Synthesis and Structural Characterization of the Copper(II) Complex with 2-(Ethylthiomethyl)-benzimidazole†

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The blue copper proteins (type I) include plastocyanin, azurin, stellacyanin and multiple copper oxidases, etc. The small blue proteins have invariably been found to contain Cu(II); they have an absorption maximum close to 600 nm with an absorption coefficient in the range 3000 to 5000 M^{-1} cm^{-1} and a unique EPR spectrum with a small hyperfine coupling constant [1]. The redox potential of the type I site is exceptionally high compared to Cu(II)/Cu(I) in aqueous solution [2]. The high resolution X-ray structures of poplar plastocyanin [3] and of *Pseudomonas* azurin [4] were published in 1978. The copper atom in plastocyanin and azurin is surrounded by two coordinating imidazole nitrogen atoms of histidine, a thioether sulfur atom of methionine and a thiolate sulfur atom of cysteine in a distorted tetrahedral arrangement. The biological role of copper ions in the blue single copper proteins is that of electron mediator. None of the above spectral properties has been successfully reproduced in low-molecular-weight Cu(II) complexes [2]. Recent works have shown that the model compounds were designed by incorporating thioether donor(s) in a multidentate ligand, and varying the relative positions of the thioether sulfurs in the ligand to control the stereochemistry of the complexes [5–11]. We report the synthesis of a new bidentate ligand, 2-(ethylthiomethyl)benzimidazole (etmb), and the determination of the crystal structure of $Cu(etmb)_2Cl_2$ by the X-ray method.

Experimental

The ligand 2-(ethylthiomethyl)benzimidazole (etmb) was prepared by reaction of ethylthioacetic acid and *o*-phenylene diamine in 4 mol dm^{-3} hydrochloric acid solution. The solution was refluxed for 18 h. Addition of cold concentrated NH_4OH to the residue gave a solid which was recrystallized twice from 60% EtOH to give colorless crystals of 2-CH_3CH_2–S–CH_2–Z (Z = benzimidazolyl). The complex $Cu(etmb)_2Cl_2$ was formed by reaction of etmb and $CuCl_2 \cdot 2H_2O$ in the molar ratio 2:1 in MeOH–EtOH. Recrystallization from MeOH–EtOH afforded the blue–green crystalline complex $Cu(etmb)_2Cl_2$.

Results and Discussion

$Cu(etmb)_2Cl_2$ crystallizes in the monoclinic space group $P2_1/C$ with $a = 9.707(1)$, $b = 14.977(2)$, $c = 8.525(1)$ Å, $\beta = 112.03(1)°$, $V = 1148.8$ Å^3 and $Z = 2$. The final residual value of R was 0.041 for 1488 reflections ($I \geqslant 3\sigma(I)$).

Positional parameters are given in Table I and bond lengths and bond angles are given in Tables II and III, respectively. In the crystals of $Cu(etmb)_2Cl_2$ the coordination geometry around Cu(II) is best described as distorted octahedral with two benzimidazole nitrogen atoms and two chloride ions occupy-

TABLE I. Positional Parameters and their Estimated Standard Deviations

Atoms	*x*	*y*	*z*	*B* (Å^2)
Cu	1.000	0.000	1.000	1.96(2)
Cl	1.0911(2)	0.0846(1)	0.8320(2)	2.82(3)
S	1.2541(2)	0.0756(1)	1.2938(2)	3.24(4)
N(1)	0.9136(6)	0.1087(3)	1.0643(6)	2.1(1)
N(2)	0.9166(6)	0.2366(4)	1.1932(8)	3.0(1)
C(1)	1.2054(9)	0.0596(6)	1.478(1)	4.3(2)
C(2)	1.274(1)	−0.0278(7)	1.561(1)	5.9(3)
C(11)	0.7684(7)	0.1303(4)	1.0414(7)	1.9(1)
C(12)	0.6351(7)	0.0860(5)	0.9588(8)	2.4(1)
C(13)	0.5068(8)	0.1242(5)	0.9590(9)	3.1(2)
C(14)	0.5113(8)	0.2061(6)	1.0414(9)	3.6(2)
C(15)	0.6387(8)	0.2505(5)	1.122(1)	3.5(2)
C(16)	0.7682(7)	0.2115(5)	1.1207(8)	2.6(1)
C(17)	0.9996(7)	0.1774(5)	1.1561(8)	2.5(1)
C(18)	1.1635(8)	0.1803(5)	1.2129(9)	3.1(2)

TABLE II. Bond Lengths (Å)

Cu–Cl	2.322(2)	N(2)–C(17)	1.345(10)
Cu–S	3.001(2)	C(1)–C(2)	1.521(13)
Cu–N(1)	2.000(5)	C(11)–C(12)	1.388(8)
S–C(1)	1.814(10)	C(12)–C(13)	1.372(11)
S–C(18)	1.803(7)	C(13)–C(14)	1.406(11)
N(1)–C(11)	1.386(8)	C(14)–C(15)	1.345(10)
C(11)–C(16)	1.393(9)	C(15)–C(16)	1.390(11)
N(1)–C(17)	1.336(8)	C(17)–C(18)	1.482(10)
N(2)–C(16)	1.389(9)		

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TABLE III. Bond Angles (deg)

Cl–Cu–S	85.70(6)	C(11)–C(12)–C(13)	118.3(6)
Cl–Cu–N	91.2(2)	C(16)–N(2)–C(17)	108.7(6)
S–Cu–N(1)	76.2(1)	S–C(1)–C(2)	107.9(7)
Cu–S–Cl	105.8(3)	N(2)–C(16)–C(11)	105.2(6)
Cu–S–C(18)	83.0(2)	N(1)–C(11)–C(16)	108.8(5)
C(1)–S–C(18)	101.4(4)	C(11)–C(16)–C(15)	122.6(6)
N(1)–C(11)–C(12)	131.7(6)	C(12)–C(11)–C(16)	119.5(6)
Cu–N(1)–C(11)	131.2(4)	S–C(18)–C(17)	112.5(5)
Cu–N(1)–C(17)	121.7(5)	C(12)–C(13)–C(14)	120.4(6)
N(1)–C(17)–N(2)	110.5(6)	C(13)–C(14)–C(15)	122.5(8)
C(11)–N(1)–C(17)	106.9(6)	C(14)–C(15)–C(16)	116.6(7)
N(1)–C(17)–C(18)	126.4(7)	N(2)–C(16)–C(15)	132.2(7)
N(2)–C(17)–C(18)	123.1(6)		

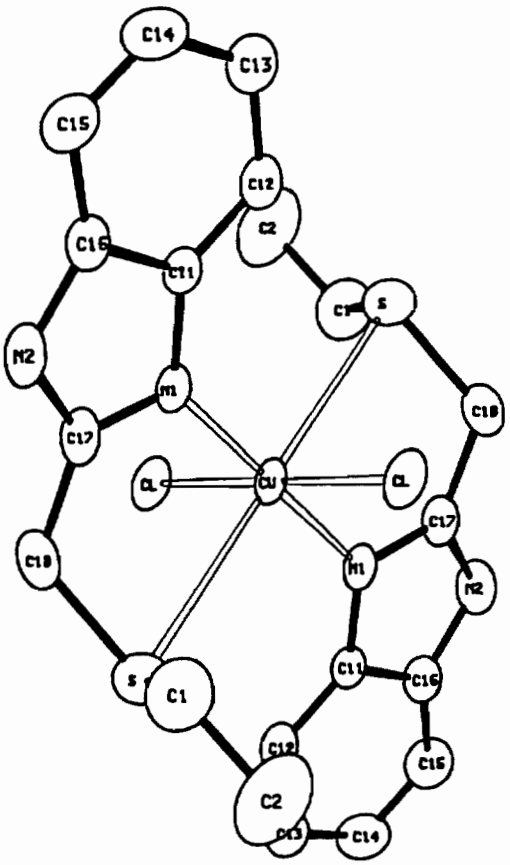

Fig. 1. ORTEP drawing of $Cu(etmb)_2Cl_2$.

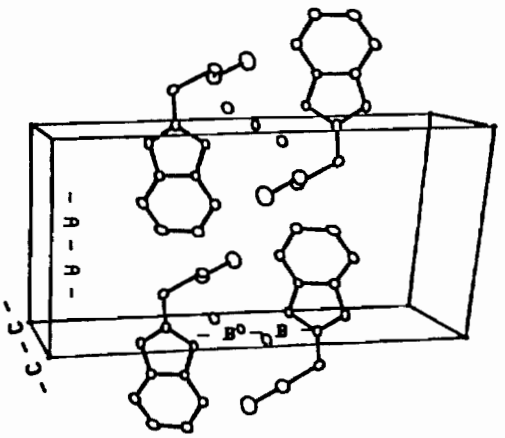

Fig. 2. Drawing of the unit cell contents of $Cu(etmb)_2Cl_2$.

ing equatorial positions and two thioether sulfur atoms in the two axial positions. The structure and unit cell of $Cu(etmb)_2Cl_2$ are shown in Figs. 1 and 2.

The N_2Cl_2 and N_2S_2 units are planar. The Cu–N bond length of 2.000(5) Å and Cu–Cl bond length of 2.322(2) Å are in good agreement with analogous interatomic distances in other published compounds [7, 9–11]. The Cu–S bond length of 3.001(2) Å is an apical Cu(II)–thioether bond. A Cu–thioether bond of similar length (2.90 Å) has been reported for plastocyanin [12]. The only other known examples of apical Cu(II)–S interactions are those in Cu–thioether (2.824(5) Å) [13], apical Cu–thiourea (2.943(1), 2.927(1) Å) [14] and apical Cu–disulfide (3.057(10), 3.138(9)) [15], (3.16(1), 3.28(1) Å) [16]. Finally, the bond lengths of $Cu(etmb)_2Cl_2$ are very similar to those of $Cu(bidhp)Cl_2$: Cu–Cl, 2.395 and 2.457 Å; Cu–S, 2.886 and 2.970 Å; Cu–N, 1.949 and 1.955 Å [17].

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