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Structure of a copper(II) bis(chelate) with 1-amino-3-methylbenzimidazole-2-thione salicylidenimine

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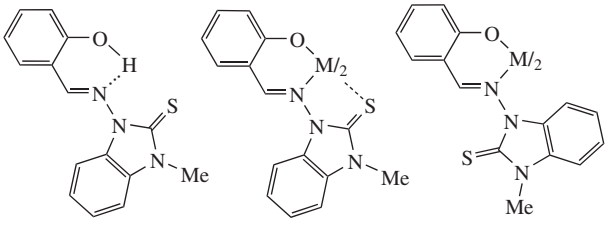
X-ray diffraction data confirm the formation of a CuL_2 complex based on 1-salicylideneimino-3-methylbenzimidazole-2-thione with different coordination modes of ligand binding – N,O,S and N,O.

Copper complexes with a NOS donor environment are of permanent interest as potential models simulating the active centers of non-heme metalloproteins.[1]

Recently, we described novel ligand systems based on the imines of 1-amino-3-methylbenzimidazole-2-thione **1**, whose complexes were attributed to an N_2S(NOS)-donor environment according to spectral data.[2,3] Here, we describe the structure of the copper chelate obtained from salicylideneimine derivative **2** (**3**).†



1 **2** **3**

Ligand system **1** under complex formation with bivalent metal ions can form chelates either with six-coordinated central atoms[4] or with four-coordinated metal ion **3**,[5] and in some cases five-coordinated ones with the one ligand bound by the type **2** and another, by the type **3**.[6]

X-ray data revealed‡ (Figure 1) that the type of coordination of two ligands is fundamentally different within the same molecule of **2** (M = Cu). One ligand (**A**) acts as a tridentate one and coordinates the copper atom by the S(1), O(1) and N(3) atoms, whereas the second one (**B**) is bidentate [involved in the coordination by the atoms O(1′) and N(3′)]. These differences are apparently due to the large volume of the imine molecules encumbering the tridentate coordination of both ligands. Thus, the coordination number of copper in the chelate is five, and the coordination polyhedron of Cu(1) can be described as a distorted

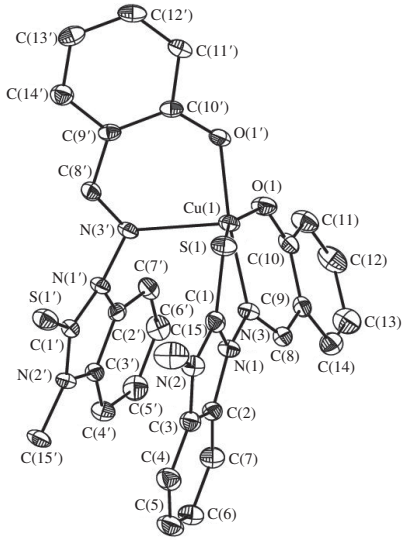


Figure 1 General view of the molecule of compound **2** (M = Cu). Selected bond lengths (Å): Cu(1)–O(1′) 1.899(1), Cu(1)–O(1) 1.939(2), Cu(1)–N(3) 1.970(2), Cu(1)–N(3′) 2.212(2), Cu(1)–S(1) 2.4072(7), O(1)–C(10) 1.283(3), C(1)–N(2) 1.342(3), C(1)–N(1) 1.362(3), C(1)–S(1) 1.687(2), N(1)–N(3) 1.398(3), N(1)–C(2) 1.406(3), N(2)–C(3) 1.390(3), N(3)–C(8) 1.297(3), O(1′)–C(10′) 1.296(3), N(1′)–C(2′) 1.386(3), N(1′)–C(1′) 1.393(3), N(1′)–N(3′) 1.407(2), C(1′)–N(2′) 1.372(3), C(1′)–S(1′) 1.657(2), N(2′)–C(3′) 1.386(3), N(3′)–C(8′) 1.292(3); selected bond angles (°): O(1′)–Cu(1)–O(1) 91.08(7), O(1′)–Cu(1)–N(3) 172.51(8), O(1)–Cu(1)–N(3) 90.23(7), O(1′)–Cu(1)–N(3′) 89.19(7), O(1)–Cu(1)–N(3′) 106.56(7), N(3)–Cu(1)–N(3′) 97.50(8), O(1′)–Cu(1)–S(1) 91.08(5), O(1)–Cu(1)–S(1) 159.76(6), N(3)–Cu(1)–S(1) 85.17(6), N(3′)–Cu(1)–S(1) 93.59(5).

† Synthesis of ligand **1** and complex **2** (M = Cu) was described elsewhere.[1,2]

‡ *Crystallographic data*: at 160 K crystals are monoclinic, space group $P2_1/n$, a = 7.134(2), b = 18.838(4) and c = 20.051(3) Å, β = 93.13(2)°, V = 2690.7(10) Å^3, Z = 4, M = 628.21, d_{calc} = 1.551 g cm^{-3}, μ(MoKα) = = 10.09, F(000) = 1292. The intensities of 8034 reflections were measured on a Syntex $P2_1$ diffractometer at 160 K [λ(MoKα) = 0.71072 Å, $\theta/2\theta$ scanning, $2\theta < 54°$], of which 5870 independent reflections (R_{int} = 0.0074) were used for further processing. The structure was solved by direct methods and refined by the full-matrix least-squares technique in anisotropic-isotropic approximation of F^2. Hydrogen atoms were localized by Fourier synthesis and refined in an isotropic approximation. The final divergence factors wR_2 = 0.0818 and GOF = 0.909 for all independent reflections [R_1 = 0.0336 was calculated against F for 4019 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using the SHELXTL PLUS 5.0 program.[7]

CCDC 1411444 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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trigonal bipyramid: the atoms S(1), O(1) and N(3′) form the equatorial plane, and N(3) and O(1′) are in the axial positions. The deviation of the Cu(1) atom from the equatorial plane is 0.03 Å.

The conformation of the six-membered ring Cu(1)–O(1′)–N(3′)–C(8′)–C(9′)–C(10′) is 'sofa' with a deviation of the atom Cu(1) by 0.516 Å, and for Cu(1)–O(1)–N(3)–C(8)–C(9)–C(10) cycle is 'bath' with the release of C(10) and N (3) atoms of the plane at 0.135 and 0.06 Å, respectively. The conformation of the five-membered metallocycle Cu(1)–S(1)–N(1)–N(3)–C(1) is 'envelope' with the deviation of the Cu(1) atom by 0.63 Å.

The differences in the bond lengths Cu–O [1.939(2) and 1.899(1) Å] and Cu–N [1.970(2) and 2.212(2) Å] in ligands **A** and **B**, respectively, are apparently caused by the trans effect. Variation of the Cu–O and Cu–N bond lengths leads to antibatic changes in the C–O, C–N and N–N bond lengths in ligands **A** and **B**. For example, the reduction of the Cu(1)–O(1′) bond length results in an elongation of the C(10′)–O(1′) bond to 1.296(3) Å as compared with the C(10)–O(10) bond [1.283(3) Å]. Difference in the coordination of ligands **A** and **B** also leads to a rather large variation in bond lengths in the imidazole cycle. In addition to the expected reduction of the C(1′)–S(1′) bond length [1.657(2) Å] in an uncoordinated C=S group, as compared with the coordinated bond C(1)–S(1) [1.687(2) Å], the C–N bonds in ligand **A** are straightened and are much shorter than the corresponding values for ring **B**.

Note that the bicyclic fragments of ligands **A** and **B** are virtually parallel (the dihedral angle is 6°) with distances between the ring planes of ~3.42 Å, which may indicate the presence of intramolecular π–π stacking interactions.

The remaining intra- and intermolecular contacts in the crystals of the compound are close to usual van der Waals distances.

Thus, we found that, as in other complexes of a copper-based tridentate ligand,[8] the copper bis(chelate) of 1-salicylideneimino-3-methylbenzimidazole-2-thione possesses the pentacoordinated central atom (CuN_2O_2S).

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References

1 *Copper Metalloproteins*, eds. R. H. Kretsinger, V. N. Uversky and E. A. Permyakov, Springer, New York, 2013.
2 I. S. Vasilchenko, T. A. Kuz'menko, T. E. Shestakova, R. N. Borisenko, L. N. Divaeva, A. S. Burlov, N. I. Borisenko, G. S. Borodkin, I. E. Uflyand and A. D. Garnovskii, *Arkivoc*, 2005, **vii**, 82.
3 I. S. Vasil'chenko, T. A. Kuz'menko, T. E. Shestakova, R. N. Borisenko, L. N. Divaeva, A. S. Burlov, N. I. Borisenko, I. E. Uflyand and A. D. Garnovskii, *Russ. J. Coord. Chem*., 2005, **31**, 747 (*Koord. Khim*., 2005, **31**, 786).
4 E. K. Beloglazkina, E. S. Barskaya, A. G. Majouga and N. V. Zyk, *Mendeleev Commun*., 2015, **25**, 148.
5 K. A. Lyssenko, A. V. Vologzhanina, Yu. V. Torubaev and Yu. V. Nelyubina, *Mendeleev Commun*., 2014, **24**, 216.
6 A. D. Garnovskii and I. S. Vasil'chenko, *Russ. Chem. Rev.*, 2005, **74**, 193 (*Usp. Khim*., 2005, **74**, 211).
7 G. M. Sheldrick, *SHELXTL PLUS, PC Version, a. System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data*, Rev. 502, Siemens Analytical X-Ray Instruments Inc., 1994.
8 I. S. Vasilchenko, A. S. Antsyshkina, A. S. Burlov, G. G. Sadikov, A. I. Uraev, A. L. Nivorozhkin, D. A. Garnovskii, V. S. Sergienko, V. P. Kurbatov, O. Yu. Korshunov and A. D. Garnovskii, *Russ. J. Inorg. Chem*., 1999, **44**, 1205 (*Zh. Neorg. Khim*., 1999, **44**, 1278).

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