Crucial Role of Cu−S Bonding for Structural Changes Accompanying the Reversible Cu^{I}/Cu^{II} Transition in an Unrestrained $Cu(N\wedge S)_2$ Coordination Arrangement. An Experimental and DFT Study

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The structure of reversibly oxidizable $[Cu(mmb)_2](BF_4)$ with 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) as bidentate N,S-donor ligand has been determined and compared with that of the copper(II) species $[Cu(mmb)_2(\eta^1\text{-}ClO_4)](ClO_4)$. In the complex ions of the equilibrium $[Cu^{I}(mmb)_2]^+ + ClO_4^- \rightleftharpoons e^- + [Cu^{II}(mmb)_2(\eta^1\text{-}ClO_4)]^+$ the almost linear N−Cu−N backbone is invariant whereas the bonds to the thioether sulfur centers and especially the changing S−Cu−S angle (145.18(5)° for the Cu^{II} species, 109.33(3)° for the Cu^{I} form) reflect the metal oxidation state. In contrast to the perchlorate coordinating copper(II) species, $[Cu^{I}(mmb)_2](BF_4)$ contains a cation with a very large vacant site at the metal center, resulting in elliptical channels within the crystal. DFT calculations on $[Cu^{I}(mb)_2]^+$, $[Cu^{II}(mb)_2]^{2+}$, and $[Cu^{II}(mb)_2(OClO_3)]^+$ with mb = 2-methylthiomethyl-1*H*-benzimidazole confirm the essential role of the metal−sulfur bonds in responding to the reversible $Cu^{I/II}$ electron transfer process, even in the absence of electronically stronger interacting thiolate sulfur centers or sophisticated oligodentate ligands.

Introduction

The very different coordination preferences of copper(I) with its d^{10} configuration (linear, trigonal-planar, or tetrahedral geometry) and the prototypical Jahn−Teller ion Cu^{2+} (d^9 configuration: square-planar or square-pyramidal coordination) have long been associated with the unusually large reorganization effects observed for Cu^{I}/Cu^{II} transitions in complexes $[CuL_m]^{n+}$.[1] The biochemical occurrence of this couple in "blue copper" proteins and "type 1" copper-containing enzymes has therefore received special attention;[2−4] the rapid electron transfer observed there has been attributed to an enforced geometry ("entatic state"), representing a compromise between the Cu^{I} and Cu^{II} energy minimum coordination structures.[4]

The type 1 copper centers exhibit one cysteinate and two histidine residues as the invariable primary coordination sphere and an additional, more weakly bonded ligand, usually the thioether part of methionine.[2] Native systems, mutants, and several model compounds of varying degrees of sophistication have been studied in the past decades;[2,3,5,6] however, the approach[6] to use polychelate or bulky ligands to restrict the degrees of freedom (and ensure stability) could not by its very nature fully elucidate the intrinsic coordination change for a reversible Cu^{I}/Cu^{II} transition with an N_2S_2 set of donor atoms. We now present a rather straightforward model system with just bidentate ligands which allows for more geometrical freedom but shows surprising conceptual parallels to what is known of the biological systems.

The 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) ligand has been recently used in copper chemistry to effect a remarkable valence tautomerism which bears some resemblance to physiologically essential phenomena in amine oxidase enzymes.[7] Mimicking one histidine and one methionine binding site, the neutral mmb ligand can form five-membered chelate rings with metal centers.[8,9] The benzimidazole N and thioether S donor atoms are both weakly π accepting but of different "softness", so that both Cu^{I} and Cu^{II} complexes can form; crystal

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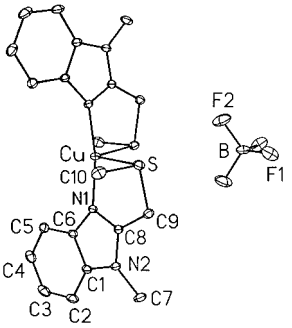

Figure 1. Molecular structure of $[Cu^{I}(mmb)_2](BF_4)$.

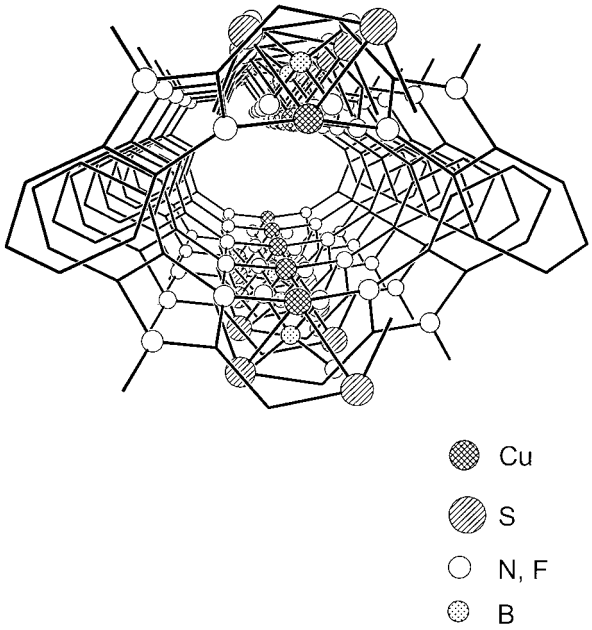

Figure 2. View along the channel formed by the coordinatively unsaturated cations in the crystal of $[Cu^{I}(mmb)_2](BF_4)$.

structures of $[Cu^{I}(mmb)(PPh_3)_2](BF_4)$ and of poorly soluble $[Cu^{II}(mmb)_2(\eta^1\text{-}ClO_4)](ClO_4)$ were reported recently.[8]

mmb

Results and Discussion

Although the new copper(I) species $[Cu(mmb)_2](BF_4)$ proved to be a very air-sensitive substance, we were able to determine its crystal structure (Figures 1 and 2, Tables 1 and 2) and study its electrochemistry.

Complex $[Cu(mmb)_2](BF_4)$ undergoes electrochemically reversible reduction at 0.31 V vs $FeCp_2^{+/0}$ in noncoordinating CH_2Cl_2/0.2 M Bu_4NPF_6. The peak-to-peak potential differences between 70 mV at 20 mV/s and 113 mV at 1 V/s scan rate coincide with that of the internal ferrocene standard and thus imply rather little geometrical reorganization,[1] in contrast to the behavior of many other simple complexes of the Cu^{I}/Cu^{II} couple.

The structural comparison in Table 2 of the complex ions in the equilibrium

$$[Cu^{I}(mmb)_2]^+ + ClO_4^- \rightleftharpoons [Cu^{II}(mmb)_2(\eta^1\text{-}ClO_4)]^+ + e^- \quad (1)$$

reveals the following features:

Table 1. Crystallographic Data for $[Cu(mmb)_2](BF_4)$

empirical formula	$C_{20}H_{24}BCuF_4N_4S_2$	fw	534.90
cryst syst	monoclinic	space group	*C*2/*c*
a, Å	18.910(2)	*T*, K	173
b, Å	10.0519(11)	*λ*, Å	0.71073
c, Å	12.8339(12)	ρ_{calc}, g cm^{-3}	1.553
β, deg	110.301(7)	*μ*, mm^{-1}	1.185
V, Å^3	2288.0(4)	R1[a]	0.0399
Z	4	wR2[a]	0.0947

[a] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o^4)]\}^{1/2}$.

Table 2. Comparison of Structural Data

	$[Cu^{I}(N\wedge S)_2]^+$		$[Cu^{II}(N\wedge S)_2(OClO_3)]$		$[Cu^{II}(N\wedge S)_2]^{2+}$
	exptl[a]	calcd[b]	exptl[c]	calcd[b]	calcd[b]
			Bond Lengths (Å)		
Cu−N	1.9199(18)	1.963	1.941(3)	2.011	1.957
			1.949(3)	2.024	
Cu−S	2.6216(7)	2.711	2.4193(13)	2.599	2.550
			2.4436(13)	2.634	
Cu−O			2.236(9)	2.108	
			Bond Angles (deg)		
N−Cu−N′	169.75(11)	166.3	172.53(14)	164.68	162.6
S−Cu−S′	109.33(3)	112.2	145.18(5)	136.40	120.0
N−Cu−S[d]	82.47(6)	81.8	83.07(11)	80.65	83.2
			83.56(11)	81.48	
N−Cu−S[e]	103.56(6)	106.9	92.31(10)	90.67	106.1
			96.86(11)	95.86	

[a] From crystal structure of tetrafluoroborate ($N\wedge S$ = mmb). [b] $N\wedge S$ = mb. [c] From crystal structure of perchlorate salt (hemimethanolate, $N\wedge S$ = mmb), see ref 8. [d] Intrachelate angles. [e] Extrachelate angles.

(i) The N−Cu−N backbone is essentially invariant, because that almost linear arrangement can be part of several ideally preferred structures, whether the linear geometry of copper(I) systems or the square-pyramidal or trigonal-bipyramidal structures of Cu^{II}. In fact, the metal coordination geometry in $[(Cu^{II}(mmb)_2(\eta^1\text{-}ClO_4)]^+$ lies midway between the sp and tbp situations,[8] giving rise to a large value $g_{||} = 2.358$ and a small EPR coupling constant $A_{||} = 13.4$ mT.[8] In contrast, $[Cu^{I}(mmb)_2]^+$ exhibits a "2 + 2" coordination with primary N (linear) and secondary S coordination (distorted tetrahedral arrangement) to copper(I).

(ii) The bonds to the thioether sulfur centers reflect the changes at the metal, i.e., the higher ionization of Cu^{II} (causing ca. 7% shorter Cu−S distances) and the capacity for π back-donation from Cu^{I} to the weakly π acidic thioether atoms. A qualitatively similar situation as for $[Cu^{I}(mmb)_2](BF_4)$ had been observed previously for $[Cu^{I}(BBDHp)](X)$, X = PF_6, BF_4, or ClO_4, in which the tetradentate 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane (BBDHp) ligand resembles a doubled N−S system as used here.[6a,10] However, the significantly longer Cu−S distances of about 2.88 Å in these systems indicate rather weak bonding, probably caused by the conformational restraints after formation of the macrocyclic chelate ring. The 2.62 Å distances found for the Cu−S bonds in $[Cu^{I}(mmb)_2](BF_4)$ are shorter than most copper/thioether distances in type 1 Cu centers;[2,3] a comparable value of 2.61 Å has been reported for the copper(II) state of cucumber basic protein.[11]

(iii) The distinctly changed S−Cu−S angle reflects the limits of the compromise situation: The large value of 145° for the

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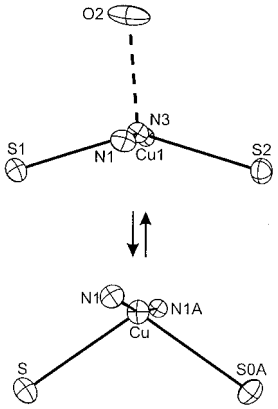

Figure 3. Projections of the coordination arrangements of $[Cu^{I}(mmb)_2]^+$ (bottom) and $[Cu^{II}(mmb)_2(\eta^1\text{-}OClO_3)]^+$ (top) in the CuS_2 plane.

copper(II) complex signifies the "flattening" tendency toward a planar situation for the $Cu^{II}N_2S_2$ core, whereas the angle of 109.3° for the copper(I) complex would be close to the ideal value in a tetrahedral situation (Figure 3).

(iv) The coordinative unsaturation of the primary $Cu^{II}N_2S_2$ coordination allows for addition of a fifth, weakly bonded ligand, here η^1-ClO_4^-. Similarly, in type 1 copper centers the $Cu^{II}(His)_2(Cys^-)$ primary coordination sphere is usually complemented by methionine and, in some cases, by a very weakly coordinated fifth O-donor ligand.[2,3] The large vacant site at the very unusually coordinated Cu^{I} center in $[Cu(mmb)_2]^+$ explains the high air sensitivity in solution and in the solid: Remarkably, the molecules pack with the open coordination sites directed at each other to form approximately elliptical channels in the crystal with axes of about 3.5 and 5.1 Å (Figure 2).

DFT calculations[12] were performed for the $[Cu^{I}(mb)_2]^+$, $[Cu^{II}(mb)_2]^{2+}$, and $[Cu^{II}(mb)_2(\eta^1\text{-}ClO_4)]^+$ ions (mb = 2-(methylthiomethyl)-1*H*-benzimidazole). The $[Cu^{II}(mb)_2]^{2+}$ ion was studied because the oxidation of $[Cu^{I}(mmb)_2](BF_4)$ primarily produces a tetracoordinate rather than pentacoordinate copper(II) center. The DFT(ADF) optimized geometry of $[Cu^{I}(mb)_2]^+$ reasonably reproduces the essential features of the experimental structure of $[Cu^{I}(mmb)_2](BF_4)$ (Table 2). The DFT(ADF) optimization overestimates the Cu−N and Cu−S bond lengths by a few percent; the bond lengths within the ligand part of the complex are reproduced with ±0.02 Å accuracy.

The one-electron scheme of $[Cu^{I}(mb)_2]^+$ as calculated by the DFT(ADF) method is shown in Figure 4. Molecular orbitals of a and b symmetry are characterized by antisymmetrical or symmetrical combinations of contributing ligand orbitals, respectively. The highest molecular orbitals 34a and 33b of this complex are mainly formed by combinations of d orbitals of the Cu atom with p orbitals of S, providing electron density for the "open" coordination site (Figure 5). The HOMO (34a) is calculated with 59.3% d and 6% s orbital contributions from the Cu atom and with 21.7% p orbital contributions from the S atom. The lower lying orbital 33b is composed from 61% d orbitals of the Cu center and 30.5% p orbitals of the S atom. The lower lying set of occupied MOs is metal-localized (more than 80% Cu contribution). The lowest lying unoccupied molecular orbitals 35a and 34b are composed from π^* orbitals of the ligand with less than 1.5% contribution from the Cu atom. The HOMO and LUMO of $[Cu^{I}(mb)_2]^+$ are depicted in Figure 5.

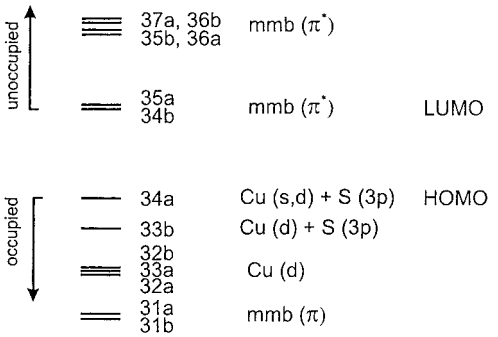

Figure 4. Molecular orbital scheme for $[Cu^{I}(mb)_2]^+$ as calculated by the DFT-ADF method.

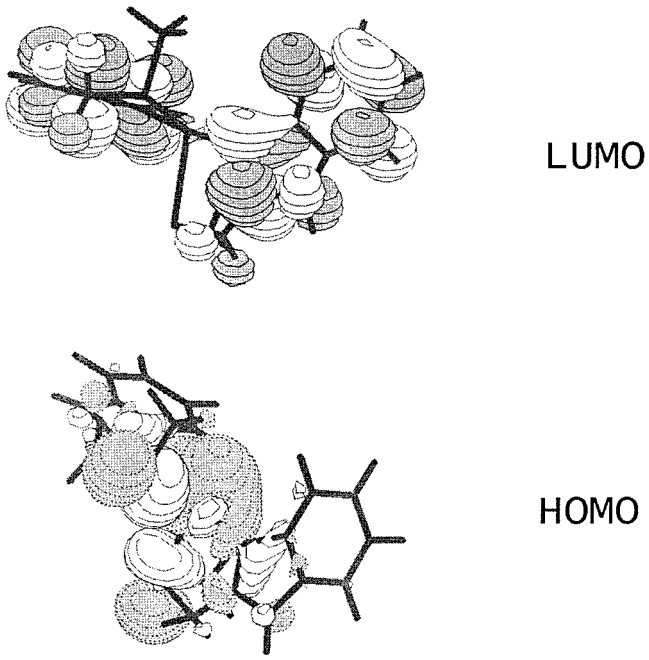

Figure 5. Composition of the LUMO and HOMO of $[Cu^{I}(mb)_2]^+$.

The withdrawing of an electron from $[Cu^{I}(mb)_2]^+$ mainly affects the S−Cu−S fragment of the complex. The Cu atom is then accessible to further coordination, due to the character of the singly occupied MO (SOMO), the modified former HOMO of $[Cu^{I}(mb)_2]^+$. However, the Cu contribution is calculated to be lower (ca. 40%) than in the HOMO of $[Cu^{I}(mb)_2]^+$, which correlates with the diminished $A_{\|}$ value of 13.4 mT for $[Cu^{II}(mmb)_2(OClO_3)](ClO_4)$.[8]

The geometry optimization of the $[Cu^{II}(mb)_2(ClO_4)]^+$ and $[Cu^{II}(mb)_2]^{2+}$ complex ions reveals hardly any variation of the ligand part of the system in comparison with $[Cu^{I}(mb)_2]^+$, in agreement with the experiment using mmb. In contrast, the region close to the copper center is strongly influenced by the change of charge and the coordination of ClO_4^- (Table 2). There is a better agreement of the experimental structure data of the copper(II) compound with the bond lengths calculated for $[Cu^{II}(mb)_2]^{2+}$ because the interaction with the perchlorate is

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obviously overestimated. On the other hand, the angles are better reproduced (Table 2) by the calculations of $[Cu^{II}(mb)_2(OClO_3)]^+$ which take ligand/ligand interactions better into account.

Summarizing, the structural response to the reversible $Cu^{I}N_2S_2/Cu^{II}N_2S_2$ transition in the simple and geometrically rather *unrestrained* $[Cu(mmb)_2]^{n+}$ complex system involves changes in the Cu−S bonding, especially of the S−Cu−S angle, whereas the almost linear N−Cu−N backbone remains virtually unchanged. The effects are reproduced by DFT calculations albeit with varying accuracy. The results thus confirm the special role of S donors in facilitating reversible electron transfer, even in the absence of electronically stronger interacting[2,3] thiolate sulfur centers or sophisticated oligodentate ligands. The new $[Cu^{I}(mmb)_2](BF_4)$ complex contains a cation with an unusual coordination geometry, involving a large and, in the crystal, channel-forming vacant site at the d^{10} metal center.

Experimental Section

Instrumentation. ^{1}H- and ^{13}C NMR spectra were taken on a Bruker AC 250 spectrometer. UV/vis/near-IR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out at a scan rate of 100 mV/s in dichloromethane/0.2 M Bu_4NPF_6 using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

Synthesis of $[Cu(mmb)_2](BF_4)$. A solution of 100 mg (0.52 mmol) of mmb in 50 mL of acetone was added to 81.8 mg (0.26 mmol) of $[Cu(CH_3CN)_4](BF_4)$ and stirred for 30 min at room temperature under an argon atmosphere. After reduction of the solution to about 15 mL and cooling to 4 °C, a colorless, partially crystalline and highly air-sensitive precipitate was obtained and dried to yield 118 mg (85%). Calcd for $C_{20}H_{24}BCuF_4N_4S_2$ (534.90): C, 44.91; H, 4.52; N, 10.47. Found: C, 44.98; H, 4.52; N, 10.14. ^{1}H NMR (acetone-d_6): δ = 2.45 (s, 6H, SCH_3), 4.04 (s, 6H, NCH_3), 4.50 (s, 4H, CH_2SCH$_3$), 7.27−7.44 (m, 4H, arom), 7.58−7.61 (m, 2H, arom), 7.70−7.73 (m, 2H, arom). ^{13}C NMR (acetone-d_6, assignment based on DEPT 135 spectroscopy): δ = 19.20 (SCH$_3$, 31.08 (NCH$_3$), 32.12 (CH$_2$SCH$_3$), 111.76, 118.96 (*C*-5,6), 124.19, 124.63 (*C*-4,7), 137.34, 140.59 (*C*-3a,7a), 155.08 (*C*-2).

Single crystals of $[Cu(mmb)_2](BF_4)$ as obtained from the reaction solution were immersed in Nujol. Measurements were performed for a colorless block (0.4 × 0.4 × 0.6 mm) on a Siemens P4 diffractometer (Table 1); cell constants were obtained with 65 reflections ($10° \le 2\Theta \le 25°$), ω-scan; 3651 reflections were collected ($4° \le 2\Theta \le 58°$, $-1 \le h \le 25$, $-1 \le k \le 13$, $-17 \le l \le 16$), of which 3027 are independent and 2235 have $I_o \ge 2\sigma(I_o)$, 194 parameters. Empirical absorption correction (Ψ-scan, $0.74 < T < 1.00$). The structure was solved by direct methods, and refinement on F^2 was carried out (SHELXTL 5.1);[13] hydrogen atoms were refined freely with isotropic temperature factors, and anisotropic temperature factors were used for all other atoms. GOF = 1.026; min/max remaining electron densities −0.470/0.472 e Å^{-3}.

Calculation Procedures. In all calculations the CH_3 group attached to N in mmb was replaced by a hydrogen atom (ligand mb). Ground state electronic structure calculations of the $[Cu(mb)_2]^+$, $[Cu(mb)_2]^{2+}$, and $[Cu(mb)_2(ClO_4]^+$ complex ions have been done by density functional theory (DFT) methods using the ADF-1999[12] program package.

Within the ADF program Slater type orbital (STO) basis sets of double-ζ quality with polarization functions for H, B, C, N, O, F, and Cl atoms and triple-ζ quality with one additional polarization function for Cu and S were employed. Inner shells were represented by the frozen core approximation (1s for B, C, N, O, F; 1s−2p for S and Cl; 1s−3s for Cu). Within ADF the functional including Becke's gradient correction[14] to the local exchange expression in conjunction with Perdew's gradient correction[15] to local density approximation (LDA) with VWN parametrization of electron gas data (ADF-BP) was used.

Calculations on $[Cu(mb)_2]^+$ and $[Cu(mb)_2]^{2+}$ were done in constrained C_2 symmetry, and the *z* axis was identified with the C_2 axis.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for $[Cu(mmb)_2](BF_4)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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