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Mixed-Ligand Copper Complexes with 8-Methylthioquinoline and Triphenylphosphane or the *o*-Semiquinone/Catecholate Redox System

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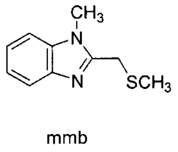
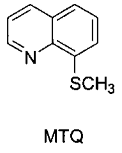
The complex $[Cu(MTQ)(PPh_3)_2](BF_4)$, MTQ = 8-methylthioquinoline, exhibits distorted tetrahedral coordination at the copper(I) center. One of two crystallographically independent molecules found in the unit cell exhibits a more pronounced inclination towards a (3+1) coordination arrangement. In comparison to the analogous complex with the related imine/thioether chelate ligand 1-methyl-2-(methylthiomethyl)-*1H*-benzimidazole, the cation $[Cu(MTQ)(PPh_3)_2]^+$ shows stronger bonding of Cu^I to S and weaker interaction with N. With 3,5-di-*tert*-butyl-*o*-semiquinone as co-ligand instead of two PPh_3 ligands a valence-tautomer equilibrium situation involving the copper(II)-catecholate state can be observed by EPR spectroscopy, showing an unusually large isotropic $^{63,65}Cu$ hyperfine coupling of 2.1 mT and an untypically small isotropic *g* value of 1.975.

Introduction

Imino and thioether donor atoms have different characteristics for metal ions, especially for copper in its two biorelevant oxidation states +1 and +2.[1,2] While a "soft" thioether S (such as in methionine) prefers copper(I), the imino function (as in the imidazole ring of histidine) tolerates both the Cu^I and Cu^{II} states.[1,2] In an attempt to mimic the biochemically relevant[3] valence tautomerism [Equation (1)] between the copper(I)-*o*-semiquinone and copper(II)-catecholate combinations, we have used a corresponding mixed-donor ligand system in the form of 1-methyl-2-(methylthiomethyl)-*1H*-benzimidazole (mmb) to observe such a temperature-dependent valence-tautomer equilibrium outside biological material.[4]

$$(L)Cu^I(Q^{\bullet-}) \rightleftharpoons (L)Cu^{II}(Q^{2-}) \qquad Q = o\text{-quinone} \tag{1}$$


mmb


MTQ

Valence-tautomer (or redox isomer) equilibria are not only of interest for the enzymatic mechanism of copper-dependent amine oxidases;[3] (1) has also been implicated in catechol-enhanced Fenton processes for wood decay.[5] In general, valence-tautomer equilibria[6] involving cobalt,[7] manganese, copper,[4,8] nickel,[9] and iron[10] have been discussed with respect to potential applications in molecular electronics ("switching").[6–11]

While thioether (methionine) coordination to biological copper(I/II) is observed for electron transfer proteins[1,2a] and enzymes,[12] there has also been a recent report describing N–S five-membered ring chelate binding of copper in methanobactin.[13]

Extending our previous approach[4] to other N–S chelate ligands we have focused on 8-methylthioquinoline (MTQ),[14–16] which contains an azine (pyridyl) nitrogen donor instead of the more basic but less π-accepting azole (imidazole) N in mmb. Also, mmb contains a flexible dialkylthioether substituent, whereas MTQ offers an arylalkythioether sulfur in a more rigid chelate setting. Accordingly, a comparison between mmb and MTQ compounds with d^6-configured metal complex fragments has revealed considerable differences in the metal–donor bond lengths within the five-membered chelate ring.[15] A homoleptic complex of MTQ with copper(I), $[Cu(MTQ)_2](ClO_4)$, was also reported recently,[16] showing relatively short bonds from the metal to N (2.0165 Å) and S (2.3242 Å).

Results and Discussion

The chelate ligand MTQ forms a stable complex with $[Cu(PPh_3)_2]^+$ [Equation (2)]. The results of the structural analysis as shown in Figure 1 and summarized in Table 1

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Table 1. Selected bond lengths [Å] and angles [°] for $[Cu(MTQ)(PPh_3)_2](BF_4)$ and calculated values for $[Cu(MTQ)(PH_3)_2]^+$.

	Exp.				Calcd.[a]
	Molecule 1		Molecule 2		
Cu–N	2.101(7)	(Cu–N1)	2.077(8)	(Cu2–N2)	2.051
Cu–S	2.363(3)	(Cu1–S1)	2.376(2)	(Cu2–S2)	2.387
Cu–P	2.256(3)	(Cu1–P2)	2.255(3)	(Cu2–P3)	2.281
Cu–P	2.289(3)	(Cu1–P1)	2.287(2)	(Cu2–P4)	2.304
N–Cu–S	84.2(2)	(N1–Cu1–S1)	84.9(2)	(N2–Cu2–S2)	87.1
N–Cu–P	111.0(2)	(N1–Cu1–P2)	108.3(2)	(N2–Cu2–P3)	115.9
N–Cu–P	103.0(2)	(N1–Cu1–P1)	107.2(2)	(N2–Cu2–P4)	112.4
S–Cu–P	119.88(9)	(P2–Cu1–S1)	117.08(10)	(P3–Cu2–S2)	116.7
S–Cu–P	104.84(10)	(P1–Cu1–S1)	107.51(9)	(P4–Cu2–S2)	107.8
P–Cu–P	125.19(9)	(P2–Cu1–P1)	124.34(9)	(P3–Cu2–P4)	114.0

[a] Calculation for $[Cu(MTQ)(PH_3)_2]^+$.

for the two crystallographically independent molecules reveal a slight asymmetry in the binding of the two triphenylphosphane ligands as is typical for many such copper(I) compounds.[17]

$$\mathrm{MTQ} + [Cu(CH_3CN)_2(PPh_3)_2](BF_4) \longrightarrow [Cu(MTQ)(PPh_3)_2](BF_4) + 2\,CH_3CN \quad (2)$$

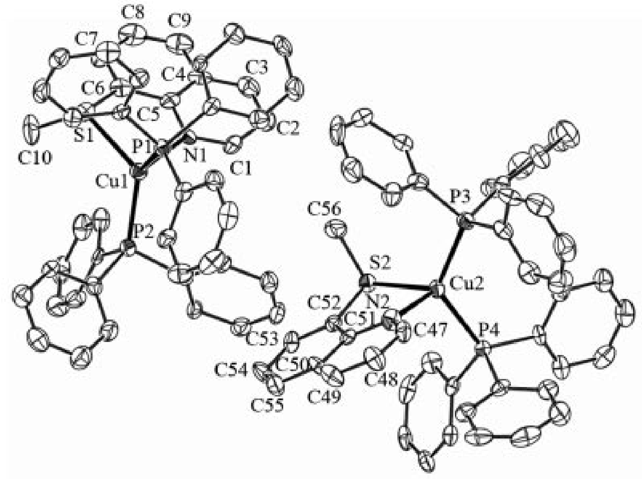

Figure 1. Molecular structures of two independent complex ions in the crystal of $[Cu(MTQ)(PPh_3)_2](BF_4)$.

The tendency of the $3d^{10}$ system for (3+1) instead of 4 coordination may be further enhanced by π–π interactions between different coordinated ligands.[17]

In comparison to the homoleptic $[Cu(MTQ)_2]^+$ ion[16] the Cu–N and Cu–S distances in $[Cu(MTQ)(PPh_3)_2]^+$ are significantly lengthened from about 2.02 to 2.09 Å and from about 2.32 to 2.37 Å, respectively. The Cu–N and Cu–S bond length data represent the average bond lengths of the two crystallographically independent molecules. Relative to several reported d^6 metal complexes[15] of MTQ, the copper(I) compound described here exhibits a balanced binding of the metal to N and S. In contrast, Ru^{II} prefers to bind to N and Pt^{IV} exhibits strong bonding to S.[15] In comparison with $[Cu(mmb)(PPh_3)_2]^+$,[18] the $[Cu(MTQ)(PPh_3)_2]^+$ ion is distinguished by longer Cu–N and shorter Cu–S bonds; the difference Δ_{NS} [d(Cu–S) – d(Cu–N)] is 0.394 Å for $[Cu(mmb)(PPh_3)_2]^{+[18]}$ but only about 0.28 Å for the two molecules of $[Cu(MTQ)(PPh_3)_2]^+$. Apparently, the higher degree of rigidity conferred by the aromatic chelate ligand MTQ enforces a more balanced coordination by the two donor atoms, whereas mmb, which has a higher flexibility due to the CH_2 group in the chelate ring, allows for a more disparate binding of N and S to the metal.

The optimized geometry of $[Cu(MTQ)(PH_3)_2]^+$ is in reasonable agreement with the experimental results. Some deviations (Table 1) result from the approximation of PPh_3 by PH_3. The highest occupied molecular orbital (HOMO) of this complex is mainly formed by a combination between d orbitals of Cu (42%) and p orbitals of S (18%). The next lower lying orbital consists of 45% d orbitals from the Cu center and 12% p orbitals on the two P atoms. The lowest unoccupied molecular orbital (LUMO) comprises π* orbitals of the ligand with about 2% contribution from Cu orbitals. The contribution of d orbitals of Cu to the LUMO can be viewed as metal-to-ligand π-back-bonding. HOMO and LUMO diagrams of $[Cu(MTQ)(PH_3)_2]^+$ are depicted in Figure 2.

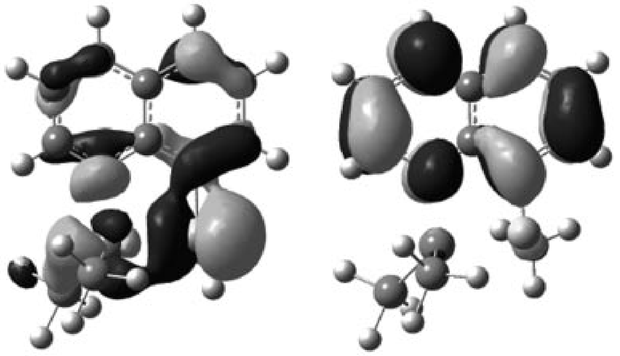

Figure 2. Composition of the HOMO (left) and LUMO (right) of $[Cu(MTQ)(PH_3)_2]^+$.

The successful use[4] of the mmb ligand in combination with the Cu^{n+}/Q_x^{n-} valence-tautomer system (n = 1 or 2; Q_x = 3,5-di-*tert*-butyl-*o*-benzoquinone) has prompted us to employ MTQ in a similar set of EPR experiments. The EPR results from mixing equimolar amounts of MTQ and

Q_x with excess activated copper[4] [Equation (3)] are shown in Figure 3.

$$\mathrm{MTQ} + \mathrm{Q_x} + \mathrm{Cu} \longrightarrow [\mathrm{Cu}^{n+}(\mathrm{MTQ})(\mathrm{Q_x})^{n-}] \qquad (3)$$
$$n = 1 \text{ or } 2$$

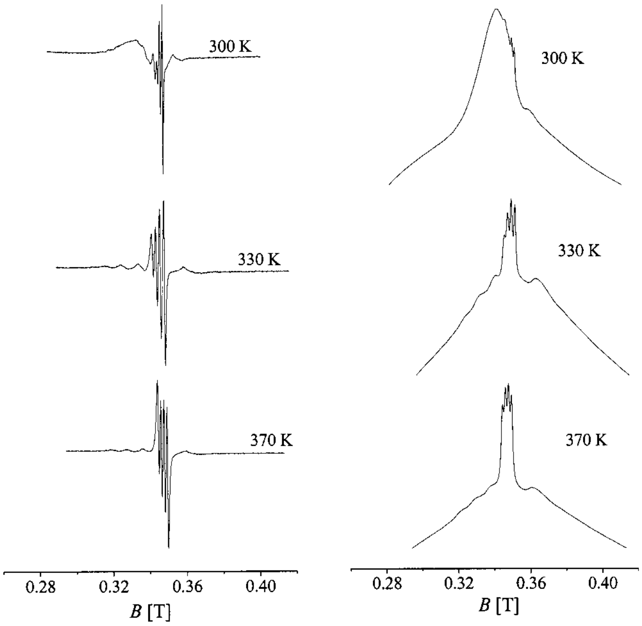

Figure 3. Temperature-dependent EPR spectra of the solution obtained by treating MTQ and 3,5-di-*tert*-butyl-*o*-semiquinone (1:1) with excess copper in toluene: derivative spectra (left) and integrated (nonderivative) spectra (right).

Although a uniform product could not be isolated from this reaction, an EPR pattern corresponding to a temperature-dependent solution equilibrium [Equation (1)] was observed with a major catecholato-copper(II) component characterized by broad signals with the typical Cu^{II} features of $a_{iso}(^{63,65}Cu) = 8.5$ mT and $g_{iso} = 2.077$ ($A_{\parallel} = 19.0$ mT, $g_{\parallel} = 2.16$, $A_{\perp} = 3.0$ mT, $g_{\perp} = 2.036$ at 110 K; ^{63}Cu: 69.2%, $I = 3/2$; ^{65}Cu: 30.8%, $I = 3/2$). The minor component, emerging to an appreciable extent at $T > 270$ K, can be expected to exhibit semiquinone/copper(I) features [$a_{iso}(^{63,65}Cu) < 1.2$ mT, $g_{iso} \approx 2.005$],[19] as for $[Cu^{I}(mmb)(Q_x^{\cdot -})]$,[4] however, the parameters observed here are very unusual: The resolved quartet from the $^{63,65}Cu$ hyperfine coupling shows a large spacing of 2.1 mT which lies between typical values of 0.5–1.2 mT for semiquinone/copper(I) species[19] and 8 mT for copper(II) systems.[20] A semiquinone–H (H^4) hyperfine coupling is not observed here because of the relatively broad lines (peak-to-peak distance ca. 2.0 mT). Even more unusual is the isotropic *g* factor at 1.975 for this quartet signal which has no precedent in either copper(II) or semiquinone/copper(I) EPR spectroscopy.[19,20] The unusually low value indicates[21] the presence of a low-energy excited state, possibly involving the π* orbital of MTQ, lying close to the doublet ground state. At this point we can only speculate that the rigidity of the unsaturated MTQ chelate ligand enforces a strictly four-coordinate copper(I) arrangement with significant contribution from the thioether S center of MTQ, whereas more flexible chelate ligands such as mmb [see Equation (2)] with partially saturated chelate ring centers allow for a 3+1 coordination. This interpretation is supported by the shorter Cu–S bond observed in $[Cu(MTQ)(PPh_3)_2](BF_4)$ relative to the mmb analogue. The electronic effect alone would favor the Cu^{I}-semiquinone alternative because MTQ is a better π acceptor than mmb.[15,16]

Experimental Section

Instrumentation: EPR spectra were recorded in the X band with a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ^{1}H NMR spectra were recorded with a Bruker AC 250 spectrometer.

Synthesis: A solution containing 130 mg (0.172 mmol) $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ and 30.5 mg (0.172 mmol) MTQ[15,16] was heated to reflux in 20 mL of dry CH_2Cl_2 for 4 h. After evaporating half of the solvent volume, the precipitate was collected by filtration and washed with cold diethyl ether to yield 117 mg (80%) of light yellow microcrystals. Single crystals were obtained from a CH_2Cl_2 solution layered with diethyl ether at –10 °C. $C_{46}H_{39}BCuF_4NP_2S$: calcd. C 64.99, H 4.62, N 1.65; found C 64.65, H 4.65, N 1.63. ^{1}H NMR (250 MHz, 300 K, $CDCl_3$): $\delta = 8.70$ (dd, $^{3}J = 4.6$ Hz, $^{4}J = 1.6$ Hz, 1 H, H2), 8.62(dd, $^{3}J = 8.4$ Hz, $^{4}J = 1.6$ Hz, 1 H, H4), 8.11 (d, $^{3}J = 8.0$ Hz, 1 H, H7), 8.06 (d, $^{3}J = 8.0$ Hz, 1 H, H5), 7.77 (t, $^{3}J = 8.0$ Hz, 8.0 Hz, 1 H, H6), 7.65 (dd, $^{3}J = 8.4$ Hz, 4.6 Hz, 1 H, H3), 7.38–7.04 (m, 15 H, aromatic), 2.15 (s, 3 H, SCH_3) ppm.

Crystallography: Data for $[Cu(MTQ)(PPh_3)_2](BF_4)$ were collected at 173 K with a Siemens P3 four-circle diffractometer using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Formula $C_{46}H_{39}BCuF_4NP_2S$; formula weight = 850.13 g·mol^{-1}; monoclinic space group *Pc*; $a = 21.520(4)$, $b = 10.607(2)$, $c = 19.993(4)$ Å; $\beta = 116.61(3)°$; $V = 4080.3(14)$ Å^3; $Z = 4$ (2 independent molecules); $F(000) = 1752$; $\rho_{calcd.} = 1.384$ g·cm^{-3}; $\mu = 0.717$ mm^{-1}, $T = 173(2)$ K; θ range 1.92 – 25.02°; number of unique reflections 7376 ($R_{int} = 0.064$), number of parameters 1011; Flack parameter = –0.009(18); $R_1 = 0.0566$, $wR2 = 0.0988$ [for, 5436 reflections with I $> 2\sigma$ (I)]; $R_1 = 0.0955$, $wR_2 = 0.1145$ (all data); $GOF = 1.073$. The structure was solved by direct methods and refined by full-matrix least-squares against F_2 of all data using the SHELXTL software package.[22] Anisotropic thermal factors were assigned to the non-hydrogen atoms. The hydrogen atoms were included in calculated positions (riding model) and refined with fixed $U_{iso} = 1.2$ U_{iso} of the carbon atoms to which they are bonded.

CCDC-275097 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.

Computational Details: Ground-state electronic structure calculations on $[Cu(MTQ)(PH_3)_2]^+$ have been done by density functional theory (DFT) methods, using the Gaussian 03 program package.[23] Within the Gaussian program, the quasirelativistic effect core potential basis sets[24] were employed for the Cu atom; for other atoms Dunning's DZP basis sets[25] were used. The geometry optimization was performed by using the pure density BP86 functional[26] at the spin-restricted level; the single point energy was calculated using the hybrid density B3LYP functional[27] with optimized geometry.

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