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Copper(I) and copper(II) complexes of the bidentate imidazole/thioether ligand 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole

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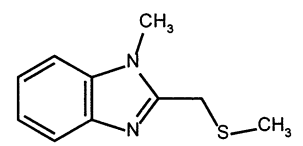
Abstract

The mixed imidazole/thioether chelate ligand 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) which has been shown earlier to effect biomimicking valence tautomerism in copper/*o*-quinone systems forms crystallographically characterized chelate complexes $[(\eta^2\text{-mmb})Cu^{I}(PPh_3)_2](BF_4)$ (**1**) and $[(\eta^2\text{-mmb})_2Cu^{II}(\eta^1\text{-}ClO_4)](ClO_4)$ (**2**). Compound **1** contains copper(I) in an approximately tetrahedral environment and complex **2**, obtained as methanol solvate, exhibits an asymmetrically (trigonal bipyramidal/square pyramidal) coordinated Cu^{II} center. Whereas bidentate mmb forms shorter N–Cu^{II} (1.945 Å) than N–Cu^{I} bonds (2.040 Å), the S(thioether)–Cu bond lengths of about 2.43 Å are independent of the metal oxidation state. Two relatively simple ligands mmb can effect similar spectroscopic responses as more complicated multidentate ligands.

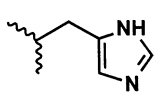
Keywords: Crystal structures; EPR; Copper complexes; Imidazole complexes; Thioether complexes

1. Introduction

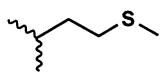
A large number of chelate ligands with sophisticated construction of imine N donor and thiolate and/or thioether S donor centers has been studied during the last two decades [1,2], in connection with attempts to mimic the structure, spectroscopy and electrochemical behavior of 'type 1' copper centers in 'blue' copper proteins [3–5]. In these centers of biological electron transfer, the metal is usually coordinated by two histidine, one cysteinate and one methionine side chain of the polypeptide backbone [3–6]. Within a different project, we have recently studied [7,8] the spectroscopically-established [9] and biologically-functional [4,10] valence tautomerism of copper/*o*-quinone complexes using a simply constructed imidazole/thioether ligand 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) which contains the donor characteristics of histidine and methionine [7].



mmb



His



Met

In combination with copper and 3,5-di-tert-butyl-*o*-quinone (Q), we were able to establish for the first time a Cu^{I}–semiquinone/Cu^{II}–catecholate valence tautomer equilibrium (Eq. (1)) outside biology [7,8]. This successful approach was based on the previous observation that all N ligands favor Cu^{II}–catecholate forms whereas all-thioether ligands stabilize the Cu^{I}–semiquinone state [11].

$$(L)Cu^{I}(Q^{\bullet -}) \rightleftharpoons (L)Cu^{II}(Q^{2-}) \quad (1)$$

In amine oxidases, ubiquitous enzymes for connective tissue maturation and other biological roles [4,10,12],

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Table 1
Crystal data for complexes **1** and **2** · 0.5CH_3OH

	1	**2** · 0.5CH_3OH
Empirical formula	$C_{46}H_{42}BCuF_4N_2P_2S$	$C_{20}H_{22}Cl_2CuN_4O_8S_2 \cdot 0.5CH_3OH$
Crystal color, form	colorless, rods	blue–green, blocks
Formula weight (g mol^{-1})	867.17	661.00
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.694(2)	10.364(3)
b (Å)	15.480(2)	11.114(2)
c (Å)	21.723(3)	12.227(3)
α (°)	90	86.15(2)
β (°)	104.810(12)	78.10(2)
γ (°)	90	75.30(2)
V (Å^3)	4126.7(11)	1332.7(6)
Z	4	2
D_{calc} (g cm^{-3})	1.396	1.647
Absorption coefficient, μ (mm^{-1})	0.711	1.231
F(000)	1792	676
Crystal size (mm)	$0.2 \times 0.2 \times 0.4$	$0.2 \times 0.2 \times 0.3$
θ Range (°)	1.66–25.08	1.70–26.00
Limiting indices	$-7 \le h \le 15; -18 \le k \le 17; -25 \le l \le 24$	$0 \le h \le 12; -12 \le k \le 13; -14 \le l \le 15$
Reflections collected	6918	5253
Independent reflections	6917	5213
R_{int}	0.2705	0.0337
Data/restraints/parameters	6567/0/515	5212/9/380
GOF on F^2	1.0009	1.064
R_1 ($I > 2\sigma(I)$)	0.0560	0.0585
wR_2 (all data)	0.1357	0.1652
Residual peaks: max., min. (e Å^{-3})	0.733, −0.438	1.010, −0.966

this process (Eq. (1)) serves to generate the copper(I) state which is essential for binding and activation of dioxygen [4,6,13].

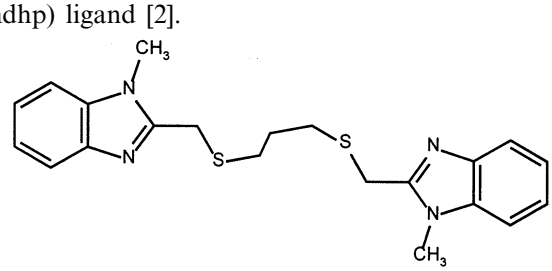
Unfortunately, structural information is not available for the system mmb/Cu^{n+}/Q^{n-} [7,8]. We therefore set out to obtain single crystals of conventional copper(I) and copper(II) compounds with the ligand mmb and arrived at compounds [(η^2-mmb)$Cu^I(PPh_3)_2$](BF_4) (**1**) and [(η^2-mmb)$_2Cu^{II}(\eta^1$-$ClO_4)$](ClO_4) (**2**). Their crystal structure, spectroscopic and electrochemical characterization are reported in this contribution.

2. Results and discussion

Compounds **1** and **2** were synthesized via conventional routes using [$Cu(PPh_3)_4$](BF_4) and $Cu(ClO_4)_2$ as metal-containing precursors. Compound **1** forms colorless, air-stable, non-luminescing crystals, and the blue–green complex **2** crystallizes with 0.5 equivalent of methanol. Crystal structure analyses were possible for both these compounds; however, no significant intermolecular interactions were found. The results are summarized in Tables 1 and 2 and Figs. 1 and 2.

Complex **1** exhibits a well-established [14] pattern for bis(triorganophosphine)copper(I) complexes of bidentate ligands, i.e. an approximately tetrahedral coordination of copper(I) (Fig. 1). The five-membered chelate ring is distinctly asymmetric with a longer Cu^I–S (2.434 Å) and a shorter Cu^I–N (2.040 Å) bond; at 2.249 and 2.296 Å the typically different [14] Cu^I–P bonds exhibit intermediate bond distances. As has been concluded from EPR studies [11], the triorganophosphines are better acceptor ligands towards Cu^I than thioether functions.

The poorly soluble complex **2** contains two η^2-mmb ligands and one disordered O-coordinated perchlorate around the copper(II) center (Figs. 2 and 3). Its coordination geometry falls between that of the trigonal bipyramidal (tbp) and square planar (sp) alternative; adopting the criteria of Reedijk and coworkers [2] (see also Schmuck and Seppelt [15]), we obtain an angular structural parameter $\tau = 0.46$ and thus a very similar value to $\tau = 0.48$ that was obtained for complex [Cu(bmdhp)(OH_2)](ClO_4)$_2$ (**3**) with one tetradentate 1,7-bis(*N* - methylbenzimidazol - 2′ - yl) - 2,6 - dithiaheptane (bmdhp) ligand [2].



bmdhp

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2** · 0.5CH_3OH

Complex ***1***			
Cu(1)–N(1)	2.040(3)	Cu(1)–P(1)	2.2491(12)
Cu(1)–S(1)	2.4336(13)	Cu(1)–P(2)	2.2961(12)
N(1)–Cu(1)–P(1)	114.53(10)	P(1)–Cu(1)–P(2)	118.30(4)
N(1)–Cu(1)–P(2)	111.42(10)	P(1)–Cu(1)–S(1)	117.32(5)
N(1)–Cu(1)–S(1)	84.25(10)	P(2)–Cu(1)–S(1)	105.96(5)
2 · *0.5CH_3OH*			
Cu(1)–N(3)	1.941(3)	Cu(1)–S(2)	2.4436(13)
Cu(1)–N(1)	1.949(3)	Cu(1)–O(2)	2.236(9)
Cu(1)–S(1)	2.4193(13)	Cu(1)–O(2A)	2.287(10)
N(3)–Cu(1)–N(1)	172.53(14)	N(1)–Cu(1)–S(1)	83.07(11)
S(1)–Cu(1)–S(2)	145.18(5)	O(2)–Cu(1)–S(1)	102.9(5)
N(3)–Cu(1)–O(2)	99.8(3)	O(2A)–Cu(1)–S(1)	122.7(4)
N(1)–Cu(1)–O(2)	86.9(3)	N(3)–Cu(1)–S(2)	83.56(11)
N(3)–Cu(1)–O(2A)	98.0(4)	N(1)–Cu(1)–S(2)	96.86(11)
N(1)–Cu(1)–O(2A)	89.5(4)	O(2)–Cu(1)–S(2)	111.9(5)
N(3)–Cu(1)–S(1)	92.31(10)	O(2A)–Cu(1)–S(2)	92.1(4)

$$\tau = (\beta - \alpha)/60° \quad (2)$$

where τ is the angular structural parameter (index of trigonality) and α,β are basal angles.

$\tau = 0$ for ideal sp ($\alpha = \beta = 180°$); $\tau = 1$ for ideal tbp ($\alpha = 120°$, $\beta = 180°$)

$[(\eta^2\text{-mmb})_2Cu^{II}(\eta^1\text{-}ClO_4)](ClO_4) \cdot 0.5CH_3OH$:

α(N3–Cu–N1) = 172.53(14)°; β(S1–Cu–S2) = 145.18(5)°; $\tau = 0.46$.

The higher charge on the metal in **2** relative to **1** results in the expected shortening of the Cu–N bonds from 2.040 to about 1.945 Å. However, at 2.419 and 2.444 Å, the Cu–S bond lengths in **2** are virtually identical to those in **1** (2.434 Å), supporting the notion of relatively little change in the copper–thioether bond on metal oxidation. Such effects have been used to understand the function of type 1 copper electron transfer centers of 'blue' copper proteins [5]; they may also be used to interpret the electron transfer function of methionine-binding heme groups which occur e.g. in cytochrome *c* [16].

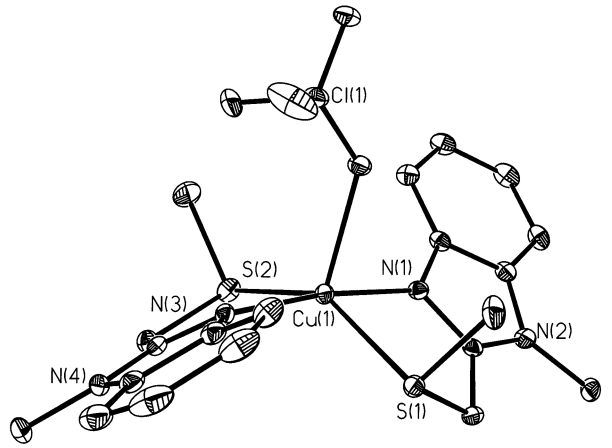


Fig. 2. Molecular structure of the cation $[(\eta^2\text{-mmb})_2Cu(\eta^1\text{-}ClO_4)]^+$ in the crystal of **2** · 0.5CH_3OH (only one orientation of the disordered perchlorate ligand shown).

Data from absorption and EPR spectroscopy support the structural results: the copper(I) center in **1** has a d^{10} configuration and displays no EPR activity, long-wavelength metal-to-ligand charge transfer absorption [14,17] or strong luminescence [14] after irradiation in the UV region. On the other hand, the d^9 copper(II) center in **2** exhibits an EPR spectrum with $g_{\|} = 2.358$, $g_{\perp} = 2.074$ and $A_{\|} = 13.4$ mT; these parameters are rather close to those of $[Cu(bmdhp)(OH_2)](ClO_4)_2$ (**3**) [2] because of similar geometrical configuration. At 750(sh) and 666 nm in acetonitrile solution the ligand-field transitions are also similar to those of **3** [2].

Cyclic voltammetry reveals that both the oxidation of **1** (at $E_{pa} = 0.90$ V) and the reduction of **2** (at $E_{pc} = 0.01$

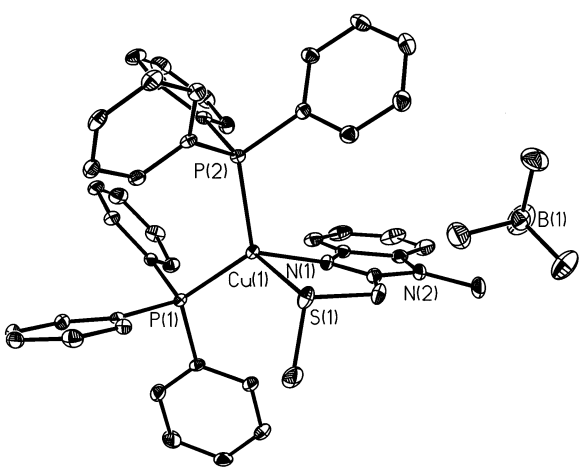


Fig. 1. Molecular structure of $[(\eta^2\text{-mmb})Cu(PPh_3)_2](BF_4)$ (**1**) in the crystal.

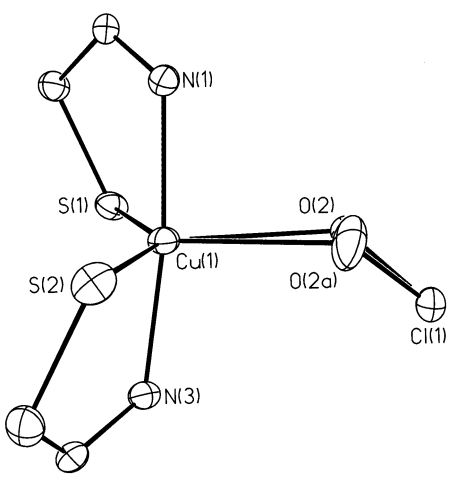


Fig. 3. Coordination of the copper(II) center in **2** · 0.5CH_3OH with both orientations of the disordered perchlorate ligand.

V, all peak potentials versus $Fc^{+/o}$ in CH_3CN/0.1 M Bu_4NPF_6) are irreversible processes due to extensive structural changes, including dissociation. The large difference between these potentials reflects the influence of two π-acidic triorganophosphine ligands in **1** which stabilize the copper(I) state (anodic shift).

Summarizing, we have confirmed that mmb can bind as chelate ligand to both Cu^I and Cu^{II} centers with surprisingly little variation of the metal–S bond length. The structural and spectroscopic results for the copper(II) complex are very similar to those obtained with corresponding tetradentate ligands [2] which suggests the use of this simple ligand in combination with other metal complex fragments.

3. Experimental

3.1. Synthesis

The preparation of the ligand mmb via Phillips condensation has been previously described [7].

3.1.1. [(η^2-mmb)Cu(PPh_3)$_2$](BF_4) (1)

A suspension of 200 mg (0.167 mmol) $[Cu(PPh_3)_4](BF_4)$ and 32 mg (0.166 mmol) mmb in toluene/chloroform (10:1) was reacted at 80°C for 1 h. Filtration of the hot solution and washing of the solid residue with toluene (2 ml) yielded the crude product which was dissolved in chloroform and reprecipitated with n-pentane to yield 85 mg (59%) of colorless air-stable **1**. Calc. for $C_{46}H_{42}BCuF_4N_2P_2S$ (867.22): C, 63.71; H, 4.88; N, 3.23. Found: C, 63.64; H, 4.88; N, 3.26%.

^1H NMR (CD_3CN) δ: 1.91 (s, 3H, SCH_3), 3.62 (s, 2H, CH_2SCH_3), 3.74 (s, 3H, NCH_3), 7.13–7.56 (m, 34H, CH) ppm. ^{13}C NMR (CD_3CN) δ: 19.1 (SCH_3), 31.3 (NCH_3), 32.8 (CH_2SCH_3), 111.8, 119.2 (*C*-5,6 mmb), 123.8, 124.4 (*C*-4,7 mmb), 129.9 (d, $J_{CP} = 9.0$ Hz, PPh_3), 131.3 (s, PPh_3), 133.7 (d, $J_{CP} = 28.1$ Hz, PPh_3), 134.3 (d, $J_{CP} = 14.9$ Hz, PPh_3), 137.9, 140.7 (*C*-3a,7a mmb), 153.7 (*C*-2 mmb) ppm.

UV–Vis (CH_3CN) $\lambda_{max}(\varepsilon)$: 287(sh), 270(sh), 259 (27 000 M^{-1} cm^{-1}) nm.

3.1.2. [(η^2-mmb)$_2$Cu(η^1-ClO_4)](ClO_4) (2)

A solution of 83 mg (0.432 mmol) mmb in 6 ml CH_3OH was slowly added to 80 mg (0.216 mmol) $Cu(ClO_4)_2 \cdot 6H_2O$, dissolved in 6 ml CH_3OH. Within 24 h a greenish precipitate is formed which is collected by filtration, washed with 20 ml of n-pentane and dried under vacuum to yield 115 mg (82%) of green **2**. The compound is soluble in DMF, CH_3CN and CH_3NO_2 but insoluble in other conventional solvents. Calc. for $C_{20}H_{24}Cl_2CuN_4O_8S_2$ (647.01): C, 37.13; H, 3.74; N, 8.66. Found: C, 37.13; H, 3.74; N, 8.58%. UV–Vis (CH_3CN) $\lambda_{max}(\varepsilon)$: 750(sh), 666 (560), 358 (3200), 281 (16 000), 273 (17 000), 268(sh), 254 (15 000 M^{-1} cm^{-1}) nm.

3.2. Instrumentation

EPR spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer. UV–Vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in acetonitrile/0.1 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.

3.3. Crystallography

Single crystals of **1** were obtained through slow cooling to 4°C of a chloroform/n-pentane solution (1:1). Single crystals of $\mathbf{2} \cdot 0.5CH_3OH$ were synthesized by slow interdiffusion of cold (4°C), methanolic solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and mmb in methanol through a porous glass frit.

Reflections were collected on a Siemens P3 diffractometer at 173 K with graphite-monochromated Mo Kα radiation (ω-scans). The structures were solved by direct methods using the SHELXTL-PLUS package [18], the refinement was carried out with SHELXL-93 [19] employing full-matrix least-squares methods. In the center of the unit cell of the Cu^{II} complex the space allows for occupation by only one methanol molecule which is disordered on two positions. For $\mathbf{2} \cdot 0.5CH_3OH$, the coordinated perchlorate was also found to be disordered (ratio 51:49). Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms were added to the structure model on calculated positions with isotropic temperature factors 20% (CH) or 50% (CH_3) higher than those of the corresponding carbon atoms.

4. Supplementary material

A full list of data collection and refinement details, tables of positional parameters for all atoms, bond distances and angles, anisotropic temperature factors, as well as calculated and observed structure factor amplitudes, have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-410009 for $[Cu(mmb)(PPh_3)_2](BF_4)$ (**1**) and CSD-410010 for

$[Cu(mmb)_2](ClO_4)_2 \cdot 0.5CH_3OH$ (**2**) and the full journal citation.

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