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# Direct Methylation of Bis(benzimidazole-2-*N*-phenylcarbothioamidato)copper(II)

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**Abstract**—Methylation of the coordinated heterocyclic thioamide ligand with dimethyl sulfate is studied. When boiled in dimethyl sulfate, bis(benzimidazole-2-*N*-phenylcarbothioamidato)copper(II) forms copper(II) complexes containing *N*-phenylbenzimidazole-2-(S-methylcarboisothioamide). The mechanism of this process is considered, and the reaction products are isolated and identified.

## INTRODUCTION

Only few works have been devoted to the complexation of isothioamide ligands with transition-metal ions [1, 2], evidently, due to the difficulty of their synthesis and isolation in the solid state. For example, the authors of [3] did not succeed in selecting optimum conditions and in isolating the expected complex compounds when they studied the reaction of aliphatic and aromatic isothioamides with potassium tetrachloroplatinate [3].

In this work, we studied the direct methylation of the Cu(II) complex containing benzimidazole-2-*N*-phenylcarbothioamide ($HL^1$) $CuL^1_2$ with dimethyl sulfate and the isolated copper(II) complexes that formed.

## EXPERIMENTAL

The starting $HL^1$ was prepared in accordance with [4]. Complex $CuL^1_2$ was prepared as described in [5].

Aniline was analyzed chromatographically on a Chrom-5 instrument using a column packed with 15% APIEZONE L on Inerton N-AW, the temperature of the column being 70–200°C. The temperature was programmed from 70 to 150°C with a heating rate of 12 K/min and from 150 to 200°C with a heating rate of 20 K/min. The column was stored for 26 min at 200°C. The purity of the compounds synthesized was monitored by thin-layer chromatography on Silufol UV-254 plates using chloroform as an eluent. The chromatograms obtained were developed in iodine vapor.

IR spectra of the compounds in the 400–4000 $cm^{-1}$ interval were recorded on a Specord 75-IR spectrophotometer with samples prepared as pellets with KBr.

**Di(methylsulfato)-N-phenylbenzimidazole-2-(*S*-methylisocarbothioamide)copper(II) ($CuL^2(CH_3SO_4)_2$).** Dimethyl sulfate (2.5 ml) dissolved in methanol (40 ml) was added to $CuL^1_2$ (2.84 g, 0.005 mol), and the reaction mixture was boiled with stirring for 8 h. The obtained dark green precipitate was filtered off, thoroughly washed with ethanol, and dried in air. The yield of the complex was 69% (1.92 g); mp 180–185°C (decomp.).

**Sulfato(benzimidazole-2-*N*-phenylcarbothioamide)copper(II) ($Cu(HL^1)SO_4$).** Copper(II) sulfate (1.25 g, 0.005 mol) dissolved in 44 ml of a mixture of methanol and water (10 : 1) was added to $HL^1$ (1.26 g, 0.005 mol) dissolved in methanol (50 ml). A brown precipitate was formed on stirring of the reaction mixture. Concentrated sulfuric acid (2 ml) was added to the reaction mixture, and the resulting mixture was stirred for 1 h at room temperature and left for a day. The green precipitate that formed was filtered off, washed several times with hot and then with cold methanol, and dried for 5 h in a desiccator at 75°C. The yield of the complex was 98% (2.02 g); mp 269–270°C (decomp.).

***N*-Phenylbenzimidazole-2-(*S*-methylisocarbothioamide) methyl sulfate ($(L^2H)CH_3SO_4$).** Hydrogen sulfide preliminarily dried above $CaCl_2$ was bubbled with vigorous stirring through a suspension of $CuL^2(CH_3SO_4)$ (2.77 g, 0.005 mol) in isopropyl alcohol (60 ml) for 6 h at room temperature. Then, the temperature of the reaction mixture was raised to 65°C and the mixture was stored for another 30 min with bubbling hydrogen sulfide. The precipitate of copper(II) sulfide was filtered off, washed with ethanol, and dried. The yield of the product was 96% (0.46 g). The orange filtrate was treated with activation carbon in the cold, filtered, and concentrated in vacuum to a volume of 7 ml. The orange crystals were filtered off on cooling, washed with ethanol, and dried in air. The yield of the product was 70% (1.32 g); mp 103–105°C.

***N*-phenylbenzimidazole-2-(*S*-methylisocarbothioamide) ($L^2$).** KOH (0.28 g, 0.005 mol) dissolved in methanol (5 ml) was added dropwise with intense stirring and cooling to $(L^2H)CH_3SO_4$ (1.89 g, 0.005 mol) dissolved in isopropyl alcohol (30 ml). The reaction medium was brought to pH ~7. The reaction mixture

**Table 1.** Results of elemental analysis of the synthesized compounds

| Compound | Molecular formula | Content (found/calculated), % | | |
|---|---|---|---|---|
| | | N | S | Cu |
| $CuL^2(CH_3SO_4)_2$ | $C_{17}H_{19}N_3O_8S_3Cu$ | 7.97/7.60 | 17.02/17.39 | 11.12/11.49 |
| $Cu(HL^1)SO_4$ | $C_{14}H_{11}N_3O_4S_2Cu$ | 9.84/10.18 | 15.25/15.53 | 15.04/15.39 |
| $(L^2H)CH_3SO_4$ | $C_{16}H_{17}N_3O_4S_2$ | 11.24/11.07 | 16.45/16.90 | |
| $L^2$ | $C_{15}H_{13}N_3S$ | 15.34/15.72 | 12.25/11.99 | |
| $CuL^2SO_4$ | $C_{15}H_{13}N_3O_4S_2Cu$ | 10.14/9.84 | 14.75/15.02 | 14.40/14.88 |

was diluted with water until a bulky yellow precipitate was formed. The precipitate was filtered off, washed with cool water, and dried in air. The yield of the compound was 95% (1.27 g); mp 165.5–167°C.

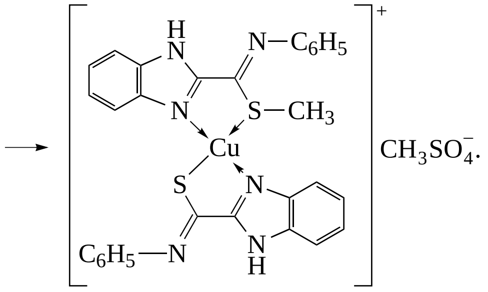
**Sulfato-*N*-phenylbenzimidazole-2-(*S*-methylisocarbothioamide)copper(II) ($CuL^2SO_4$).** Copper(II) sulfate (1.25 g, 0.005 mol) dissolved in a mixture (44 ml) of methanol and water (10 : 1) was added with stirring at room temperature to $L^2$ (1.33 g, 0.005 mol) dissolved in methanol (80 ml). This resulted in precipitation of a dark substance. Concentrated sulfuric acid (0.5 ml) was added to the reaction mixture, and the resulting mixture was stirred for 30 min and stored under these conditions for 12 h. The green precipitate that formed was filtered off, washed several times with hot and then with cold methanol, and dried for 5 h in a desiccator at 75°C. The yield of the complex was 81% (1.73 g); mp > 340°C (with decomp.).

The results of elemental analysis of the synthesized compounds are presented in Table 1.

## RESULTS AND DISCUSSION

The methylation of the $CuL^1_2$ complex on boiling in dimethyl sulfate results, evidently, in the formation of an intermediate,

$CuL^1_2 + (CH_3)_2SO_4$

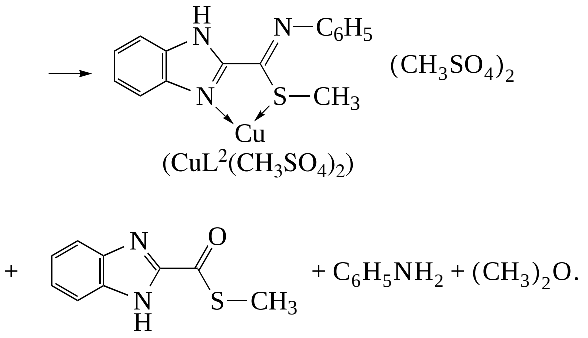


(1)

$([CuL^1L^2]^+)$

The methyl sulfate anion no longer remains the active alkylating agent [6] and acts as an outer-sphere anion in the $[CuL^1L^2]CH_3SO_4$ complex that formed. This is also confirmed by the fact that we failed to alkylate $CuL^1_2$ and $HL^1$ with isobutyl iodide, which is a weaker alkylating agent, under similar conditions. The intermediate formed as dark brown crystals was not isolated as an individual compound but was further boiled to give a $CuL^2(CH_3SO_4)_2$ complex, aniline, and methyl benzimidazole-2-thiocarboxylate:

$[CuL^1L^2]CH_3SO_4 + (CH_3)_2SO_4 + 2CH_3OH$



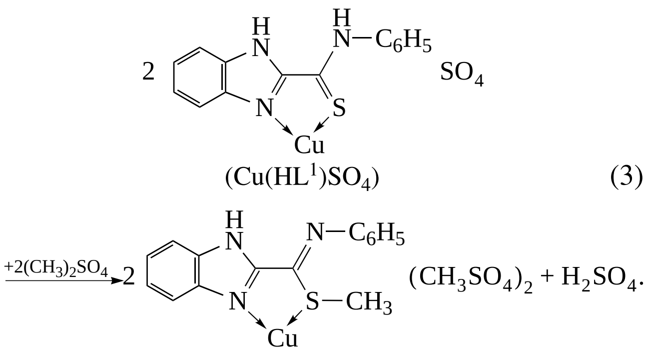
(2)

$(CuL^2(CH_3SO_4)_2)$

Complexes with the general formula $CuL_2$ with heterocyclic thioamide ligands, as a rule, have square-planar *trans*-isomeric structure and are crystalline brown or even black substances [7]. The dark green *S*-methylated $CuL^2(CH_3SO_4)_2$ complex can be presented as a compound with tetrahedral configuration.

Heterocyclic thioamides do not undergo hydrolysis in an acidic medium, and even on heating with strong mineral acids, they form the corresponding salts. However, the chemical activity of a nonmethylated molecule of the thioamide ligand in the composition of the intermediate $[CuL^1L^2]CH_3SO_4$ changes so substantially that the ligand is hydrolyzed to form aniline and methyl benzimidazole-2-thiolcarboxylate.

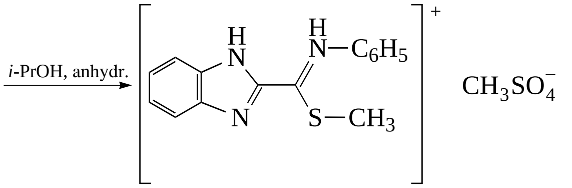
The counter synthesis of the $CuL^2(CH_3SO_4)_2$ complex was also carried out according to the scheme



(Cu(HL¹)SO₄) (3)

The possible alternative formation of the *S*- or *N*-methylated complex was proved by the decomposition of the latter after bubbling hydrogen sulfide in the heterogeneous medium for a long time followed by the isolation and analysis of *N*-phenylbenzimidazole-2-(*S*-methylcarboisothioamide) ($L^2$):

$$CuL^2(CH_3SO_4)_2 + H_2S$$



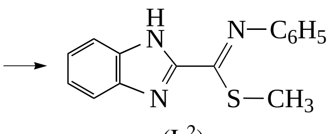
(4)

($L^2H^+$)

$$+ CuS + (CH_3)HSO_4,$$

$$(L^2H)(CH_3SO_4) + KOH$$

(5)

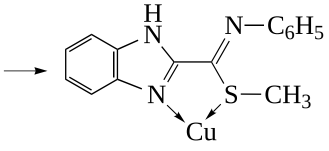


$+ (CH_3)KSO_4 + H_2O.$

($L^2$)

The reaction of the *S*-methylated thioamide ligand $L^2$ with copper(II) sulfate gave a complex, which, unlike $CuL^2(CH_3SO_4)_2$ contained the sulfate anion

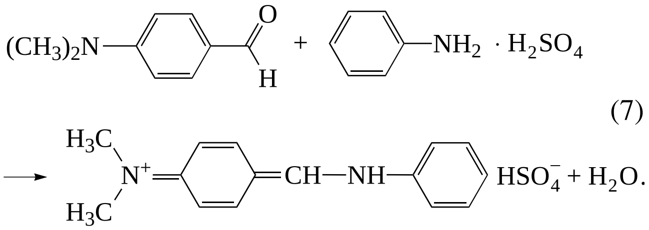
$L^2 + CuSO_4 \longrightarrow$



$SO_4.$ (6)

($CuL^2SO_4$)

The presence in the reaction mixture of the hydrolysis products of the second molecule of the thioamide ligand after the isolation of $CuL^2(CH_3SO_4)_2$ was established by chromatographic analysis and the qualitative reaction of 4-dimethylaminobenzaldehyde for aniline [8]:



(7)

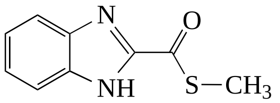
The azomethine salt formed in this reaction has a characteristic bright yellow color. The reaction mixture was neutralized with an alkaline solution to transform aniline into the basic form. Chromatographic analysis of this solution confirmed the presence of aniline in the reaction mixture. It is of interest that the same products of acid-catalyzed hydrolysis of arylated isothioamides were obtained in [9]: aniline and phenyl thiolbenzoate.

Thus, the overall reaction equation of $CuL_2^1$ complex methylation can be presented as

$$CuL_2^1 + 2(CH_3)_2SO_4 + 2CH_3OH$$

$$\longrightarrow CuL^2(CH_3SO_4)_2 + C_6H_5NH_2 + (CH_3)_2O$$

$+$



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The structures of the synthesized compounds were confirmed by their IR spectra. It is known [8, 10–12] that the IR spectra of thioamide ligands contain a band of stretching vibrations ν(NH) in the 3220–3050 $cm^{-1}$ region. However, the spectrum of $HL^1$ exhibits, along with the ν(NH) band of the thioamide group, a band of ν(NH) vibrations of the benzimidazole fragment. In order to assign these vibrations to a particular fragment in the $HL^1$ molecule, we studied the IR spectra of thiobenzanilide ($HL^3$) and *N*-phenylbenzthiazole-2-carbothioamide ($HL^4$) (Table 2). In the spectrum of $HL^3$, the ν(NH) band of the thioamide group lies at 3180 $cm^{-1}$, and the spectrum of $HL^4$ contains two ν(NH) bands at 3285 and 3260 $cm^{-1}$. The spectrum of $HL^1$ exhibits three bands in this region lying at 3356, 3275, and 3256 $cm^{-1}$. We assigned the two low-frequency bands, as in the case of $HL^4$, to vibrations of the NH bond of the thioamide group, and the band at 3356 $cm^{-1}$ was assigned to ν(NH) of the benzimidazole fragment.

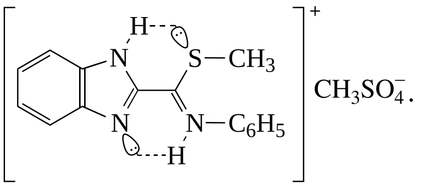
The spectrum of the *S*-methylated ligand $L^2$ contains only the ν(NH) band of the benzimidazole fragment at 3356 $cm^{-1}$ and two $\nu(CH_3)$ bands of the S–$CH_3$ fragment at 2920 and 2853 $cm^{-1}$. The spectrum of $HL^2CH_3SO_4$ also contains two $\nu(CH_3)$ bands of the S–$CH_3$ fragment (2920 and 2840 $cm^{-1}$). The intense broad bands in the 2805–2636 $cm^{-1}$ region in the spectrum of $(HL^2)CH_3SO_4$ can be interpreted as $\nu(CH_3)$ of the methyl sulfate anion and $\nu(N^+H)$ of the thioamide group [13]. The spectrum of this compound does not contain the ν(NH) band of the heterocyclic fragment

**Table 2.** Main vibrational frequencies (cm$^{-1}$) in the IR spectra of thioamide ligands and related complexes and their assignment

| Compound | ν($CH_3$) | ν(NH) | | Vibrations of the C(=S)NH group* | | | | | | Other vibrations |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C(=S)NH | hetero-cycl. | ν(CN) | δ(NH)+ν(CN) | ν(CN) | ν(CN)+ν(C=S) | ν(C=S) | ν(C=S)+ν(CN) | |
| $HL^3$ | | 3180 | | 1533 | 1372 | 1278 | 1198 | 997<br>990 | 768<br>686 | 1588, 1491, 1447, 564, 510 |
| $HL^4$ | | 3260<br>3285 | | 1536 | 1374<br>1316 | 1234 | 1188 | 1000 | 758 | 1590, 1448, 1444, 730, 684, 512 |
| $HL^1$ | | 3256<br>3272 | 3356 | 1540 | 1384 | 1216 | 1138 | 1076 | 754<br>734 | 1597, 1497, 1426, 1360, 1310, 1163 |
| $L^2$ | 2853<br>2920 | | 3356 | 1528 | 1375 | 1296 | 1139 | 948 | 754 | 2955, 1187, 1059, 586 |
| $(L^2H)CH_3SO_4$ | 2840<br>2920 | | 3010 | 1526 | 1397<br>1382 | 1187 | 1116 | 946 | 743 | 2805, 2724, 2636, 1496, 1039, 1066 |
| $Cu(HL^1)SO_4$ | | 3064<br>3150 | 3235 | 1566 | 1388<br>1325 | 1154<br>1120 | 1040 | 972 | 746 | 1595, 1515, 698, 620 |
| $CuL^2SO_4$ | 2945<br>2990 | | 3080 | 1566 | 1330 | 1250<br>1240 | 1115<br>1098 | 970 | 754 | 694, 620, 512 |
| $CuL^2(CH_3SO_4)_2$ | 2945<br>2990 | | 3210 | 1566<br>1506 | 1326 | 1273<br>1258 | 1170 | 1000<br>966 | 760 | 3150, 1602, 977, 546 |

* Vibrations with the maximum contributions are underlined.

typical of the *S*-methylated ligand $L^2$. This is associated with the formation of an intramolecular hydrogen bond [14, 15] and with the shift of this band to 3010 cm$^{-1}$ [16].



The spectra of the $CuL^2(CH_3SO_4)_2$ and $CuL^2SO_4$ complexes exhibit broad intense ν(NH) and ν($CH_3$) bands in the 3235–2940 cm$^{-1}$ region. As a result of complexation they are shifted to low- and high-frequency regions, respectively, as compared to their positions in the spectra of the ligands. The spectra of $CuL^2(CH_3SO_4)_2$ do not contain individual absorption bands of the methyl sulfate anion (similar in symmetry to the hydrosulfate anion) in the region of 1200–1050 cm$^{-1}$, whereas a very strong absorption band characteristic of the sulfate anion [17] was detected at 1098 cm$^{-1}$ in the spectrum of $CuL^2SO_4$.

The considered vibrations in the high-frequency region of the compounds studied are the most characteristic [18] and provide the most clear understanding of methylation of the $CuL_2^1$ complex. The vibrations of the thioamide ligands and related complexes in the region of 1630–510 cm$^{-1}$ have a complicated stretching-deformation nature (Table 2) and for their interpretation we used both our data [7, 10–12] and the data of [18–20].

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