Cu^{II}(Q_y \cdot)]$ with a $(\uparrow,\downarrow,\uparrow)$ ground state.

Like the planar analogue $\mathbf{1}^{[6]}$ with Q_x^{-} , the compound **2** described herein undergoes four reversible one-electron steps, two oxidations at +0.37 and -0.38 V, and two

reductions at -1.07 and -1.49 V (versus Fc^{+/0} (Fc = ferrocene) in CH₂Cl₂/0.1M Bu₄NPF₆). The results of spectroelectrochemistry investigations in the UV/Vis-NIR regions are summarized in Figure 4, Table 1, [Eq. (3)]: On oxidation to **2**⁺ the long-wavelength bands attributed to intraligand (IL) and ligand-to-metal charge transfer (LMCT) transitions are diminished and a strong band emerges at 515 nm, possibly associated with the formation of a quinone ligand in



Figure 4. Spectroelectrochemistry study of complex **2** in $CH_2Cl_2/0.1$ M Bu_4NPF_6 .

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$$[(Q_y)Cu^{II}(Q_y)]^{2^+} \xrightarrow{+e^-} [(Q_y)Cu^{II}(Q_y^{\bullet^-})]^+ \xrightarrow{+e^-} [(Q_y^{\bullet^-})Cu^{II}(Q_y^{\bullet^-})] \xrightarrow{+e^-} 2^{2^+} 2^+ 2^+ 2^+ (Q_y^{\bullet^-})Cu^{II}(Q_y^{2^-})]^- \xrightarrow{+e^-} [(Q_y^{\bullet^-})Cu^{II}(Q_y^{2^-})]^{2^-} or [(Q_y^{2^-})Cu^{II}(Q_y^{2^-})]^{2^-} 2^{2^-} 2^{2^-}$$

$$2^{-} 2^{2^-}$$

 $[(Q_y)Cu^{II}(Q_y)^-]^+$. The second oxidation to $[(Q_y)Cu^{II}(Q_y)]^{2+}$ leaves only the band arising from quinone, shifted to 528 nm. One-electron reduction could lead to either $[(Q_y)^-)Cu^{II}(Q_y)^-]^-$. Spectroelectrochemical reduction gives rise to a strong, broad $(\Delta v_{1/2} = 2600 \text{ cm}^{-1})$ band at 1940 nm (5150 cm⁻¹, Figure 4, Table 1) in addition to absorp-

Tuble 1. Absolption data of complexes.	Table 1:	Absorption	data of	f comple	exes. ^{[a}
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Compound	λ_{max} [nm] (10 ³ ε [m ⁻¹ cm ⁻¹])
2	316(15.7), 345(16.5), 446 sh(5.3), 790(5.4), 1062(3.0)
2+	259(16.5), 242(15.8), 515(11.9), 930(2.7)
2 ²⁺	238(14.2), 270(14.7), 300 sh(13.1), 424(10.5), 528(11.6)
2-	245 sh(13.2), 273(14.0), 358(14.1), 526(3.8), 695(3.6), 1940(4.5)
2 ^{2–}	247 sh(11.6), 270(12.3), 307(12.2), 364(12.4)

[a] In CH_2Cl_2 solution, charged species were electrochemically generated in $CH_2Cl_2/0.1$ M Bu_4NPF_6 .

tions at 526 and 695 nm. The intense band (oscillator strength $f=5.4 \times 10^{-2}$) in the near infrared is more compatible with the ligand-to-ligand intervalence charge-transfer transition^[13] for a $[(Q_y^{-})Cu^{II}(Q_y^{2-})]^-$ formulation, however, the structure of this species is not known. The second reduction to either $[(Q_y^{-})Cu^{I}(Q_y^{2-})]^{2-}$ or $[(Q_y^{2-})Cu^{II}(Q_y^{2-})]^{2-}$ does not produce intense absorptions above 450 nm. More detailed assignments of oxidation state combinations and electronic transitions will require high-quality excited-state TD-DFT calculations.

Summarizing, we have found an additional factor in determining the oxidation and spin state for the already complicated interaction^[3-6] between the copper(II,I) couple and quinonoid ligands, that is, the possible structural distortion caused by secondary coordination. While radical anion ligands^[12] already yield unusual complexes with transition metals in "normal" configurations,^[3b,6,14,15] the geometrical distortion can add, literally, another twist to this remarkable class of compounds, allowing for a striking switch of spin combinations. The behavior of the $Q_y^{0,-,2-}$ redox system as a ligand towards other transition metals is currently being investigated.

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- [8] Preparation of Q_y : A solution of 2-(methylthio)aniline (1.44 mL, 11.5 mmol) in *n*-heptane (4 mL) was added dropwise to a suspension of 3,5-di-*tert*-butylcatechol (2.56 g, 11.5 mmol) and triethylamine (0.15 mL) in *n*-heptane (10 mL). The solution was heated to reflux for 3 h, the solvent then evaporated to dryness, and the residue washed with cold *n*-heptane to yield a colorless solid. Yield 2.37 g (60%). ¹H NMR (250 MHz, 300 K, CDCl₃): $\delta = 6.35-7.48$ (m, 6H, arom), 2.45 (s, 3H, SCH₃), 1.44 (s, 9H, C(CH₃)₃), 1.26 ppm (s, 9H, C(CH₃)₃). Elemental analysis (%) calcd for C₂₁H₂₉NOS: C 73.42, H 8.51, N 4.08; found: C 73.49, H 8.42, N 4.07.
- [9] Synthesis of **2**: A solution of Q_y (736 mg 2.14 mmol), NEt₃ (0.5 mL), and CuCl (106 mg, 1.07 mmol) was heated to reflux in acetonitrile (25 mL) for 4 h in the presence of air. The dark precipitate was collected by filtration, then washed with cold acetonitrile. A dark green microcrystalline material was obtained. Yield 520 mg (65%). Elemental analysis (%) calcd for C₄₂H₅₄CuN₂O₂S₂: C 67.57, H 7.29 N 3.75; found: C 67.30, H 7.31, N 3.73. Single crystals were obtained from a dichloro-

methane solution of 2 layered with *n*-hexane. Crystal data: $C_{42}H_{54}CuN_2O_2S_2$ (746.53); monoclinic $P2_1/n$; a = 16.3439(2), b =14.5226(2), c = 16.9358(3) Å; $\beta = 90.140(1)^{\circ}$; V = 4019.8(1) Å³; Z = 4; $\rho_{\text{calcd}} = 1.234 \text{ g cm}^{-3}$; $\mu = 0.683 \text{ mm}^{-1}$; T = 100(2) K; number of unique reflections 9142, number of parameters 498; $R1 = 0.0475, wR2 = 0.1143 (I > 2\sigma(I)); R1 = 0.0570, wR2 =$ 0.1203 (all data); GOOF = 1.044. The structure was solved by direct methods and refined using the SHELXS-97/SHELXL-97 program package (G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997, G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997). The scattering factors for the neutral atoms were those incorporated in the programs. CCDC-251450 contains 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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- [11] a) The magnetic susceptibility measurements were performed on a powder sample of 2 using a Quantum Design MPMSXL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions to the molar magnetic susceptibility using Pascal's constants and for temperature-independent paramagnetism (TIP = $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$); b) The following constraints were used: The g values of the radicals and the Cu^{II} center were taken to be 2.00 (see EPR discussion). Furthermore, the difference between the two exchange interaction parameters was not allowed to decrease below 300 cm⁻¹ in order to keep the excited S = 1/2 state at high energies. From the fit (T > 50 K), the following parameters are obtained: $J = -414 \text{ cm}^{-1}$, and J' = -114 cm^{-1} ($\pm 6 \text{ cm}^{-1}$). If not constrained, the radical-radical exchange interaction tends to increase, leading to similar values for both exchange parameters, $J = -367 \text{ cm}^{-1}$, and J' = -357 cm^{-1} , without significantly improving the fit.
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