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Reduction and Aerobic Oxidation of Hexaketocyclohexane (C_6O_6) by Reaction with Metallic Copper

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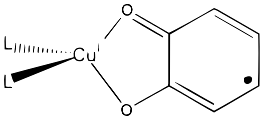
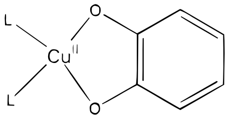
Introduction

Oxidative addition reactions between unsaturated organic molecules and nucleophilic transition metals are of fundamental importance to a wide variety of catalytic and biocatalytic processes. The *o*-benzoquinones constitute a class of organic substrates that may add to metals as either one or two electron acceptors in reactions that exhibit an interesting and important coligand dependence.[2] Complexes formed with copper illustrate these effects in a particularly clear way.[3] Compounds that contain soft-donor, π-acceptor coligands contain Cu^I coordinated by a radical semiquinone (SQ), $L_2Cu^I(SQ)$ (I), as the product of a one-electron transfer process. Hard-donor coligands increase metal-orbital energy with a shift in charge distribution to $L_2Cu^{II}(Cat)$ (II). The change in metal oxidation state results in a structural change for four-coordinate complexes, from tetrahedral for Cu^I to square planar for Cu^{II}, and changes in metal and quinone-ligand charge result in a shift in the center of paramagnetism, from the radical ligand to the metal. Complexes of both charge distributions may be conveniently prepared by treating metallic copper with an *o*-benzoquinone, and in many cases the products have been observed to react further with molecular oxygen to give dicarboxylic acids by oxidative ring cleavage (eq 1).[3,4] Observations on these reactions have been used to gain mechanistic insights into commercial and biological quinone oxidation processes.[5,6] In this report we describe preliminary results obtained from similar reactions carried out with triquinoyl octahydrate, $C_6O_6{\cdot}8H_2O$, as an extension of the copper−quinone coordination chemistry.



$L = PR_3$

(I)



L = py

(II)

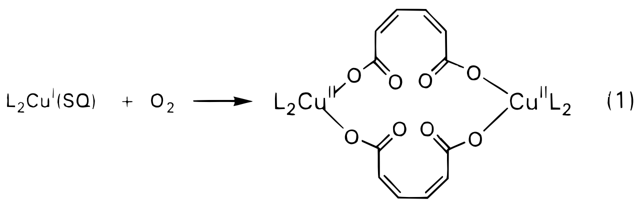


Table 1. Crystallographic Data for $[(tmeda)Cu(\mu\text{-}C_5O_5)Cu(tmeda)(\mu\text{-}C_2O_4)]_n{\cdot}H_2O$

formula	$C_{19}H_{34}N_4O_{10}Cu_2$
fw	605.6
space group	*C*2/*c*
a (Å)	17.036(3)
b (Å)	12.630(3)
c (Å)	12.897(3)
β (deg)	117.41(3)
V (Å^3)	2463.4(9)
Z	4
T (K)	158
λ(Mo Kα) (Å)	0.710 73
D_{calcd} (g cm^{-3})	1.633
μ (mm^{-1})	1.787
R, R_w	0.049, 0.092[a]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Experimental Section

Preparation of $[(tmeda)Cu(\mu\text{-}C_5O_5)Cu(tmeda)(\mu\text{-}C_2O_4)]_n{\cdot}H_2O$. Stoichiometric quantities of $C_6O_6{\cdot}8H_2O$ (0.47 g, 1.5 mmol) and metallic Cu powder (0.095 g, 1.5 mmol) were combined with 15 mL of purified acetonitrile under an atmosphere of argon. *N,N,N′,N′*-Tetramethylethylenediamine (0.23 mL, 1.5 mmol) was added at room temperature, and the color of the mixture rapidly turned to an intense orange. The atmosphere over the mixture was replaced with dioxygen. After being stirred for 2 h, the reaction mixture was dark red. A light solid was separated from the solution by filtration, and the filtrate was allowed to sit in air. The color of the solution slowly turned blue, and light blue crystals of $[(tmeda)Cu(\mu\text{-}C_5O_5)Cu(tmeda)(\mu\text{-}C_2O_4)]_n$ were obtained (0.35 g) in 78% yield based on initial quantities of Cu and tmeda.

Characterization. Mp: >350 °C. IR (KBr) [ν (cm^{-1})]: 3460 w, 3013 w, 2990 w, 2930 w, 1667 s, 1600 s, 1473 m, 1300 m, 1023 w, 960 w, 793 m. Magnetic moment: $\mu_{eff} = 3.00\ \mu_B$ (per binuclear subunit). UV−vis (DMSO) [λ_{max} (ϵ)]: 272 nm (11 400 M^{-1} cm^{-1}), 346 (10 400), 368 (11 100), 616 (225). EPR: solid, $g_{\parallel} = 2.279$, $g_{\perp} = 2.073$; MeCN, $g_{iso} = 2.12$, $A(^{63,65}Cu) = 85$ G. Anal. Found: C, 37.7; H, 5.55; N, 9.26. Calcd for $Cu_2C_{19}H_{32}N_4O_9{\cdot}H_2O$: C, 37.7; H, 5.66; N, 9.25.

Crystallography. Pale blue crystals of $[(tmeda)Cu(\mu\text{-}C_5O_5)Cu(tmeda)(\mu\text{-}C_2O_4)]_n{\cdot}H_2O$ were obtained directly from the reaction. They form in the monoclinic crystal system, space group *C*2/*c*, in a unit cell of the dimensions listed in Table 1. Data were collected on a Nicolet P3/f diffractometer, and the structure was solved using a Patterson map. Refinement converged with $R = 0.049$ and $R_w(F^2) = 0.092$ for 1503 observed independent reflections. Positions for selected atoms of the structure are listed in Table 2.

Results and Discussion

The triquinoyl ring of $C_6O_6{\cdot}8H_2O$ appears from spectroscopic characterization to be dodecahydroxycyclohexane ($C_6(OH)_{12}$),[7] but the products of amine condensation reactions show that the chemistry of this compound follows the path of hexaketocyclohexane.[8] This is particularly true of ring reduction reactions that proceed in one-electron steps to give the semitriquinoyl radical anion and the rhodizonate dianion (eq 2). With

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[8] See for example: Catalano, V. J.; Larson, W. E.; Olmstead, M. M.; Gray, H. B. *Inorg. Chem.* **1994**, *33*, 4502.

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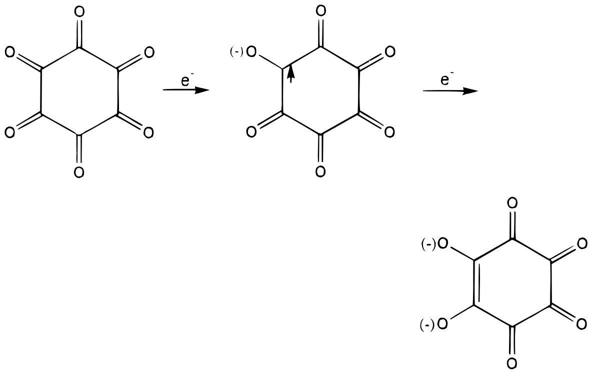
Table 2. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[a] ($Å^2 \times 10^3$) for [(tmeda)Cu(μ-C_5O_5)Cu(tmeda)(μ-C_2O_4)]

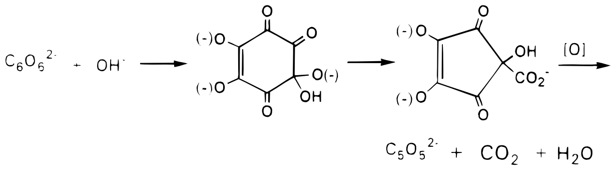
	x	*y*	*z*	U_{eq}[a]
Cu	7185(1)	6181(1)	3166(1)	21(1)
O(1)	5929(2)	6263(3)	2815(3)	32(1)
O(2)	6552(2)	4112(3)	3097(3)	36(1)
O(3)	5000	2687(4)	2500	50(2)
O(4)	7561(2)	6124(2)	4864(3)	26(1)
O(5)	7250(2)	7923(2)	3594(2)	28(1)
N(1)	6851(3)	6221(3)	1431(3)	33(1)
N(2)	8431(3)	5869(3)	3434(4)	36(1)
C(1)	5471(3)	5450(4)	2666(4)	25(1)
C(2)	5787(3)	4374(4)	2802(4)	26(1)
C(3)	5000	3661(6)	2500	33(2)
C(4)	6304(6)	7137(5)	864(5)	88(3)
C(5)	6400(3)	5239(4)	830(4)	36(1)
C(6)	7707(5)	6315(6)	1398(5)	68(2)
C(7)	8370(4)	5652(6)	2282(6)	68(2)
C(8)	8761(4)	4888(5)	4170(7)	73(2)
C(9)	9047(3)	6741(4)	4026(4)	35(1)
C(10)	7595(3)	6986(4)	5374(4)	22(1)

[a] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.



(2)

this similarity to *o*-benzoquinone, reactions with metallic copper have been investigated as an initial step in the investigation of the coordination chemistry of "C_6O_6". Stoichiometric quantities of metallic copper, $C_6O_6 \cdot 8H_2O$, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were combined in acetonitrile under an atmosphere of argon to give an intense orange product. The atmosphere over the reaction was replaced with dioxygen, and the color of the solution turned to dark red. The solution was filtered in air, and over the period of several hours pale blue crystals separated from the filtrate. Crystallographic characterization on the product obtained from the filtrate has shown that it contains a $C_5O_5^{2-}$ croconate ring bridging two Cu^{II} ions (Figure 1). Chelated to both Cu ions are oxalate ligands that bridge to adjacent metals forming a linear polymer consisting of [(tmeda)-Cu(μ-C_5O_5)Cu(tmeda)(μ-C_2O_4)]$_n$ complex units. The rhodizonate anion is known to undergo ring contraction under aerobic basic conditions to give $C_5O_5^{2-}$, CO_2, and water (eq 3).[7] The



(3)

orange product formed initially in the reaction with Cu is more likely a complex of Cu^I than Cu^{II} from the observation that Cu^{II} species are typically the color of the blue polymeric complex. EPR spectra recorded on diluted solutions of this product give a single resonance at a *g*-value of 2.012 split into four lines by weak coupling of 10 G to the $^{63,65}Cu$ nucleii. This observation is typical for an organic radical coordinated to a diamagnetic Cu center. On the basis of observed color changes, the apparent stoichiometry of the reaction, and the chemistry of *o*-benzoquinone addition reactions, it is likely that (tmeda)$Cu^I(C_6O_6^{\bullet -})$ is formed initially as the product of triquinoyl addition to metallic copper. Under aerobic conditions O_2 may add across the Cu-radical anion chelate ring to give a peroxytriquinoyl semiquinone species (eq 4), following the model for oxidation

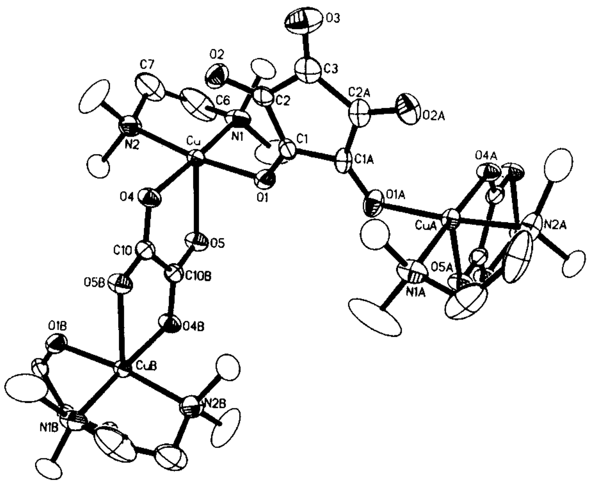
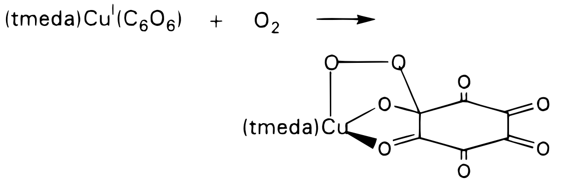


Figure 1. View showing one [(tmeda)Cu(μ-C_5O_5)Cu(tmeda)(μ-C_2O_4)] unit of the polymer. The bridging $C_5O_5^{2-}$ ligand is located along a crystallographic 2-fold axis, and the oxalate ligand is located about a center of inversion. The Cu is square pyramidal with N1, N2, O1, and O4 occupying basal positions and O5 located at the apical site. O2 is located at the remaining position of an octahedron, but the Cu−O2 separation is long. A water molecule is hydrogen bonded to O1. Selected bond lengths (Å): Cu−O1 1.976(3), Cu−O4 1.980(3), Cu−N1 2.040(4), Cu−N2 2.025(4), Cu−O5 2.259(3), Cu−O2 2.812(4), C1−O1 1.249(5), C2−O2 1.222(5), C3−O3 1.230(9).



(4)

of metal−semiquinone complexes.[3,9] Formation of the peroxo-ring O−C bond would parallel OH^- addition to $C_6O_6^{2-}$ leading to ring contraction and formation, in this case, of a coordinated CO_2 radical anion that readily dimerizes to form oxalate.

This mechanism is consistent with the high yield of product, 78% based on the stoichiometric quantities of Cu and tmeda used initially, and the assumption that the two oxalate carbon atoms are derived from separate ring contraction processes.

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Supporting Information Available: Text describing X-ray procedures and tables giving crystal data and details of the structure determination, atom coordinates and *U* values, bond lengths, bond angles, and anisotropic thermal parameters for [(tmeda)Cu(μ-C_5O_5)-Cu(tmeda)(μ-C_2O_4)]$_n \cdot H_2O$ (7 pages). Ordering information is given on any current masthead page.

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