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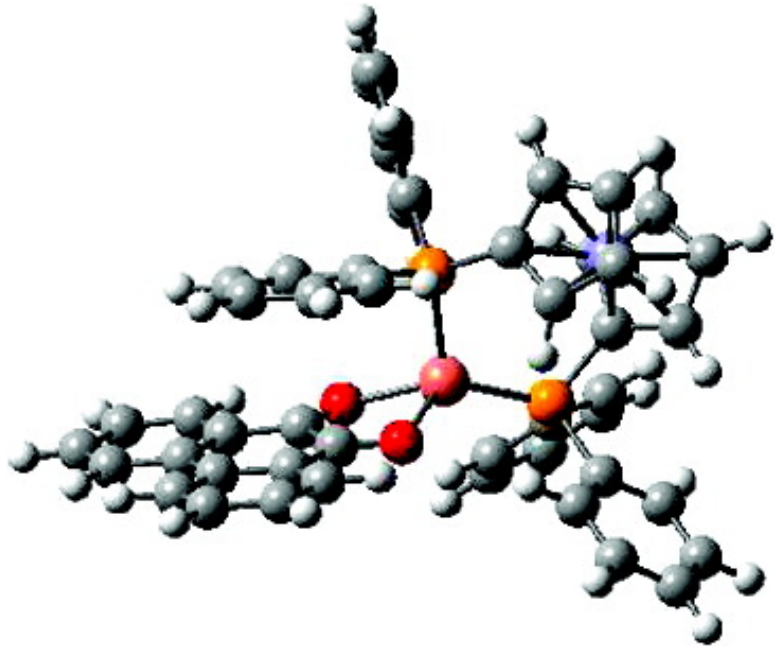

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Stabilizing the Elusive *ortho*-Quinone/Copper(I) Oxidation State Combination through π/π Interaction in an Isolated Complex

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The interaction between copper species and quinones is strongly determined by the typically comparable redox potentials of the Cu^0Cu^I or Cu^ICu^{II} and the Q^0Q^{-I} or $Q^{-I}Q^{-II}$ couples.[1] The copper/quinone interaction is relevant for research areas as diverse as biochemical systems (neurotransmitter and melanin metabolism,[2] tyrosinase,[3] polyphenol oxidase,[4] and quinoprotein oxidase function),[5] molecular devices (valence tautomerism),[1,6] biodegradation (catechol-enhanced Fenton reaction),[7] organic and industrial synthesis (copper catalysis of phenol and catechol involving reactions),[8] and photochemical charge transfer.[9]

Stable *o*-quinonemonoimine[10] and *o*-quinonediimine complexes[11] of copper(I) and copper(II) were reported, and the one-electron and two-electron reduced forms of O,O′-coordinating *o*-quinones, the semiquinones[6b,12,13] and catecholates,[6b,13b,14] have long been known to form chelate complexes with Cu^I [12] and Cu^{II}.[6b,13,14] In contrast, there has been no report yet of an isolated *o*-quinone copper(I) species with a quinone-O coordinated metal, possibly because of the lability of copper(I) vs oxygen donors and the low basicity of unreduced quinone ligands in general.[1,6a] Using an organometallic coligand for copper(I), viz, dppf = 1,1′-bis(diphenylphosphino)-ferrocene,[15] and a well established *o*-quinone in the form of PhenQ = 9,10-phenanthrenequinone, we present here the first structural, theoretical, and spectroscopic evidence for the O,O′-chelate coordination of electron-rich copper(I) by the unreduced quinone π acceptor.

The heterodinuclear $[(PhenQ)Cu(dppf)](BF_4)$ was obtained from PhenQ and $[(CH_3CN)_2Cu(dppf)](BF_4)$[16] and could be crystallized for X-ray diffraction by diffusion (CH_2Cl_2/hexane 2/1). Structural analysis confirmed the O,O′ chelate coordination of copper(I) in $[(PhenQ)Cu(dppf)]^+$ (Figure 1) and substantiated the unreduced quinone character of PhenQ via the C═O bond lengths of 1.257(11) and 1.244(10) Å (semiquinones have ≥1.27 Å) and the (O)C−C(O) single bond length of 1.499(13) Å (semiquinones have ≤1.46 Å, Table S1).

The DFT[17] calculated values are very similar at 1.227 and 1.517 Å, respectively; free PhenQ has ∼1.22 Å and 1.52 Å,[18] and weakly Cu^{II}-bonded monodentate PhenQ was reported with 1.252(18)/1.233(15) Å and 1.476(20) Å.[6c] Infrared vibrational spectroscopy in the solid phase confirms a largely unaffected C═O double bond situation with a band at 1674 cm^{-1} (free ligand: 1681 cm^{-1} in the neutral, 1561 cm^{-1} in the monoanionic state). The Cu−O bonds are remarkably different (Cu−O1 2.053(7) Å; Cu−O2 2.159(6) Å) as are the two Cu−P bonds at Cu−P1 2.208(3) Å and Cu−P2 2.254(3) Å; the stronger Cu−O1 and Cu−P1 bonds form a much larger angle at 132.3(2)° than the two longer such bonds at 99.55(19)°. Such strong distortions are not unknown in copper(I) chemistry.[19] This experimental and DFT confirmed distortion (DFT with M05-2x functional:[17] Cu−O1 2.065, Cu−O2 2.147, Cu−P1 2.237, Cu−P2 2.249 Å) found for $[(PhenQ)Cu(dppf)](BF_4)$ is absent when the phenyl groups at P are replaced by methyl in the calculation (Figure 2), suggesting as origin the obvious intramolecular π/π interaction[20] in $[(PhenQ)Cu(dppf)]^+$ (Figure 1) with short distances such as 3.155 Å for C1···C36 (calculated at 3.118 Å).

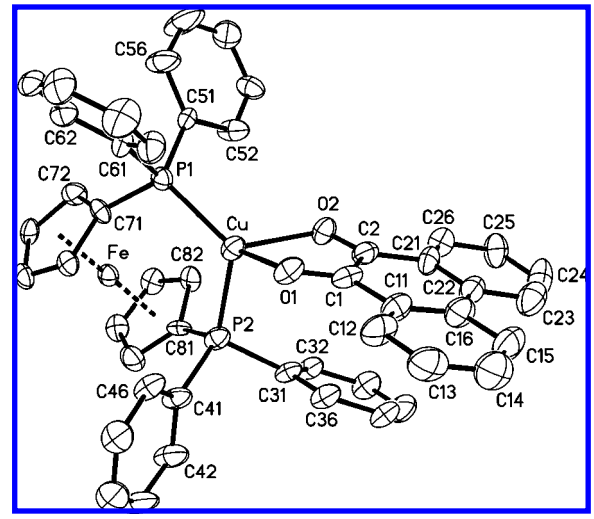

Figure 1. Molecular structure of the cation in the crystal of $[(PhenQ)Cu(dppf)](BF_4) \times CH_2Cl_2$.

Such copper-mediated intramolecular π/π and $\pi/\pi/\pi$ stacking motifs have been reported and discussed earlier in connection with radical stabilization and MLCT luminescence.[21] Emission or photoreactivity has not been observed for $[(PhenQ)Cu(dppf)](BF_4)$ in CH_2Cl_2 solution; the absorption spectrum with one long wavelength maximum at 693 nm ($\varepsilon = 3390\ M^{-1}\ cm^{-1}$) and another band at 420 nm ($\epsilon = 6540\ M^{-1}\ cm^{-1}$) is similar to that reported for a reaction mixture between PhenQ and $(Ph_3P)_2Cu(BH_4)$: λ_{max} 707 and 418 nm in CH_2Cl_2.[9] The MLCT transition d(Cu,Fe)→ π^*(PhenQ) (Figure S1), calculated by TD DFT at 741 nm, leads from the structurally established copper(I)/quinone ground state, Cu^I/Q^0, to an excited state, formulated as $Cu^{II}/Q^{\bullet-}$, i.e., to a valence-isomeric description reported earlier as ground state.[13] On a one-electron reduced level, a similar ambivalence has been reported as parts of a valence isomer equilibrium $Cu^{II}/Q^{2-} \rightleftharpoons Cu^I/Q^{\bullet-}$.[6] The 420 nm absorption comprises MLCT and LLCT transitions to π^*(PhenQ) according to TD DFT.

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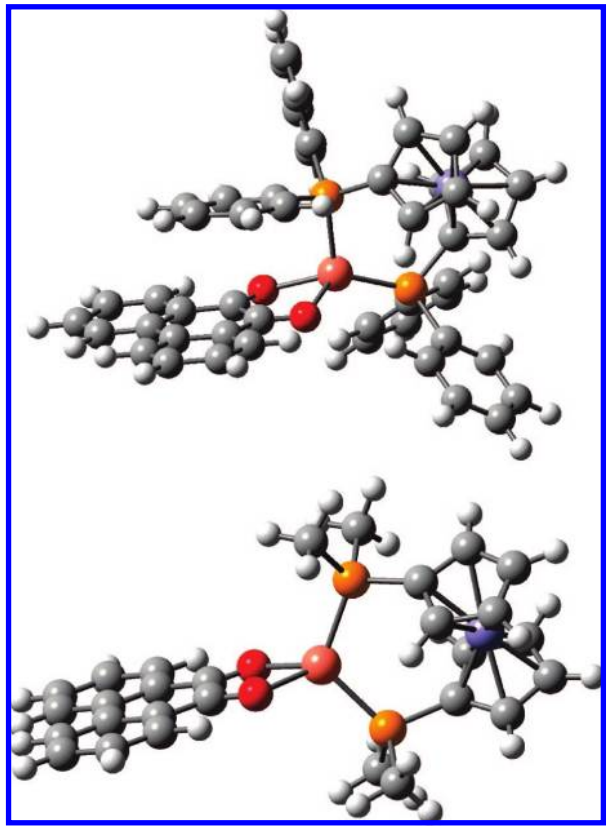

Figure 2. DFT optimized structures of $[(PhenQ)Cu(dppf)]^+$ (top) and the model with P-phenyl substituents replaced by P-methyl groups (bottom).

Intermolecular PhenQ/PhenQ π stacking is also observed in the crystal of $[(PhenQ)Cu(dppf)](BF_4) \times CH_2Cl_2$ with a distance of 3.335 Å between the planes.

In addition to the ferrocene-based oxidation at 0.28 V (295 K) or 0.15 V vs Fc (223 K; no Cu^I oxidation observed below 1.6 V), the complex $[(PhenQ)Cu(dppf)](BF_4)$ can be reversibly reduced at −0.78 V (223 K) in CH_2Cl_2/0.1 M Bu_4NPF_6 to an EPR active species $[(PhenSQ)Cu(dppf)]$ ($g_{iso} = 2.0055$ at 220 K). The hyperfine values for $^{63,65}Cu$ ($I = {}^3/_2$), ^{31}P ($I = {}^1/_2$), and ^1H ($I = {}^1/_2$) isotopes at 1.0 mT (1 Cu), 1.4 mT (2 P), and 0.15 mT (4H), respectively, agree with the phenanthrenesemiquinone data (0.165, 0.137, 0.042, 0.022 mT, 2H each)[22] and with typical values for copper(I) radical complexes.[12,23]

Using a special copper(I) complex fragment and a polycyclic *o*-quinone we have thus obtained the first isolated example of a copper(I)−quinone complex, distinguished by π/π interactions. Considering the broad relevance of copper/quinone interactions[2−9,24] and the role of π interactions within proteins,[25] it will be tempting to study its potential for electron transfer reactivity and to elucidate the role of π/π interactions in stabilizing such species.

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Supporting Information Available: Synthetic, DFT and cyrstallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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