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Synthesis and X-ray Diffraction Analysis of {Perchlorato-bis[benzimidazole-2-*N*-(4-methoxyphenyl)carbothioamidato]copper(III)} Hydroperchlorate

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Abstract—Conditions for the formation of the complex $[CuL_2(ClO_4)] \cdot HClO_4$ (where L is the deprotonated molecule of benzimidazole-2-*N*-(4-methoxyphenyl)carbothioamide) are determined and its crystal and molecular structures are studied by X-ray diffraction analysis.

INTRODUCTION

An interest in organic compounds containing N,S-donor sites has considerably increased recently. Complexes containing these sites are of great significance in modern bioinorganic chemistry, since they can be used to obtain stereochemically fixed structures and models of active sites of non-heme metalloproteins [1, 2]. For instance, the polynuclear complexes of trivalent copper, which can be used also as the functional model systems of allosteric metalloenzymes, were studied in detail [3].

We have previously obtained complexes CuL_2 and $[Cu(HL)X_2]$ based on arylamides of benzimidazole-2-thiocarboxylic acid (HL) [4]. However, the synthesis of the aforementioned complexes using perchloric acid in an anhydrous alcohol medium gave trivalent copper complexes instead of the expected copper(II) complexes. The synthesis of such complexes is not described in the literature. This work deals with the synthesis and X-ray diffraction analysis of the complex $[CuL_2(ClO_4)] \cdot HClO_4$ (**I**) prepared by the oxidation of the CuL_2 chelate (**II**) with air oxygen on heating in an anhydrous alcohol medium in the presence of excess $HClO_4$. A possible specific bioactivity of the complex is also studied.

EXPERIMENTAL

The starting thioamide HL was synthesized according to a known procedure [5]. Anhydrous $HClO_4$ was synthesized by the procedure described in [6]. Copper(II) monochloroacetate dihydrate (high-purity grade) was used in the synthesis.

Synthesis of {perchlorato-bis[benzimidazole-2-(4-methoxyphenyl)carbothioamidato]copper(III)} hydroperchlorate (I). A suspension of CuL_2 was prepared by reacting hot solutions of HL (1.41 g, 5 mmol) in anhydrous EtOH (70 ml) and $Cu(ClCH_2COO)_2 \cdot 2H_2O$ (0.72 g, 2.5 mmol) in anhydrous CH_3OH (30 ml). A solution of anhydrous $HClO_4$ was obtained from 69% $HClO_4$ (2.63 ml), HOAc (6 ml), and Ac_2O (8 ml) and added to the suspension of CuL_2. As a result, the reaction mixture became very hot and the CuL_2 precipitate dissolved. A yellow–green solution that formed was heated for another 10 min, slowly cooled to room temperature, and allowed to stand for 2 h. Black crystals precipitated were filtered off, washed several times with ethanol to pH ~ 7, and dried in air. The yield was 1.70 g (82%), and the explosion temperature was 235°C.

For $C_{30}H_{25}Cl_2N_6O_{10}S_2Cu$			
anal. calcd. (%):	N, 10.15;	S, 7.74;	Cu, 7.76.
Found (%):	N, 10.52;	S, 7.48;	Cu, 7.52.

X-ray diffraction analysis. Black, well faced crystals of compound **I** belong to the triclinic crystal system: $a = 12.710(3)$, $b = 16.370(3)$, $c = 8.498(2)$ Å, $\alpha = 100.34(3)°$, $\beta = 91.43(3)°$, $\gamma = 104.50(3)°$, $V = 1679.5(6)$ Å^3, $M = 828.12$, ρ(calcd.) $= 1.638$ g/cm^3, $Z = 2$, space group $P\bar{1}$.

A set of experimental reflections was obtained on an automated four-circle KM-4 (KUMA Diffraction) diffractometer with χ geometry using the $\omega/2\theta$ scan mode with the monochromatized MoK_α radiation ($2\theta \le 50°$). The total number of independent reflections measured was 5945. No correction for absorption was applied ($\mu = 1.001$ mm^{-1}).

The structure was solved by the direct method followed by a series of electron density syntheses. Hydrogen atoms of the methyl groups were specified geometrically. The full-matrix anisotropic refinement of non-

Table 1. Coordinates ($\times 10^4$) and isotropic thermal parameters (U_{equiv}, $\times 10^3$) of atoms in the crystal structure of complex **I**

Atom	ι	y	z	U_{equiv}, Å^2	Atom	ι	y	z	U_{equiv}, Å^2
Cu(1)	–1373(1)	–2558(1)	–302(1)	43(1)	C(23)	2175(5)	–1217(4)	–3120(7)	61(2)
Cl(1)	–1064(1)	–1410(1)	3625(2)	56(1)	C(24)	2643(6)	–1779(5)	–2579(11)	95(2)
S(1)	417(1)	–2288(1)	–1022(2)	56(1)	C(25)	3646(6)	–1872(5)	–3162(11)	99(3)
S(2)	–3189(1)	–3217(1)	–1247(2)	53(1)	C(26)	4118(6)	–1400(6)	–4209(10)	91(2)
N(1)	–1379(3)	–3649(2)	280(5)	41(1)	C(27)	3652(7)	–835(7)	–4735(11)	117(3)
N(2)	–1362(3)	–1458(2)	–837(5)	42(1)	C(28)	2704(6)	–734(6)	–4186(10)	96(3)
N(3)	–2116(3)	–5000(2)	401(5)	45(1)	C(29)	–8643(5)	–6471(4)	–5374(7)	64(2)
N(4)	–673(3)	–323(3)	–1891(5)	49(1)	C(30)	5563(8)	–1985(7)	–4441(15)	140(4)
N(5)	–3977(3)	–4928(2)	–1583(5)	44(1)	Cl(2)	6382(1)	2804(1)	–1040(3)	97(1)
N(6)	1176(4)	–1027(3)	–2636(5)	53(1)	O(7)	6416(4)	3375(4)	–2127(11)	148(3)
O(1)	–1635(5)	–2095(3)	2449(5)	104(2)	O(8)	7048(5)	2286(4)	–1498(9)	133(2)
O(2)	–1438(6)	–1559(4)	5085(6)	139(3)	O(9)	6813(10)	3291(4)	448(10)	247(6)
O(3)	–1186(5)	–630(3)	3325(8)	125(2)	O(10)	5367(6)	2268(5)	–995(14)	208(5)
O(4)	36(6)	–1356(5)	3616(13)	191(4)	H(3)	–2575	–5496	247	53
O(5)	–7929(3)	–5640(2)	–5168(5)	61(1)	H(4)	–221	39	–2331	58
O(6)	5143(5)	–1410(5)	–4759(9)	138(2)	H(4)	–4891	–3872	–2929	67
C(1)	–2237(4)	–4310(3)	–148(6)	41(1)	H(5)	–6572	–4243	–4413	75
C(2)	–3193(4)	–4221(3)	–1056(6)	41(1)	H(7)	–7110	–6658	–3726	60
C(3)	–4997(4)	–5053(3)	–2448(6)	40(1)	H(8)	–5442	–6286	–2222	58
C(4)	–5330(4)	–4432(3)	–3089(7)	56(2)	H(10)	–899	–5800	2165	74
C(5)	–6338(5)	–4657(3)	–3985(8)	63(2)	H(11)	749	–5054	3508	84
C(6)	–6982(4)	–5487(3)	–4231(6)	48(1)	H(12)	1573	–3662	3290	77
C(7)	–6667(4)	–6100(3)	–3576(7)	50(1)	H(13)	679	–2903	1898	67
C(8)	–5662(4)	–5873(3)	–2674(6)	48(1)	H(19)	–1968	827	–2074	74
C(9)	–1116(4)	–4765(3)	1260(6)	48(1)	H(20)	–3672	616	–1063	87
C(10)	–593(5)	–5226(4)	2122(7)	62(2)	H(21)	–4365	–536	154	88
C(11)	389(5)	–4780(4)	2887(8)	70(2)	H(22)	–3394	–1549	334	71
C(12)	884(5)	–3928(4)	2784(8)	64(2)	H(24)	2312	–2098	–1840	114
C(13)	365(4)	–3475(4)	1944(7)	55(1)	H(25)	3978	–2261	–2818	119
C(14)	–644(4)	–3914(3)	1173(6)	44(1)	H(27)	3985	–517	–5473	140
C(15)	414(4)	–1416(3)	–1813(6)	45(1)	H(28)	2395	–332	–4528	116
C(16)	–515(4)	–1055(3)	–1523(6)	43(1)	H(29A)	–9276	–6500	–6044	95
C(17)	–2114(4)	–966(3)	–748(6)	46(1)	H(29B)	–8860	–6592	–4348	95
C(18)	–1688(4)	–259(3)	–1436(6)	49(1)	H(29C)	–8278	–6888	–5871	95
C(19)	–2255(5)	360(3)	–1592(8)	62(2)	H(30A)	6253	–1931	–4903	210
C(20)	–3260(5)	227(4)	–987(9)	73(2)	H(30B)	5088	–2540	–4879	210
C(21)	–3685(5)	–475(4)	–259(9)	74(2)	H(30C)	5669	–1923	–3299	210
C(22)	–3109(4)	–1080(3)	–143(8)	59(2)					

Table 2. Main bond lengths and bond angles in structure **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(2)	1.931(4)	N(2)–C(16)	1.322(6)
Cu(1)–N(1)	1.935(4)	N(2)–C(17)	1.392(6)
Cu(1)–S(1)	2.326(2)	N(3)–C(1)	1.337(6)
Cu(1)–S(2)	2.342(2)	N(3)–C(9)	1.380(6)
Cu(1)–O(1)	2.383(5)	N(4)–C(16)	1.351(6)
Cl(1)–O(2)	1.380(5)	N(4)–C(18)	1.380(7)
Cl(1)–O(4)	1.379(7)	N(5)–C(2)	1.321(6)
Cl(1)–O(3)	1.391(5)	N(5)–C(3)	1.425(6)
Cl(1)–O(1)	1.391(5)	N(6)–C(15)	1.311(6)
S(1)–C(15)	1.684(5)	N(6)–C(23)	1.433(7)
S(2)–C(2)	1.680(5)	Cl(2)–O(8)	1.359(6)
N(1)–C(1)	1.320(6)	Cl(2)–O(10)	1.373(6)
N(1)–C(14)	1.386(6)	Cl(2)–O(9)	1.386(9)
Cl(2)–O(7)	1.421(6)		
Angle	ω, deg	Angle	ω, deg
N(2)Cu(1)N(1)	178.85(18)	C(2)N(5)C(3)	130.8(4)
N(2)Cu(1)S(1)	85.66(13)	C(15)N(6)C(23)	131.0(5)
N(1)Cu(1)S(1)	94.48(13)	Cl(1)O(1)Cu(1)	132.9(3)
N(2)Cu(1)S(2)	95.33(13)	N(1)C(1)N(3)	111.5(4)
N(1)Cu(1)S(2)	85.23(12)	N(1)C(1)C(2)	120.4(4)
S(1)Cu(1)S(2)	144.05(7)	N(3)C(1)C(2)	127.9(4)
N(2)Cu(1)O(1)	93.18(18)	N(5)C(2)C(1)	117.2(4)
N(1)Cu(1)O(1)	85.74(18)	N(5)C(2)S(2)	126.8(4)
S(1)Cu(1)O(1)	116.67(15)	C(1)C(2)S(2)	116.0(4)
S(2)Cu(1)O(1)	99.18(15)	N(6)C(15)C(16)	117.3(4)
C(15)S(1)Cu(1)	96.87(18)	N(6)C(15)S(1)	126.2(4)
C(2)S(2)Cu(1)	97.40(17)	C(16)C(15)S(1)	116.5(4)
C(1)N(1)C(14)	107.2(4)	N(2)C(16)N(4)	110.8(4)
C(1)N(1)Cu(1)	119.7(3)	N(2)C(16)C(15)	120.6(4)
C(14)N(1)Cu(1)	133.1(3)	N(4)C(16)C(15)	128.6(5)
C(16)N(2)C(17)	107.1(4)	O(8)Cl(2)O(10)	106.2(5)
C(16)N(2)Cu(1)	119.0(3)	O(8)Cl(2)O(9)	106.3(7)
C(17)N(2)Cu(1)	133.8(3)	O(10)Cl(2)O(9)	113.1(6)
C(1)N(3)C(9)	107.2(4)	O(8)Cl(2)O(7)	109.3(5)
C(16)N(4)C(18)	107.9(4)	O(10)Cl(2)O(7)	113.7(5)
O(9)Cl(2)O(7)	107.9(5)		

Table 3. Conditions for synthesis and the yield of the $[CuL_2(ClO_4)] \cdot HClO_4$ complex (**I**) in an anhydrous medium

No.	Reaction medium	Molar ratio of reactants	Concentration of $HClO_4$, wt %	Time, h	Yield, %
		$HL : CuX_2 : HClO_4$			
1	EtOH + MeOH + HOAc	2 : 1 : 16	100*	0.7	93
2	EtOH + MeOH + HOAc	2 : 1 : 2	100*	0.2	82
3	EtOH** + MeOH**	2 : 1 : 13	30	5.0	92
4	IPA*** + MeOH	2 : 1 : 10	69	5.0	85
5	EtOH + MeOH	2 : 1 : 16	69	1.0	70
6	EtOH + MeOH	1 : 1 : 20	69	1.5	

* Anhydrous $HClO_4$ was preliminarily prepared by a described procedure [6].

** Alcohols with concentration 95 wt %.

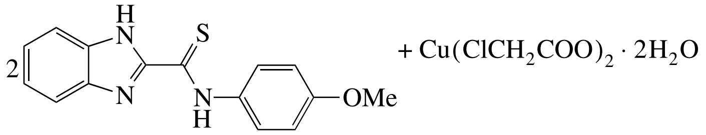
*** IPA is isopropyl alcohol with concentration 98 wt %.

hydrogen atoms by the least-squares method was completed at $R = 0.0462$ for 2768 reflections with $I \geq 2\sigma(I)$; GOOF = 0.928.

The coordinates of atoms and their temperature factors are presented in Table 1. The bond lengths and bond angles are presented in Table 2. All calculations were performed with the SHELX97 programs [7].

RESULTS AND DISCUSSION

Complex **I** was synthesized via the following scheme:



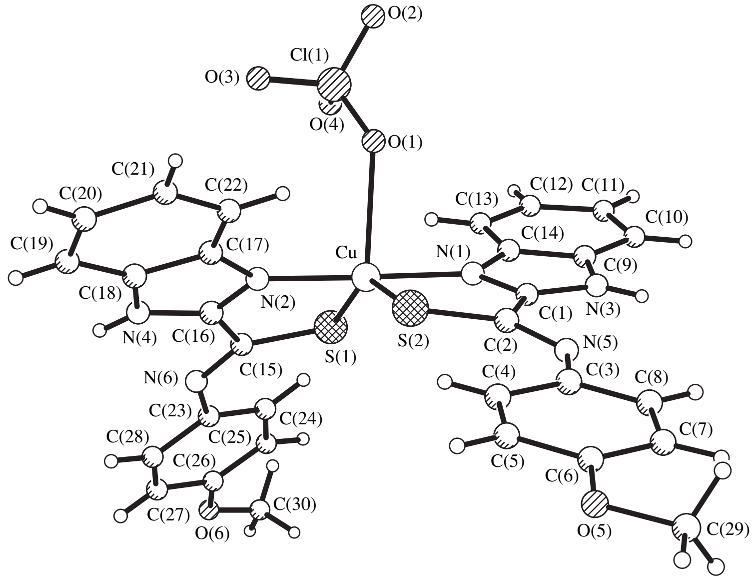
$$\xrightarrow[-2ClCH_2COOH;\ -2H_2O]{} \underset{(\mathbf{II})}{[CuL_2]} \xrightarrow[-H_2O]{+2HClO_4;\ +O_2} \underset{(\mathbf{I})}{[CuL_2(ClO_4)] \cdot HClO_4}.$$

Evidently, compound **I** is formed through the step of formation of chelate **II**, which is oxidized with air oxygen on the subsequent refluxing with $HClO_4$ in an anhydrous alcohol medium to the final product **I**. In complex **I**, the trivalent state of copper is likely to be stabilized due to the coordination of two bulky deprotonated thioamide ligands (chelate effect) and ClO_4^- anion by the central atom. This agrees with the previously published data showing that the described S- and S,N-containing thiolates, thiophosphates, and dithiocarbamates [8], which also form heterovalent Cu(III)/Cu(II) complexes [9], are organic ligands with a pronounced tendency toward stabilization of the Cu^{3+} ion in coordination compounds.

We found that the reaction carried out in an argon atmosphere (refluxing for 2 h) only yielded complex **II**, which forms complex **I** after its subsequent dissolution in $HClO_4$ and interaction with air oxygen. It was established that the forced cooling of the reaction mixture sharply inhibited the dissolution of CuL_2 and formation of complex **I**. This agrees with our previous conclusion that only the bivalent copper complex $[Cu(HL)X_2]$ is formed in a similar reaction system under less rigid conditions (without refluxing and with a smaller excess of $HClO_4$) [4, 10].

The conditions for complex **I** formation studied in this work are presented in Table 3.

Thus, compound **I** is formed when the reaction mixture contains molecular oxygen, the stoichiometric ratio of the reactants and excess $HClO_4$ ($HL : CuX_2 : HClO_4 = 2 : 1 : (12–16)$), and when an anhydrous alcohol or alcohol-acetic medium is used. When the process is homogenized and CuL_2 is rapidly dissolved, the reaction terminates for 0.2–0.7 h (Table 3, entries 1 and 2), which corresponds to the highest yield of complex **I**. A decrease in the stoichiometric amount of perchloric



General view of the molecular complex **I**.

acid (Table 3, entry 4) and the use of an alcohol aqueous medium decrease the yield of complex **I**. A general tendency is an increase in the yield of complex **I** with an increase in the reaction time (Table 2, entries 2 and 3).

The structural units of crystal **I** are molecular complexes of trivalent copper $[CuL_2(ClO_4)]$ (see figure) and perchloric acid molecules. Two bidentate chelate thioamide ligands are bound to the Cu(III) atom through the sulfur and nitrogen atoms of the benzimidazole fragment to form *trans*-arranged planar five-membered metal cycles. The O(1) atom of the perchlorate anion completes the coordination of the copper atom to a distorted square pyramide. The S(1)CuS(2) angle is equal to 144.05°.

The Cambridge Structural Database contains no examples for Cu(III) complexes with S- and N-chelating ligands; however, all bonds in the coordination polyhedron of complex **I** are typical of similar bonds of trivalent copper. The bonds in two crystallographically independent ligands L are virtually the same as the localized N(1)=C(1) and N(5)=C(2) double bonds in one ligand and similar bonds in another ligand. The benzimidazolethioamide group with the S(2) atom is planar as a whole, while in a group with the S(1) atom, the orientation of the methoxyphenyl fragment is characterized by a torsion angle C(15)N(6)C(23)C(24) of −12.2°, which is probably a consequence of the packing effect. In crystal **I**, the complexes are united by intermolecular hydrogen bonds of the $(L)N{-}H\cdots O(ClO_4)$ type $(N(4)\cdots O(3)$ 2.91 Å, the angle N(4)H(4)O(3) 158°). The N(3) atom forms an $N(3){-}H(3)\cdots O(9)$ hydrogen bond with the oxygen atom of perchloric acid $(N(3)\cdots O(9)$ 2.79 Å, angle N(3)H(3)O(9) 161°). An $O(7){-}H\cdots N(5)$ hydrogen bond between the OH group of perchloric acid and nitrogen atom of the complex is evidently formed in crystal **I** $(O(7)\cdots N(5)$ 2.90 Å). The hydrogen atom of perchloric acid is not localized; however, it is most likely to lie at the O(7) atom, because the Cl(2)–O(7) distance (1.420 Å) is the longest of the four Cl–O bonds.

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