

Syntheses and Structure Determinations of Two Copper(II)–Thione Complexes

Hilde E. Heldal and Jorunn Sletten*

Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

Heldal, H. E. and Sletten, J., 1996. Syntheses and Structure Determinations of Two Copper(II)–Thione Complexes – Acta Chem. Scand. 50: 596–602 © Acta Chemica Scandinavica 1996.

Syntheses and crystal structures of two compounds containing heteroleptic copper(II)–(2,2′-bipyridyl)thione complexes are reported, the thione ligands being 4-amino-1,2,4-triazole-5-thione (atth) and 1-(1′-imidazolin-2′-yl)-imidazolidine-2-thione (imthim), respectively. The imthim ligand resulted from copper(II)-promoted ring fusion of two molecules of imidazolidine-2-thione. Crystals of **1**, [Cu(bpy)(atth)(H₂O)](NO₃)₂·3H₂O, are triclinic, space group *P* $\bar{1}$ $a=7.294(3)$, $b=12.223(6)$, $c=12.428(4)$ Å, $\alpha=108.58(4)$, $\beta=97.26(3)$, $\gamma=97.01(4)^\circ$, $Z=2$. Crystals of **2**, [Cu(bpy)(imthim)(NO₃)](NO₃)·H₂O, are triclinic, space group *P* $\bar{1}$, $a=9.746(1)$, $b=10.370(2)$, $c=12.576(2)$ Å, $\alpha=68.21(1)$, $\beta=68.52(1)$, $\gamma=62.53(1)^\circ$, $Z=2$. The crystal structures at 95 K (**1**) and 103 K (**2**) have been determined by X-ray diffraction methods. Full-matrix least-squares refinements including 3019 and 2595 contributing reflections, respectively, converged at *R*-values of 0.029 (**1**) and 0.034 (**2**). In **1** the copper coordination geometry may best be described as distorted square pyramidal, with the sulfur and the amino nitrogen of the atth ligand and the two bpy nitrogen atoms in the equatorial plane, and a water oxygen in the apical position. In **2** the copper coordination geometry is slightly distorted trigonal bipyramidal, with sulfur, one bpy nitrogen atom and one nitrate oxygen atom in the equatorial plane, and with the second bpy nitrogen atom and an imthim imino nitrogen in the axial positions. Despite the differences in coordination geometries the Cu–S bond distances are almost identical in the two complexes [Cu–S=2.340(1) Å (**1**) and 2.347(1) Å (**2**)]. The thione ligands remain essentially in their thione form in the complexes [S–C=1.692(3) Å and 1.688(3) Å].

The copper centres in type 1 blue copper proteins are known to contain thiolate and thioether groups. It has proved difficult to prepare suitable small 'model' compounds, mainly due to the facile redox reaction converting thiolate and copper(II) to disulfide and copper(I). However, the thiolate function may be stabilized by steric or electronic constraints. Introducing multiple bond character at the donor sulfur and appropriate substituents in the ligand molecule may allow the preparation of stable systems with Cu^{II}–S bonds.^{1,2} It has been pointed out that heterocyclic, unsaturated compounds with thione substituents may be useful sources of ligands for preparing model compounds. While the free ligand may exhibit typical thione character, it may be metal-bonded in its tautomeric thiolate form.^{3–5} Detailed structural data on such compounds are still rather limited.

We have attempted the preparation and structure determination of Cu^{II} complexes with simple, small, heterocyclic thione ligands. The ligands used lack the geometrical constraints necessary to make their complexes true model compounds for the protein active sites.

However, they may give information on to which degree changes in thione/thiolate character occur in this family of ligands upon complexation to copper(II). In this paper the syntheses and structures of two heteroleptic Cu^{II} complexes with neutral, heterocyclic thione ligands are reported. Attempts to isolate the corresponding complexes after deprotonation of the sulfur-containing ligands were not successful.

Experimental

Materials. (2,2′-Bipyridyl)copper(II) nitrate trihydrate and 4-amino-1,2,4-triazole-5-thione (atth) were prepared according to the literature.^{6,7} All other chemicals were obtained from commercial sources, and were used as received.

Preparation of [Cu(bpy)(atth)(H₂O)](NO₃)₂·3H₂O (1**).**

0.25 mmol atth was dissolved in hot water; this solution was added dropwise under stirring to an aqueous solution of 0.5 mmol (2,2′-bipyridyl)copper(II) nitrate, resulting in a bright green solution. A light, colloidal precipitate forming within a few minutes was removed by filtration.

When the green filtrate was cooled in a refrigerator bright green crystals separated. The crystals disintegrated in the course of a few hours if dried in the air, but in the mother liquid they were stable over a period of several months. An X-ray crystallographic structure determination (see below) revealed the identity of compound **1**.

Preparation of [Cu(bpy)(imthim)(NO₃)](NO₃)·H₂O (2). A slurry of 0.4 mmol imidazolidine-2-thione and 0.4 mmol LiOH in water/ethanol was gradually added to a warm ethanolic solution of 0.5 mmol (2,2'-bipyridyl)copper(II) nitrate under constant stirring. A light blue microcrystalline precipitate, formed on cooling the solution, was removed by filtration. On slow evaporation at room temperature green, prismatic crystals separated. An X-ray crystallographic structure determination (see below) revealed the identity of compound **2**.

Crystal structure determinations and refinements. The crystals were sealed and mounted in paratone-n oil. Diffraction data were collected at 95 K (**1**) and 103 K (**2**) with an Enraf-Nonius CAD-4 diffractometer, equipped with a liquid-nitrogen cooling device, using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Crystal parameters and refinement results are compiled in Table 1. A total of 3419 (**1**) and 3571 (**2**) reflections were recorded in the range $2 < \theta < 25^\circ$. Three reference reflections, monitored during each data

collection, decreased by 4.1% (**1**) and 2.0% (**2**). The data were in each case corrected for Lorentz and polarization effects, for linear decay, and for absorption based on Ψ -scan measurements of six reflections [range of transmission factors 99.81–95.47% (**1**) and 99.97–94.72% (**2**)].

The intensity statistics in both cases suggested a centrosymmetric space group. The structures were solved by direct methods,⁸ and refined by full-matrix least-squares methods. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in a difference Fourier map, and were isotropically refined. For compound **1** an extinction parameter was included and adjusted in the final stages of refinement. The refinements, including 3019 (**1**) and 2595 (**2**) reflections with $I > 2\sigma$, converged at $R = 0.029$ and 0.034, respectively.

All calculations were carried out with programs in the MolEN system.⁹ Neutral atomic scattering factors were those of Cromer *et al.*¹⁰ Anomalous scattering terms were included in F_{calc} .¹¹ For non-hydrogen atoms coordinates are listed in Tables 2 and 3, bond distances and angles in Tables 4 and 5. Supplementary material contains coordinates of hydrogen atoms, anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms, hydrogen bond parameters, equations of least-squares planes and structure-factor tables.

Results

Description of the structure of [Cu(bpy)(atth)(H₂O)](NO₃)₂·3H₂O (1). The structure is built of

Table 1. Crystallographic data for [Cu(bpy)(atth)(H₂O)](NO₃)₂·3H₂O (**1**) and [Cu(bpy)(imthim)(NO₃)](NO₃)·H₂O (**2**).

Compound	1	2
Chemical formula	C ₁₂ H ₂₀ CuN ₈ O ₁₀ S	C ₁₆ H ₂₀ CuN ₈ O ₇ S
Formula weight	531.94	531.99
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
$a/\text{\AA}$ ^a	7.294(3)	9.746(1)
$b/\text{\AA}$	12.223(6)	10.370(2)
$c/\text{\AA}$	12.428(4)	12.576(2)
$\alpha/^\circ$	108.58(4)	68.21(1)
$\beta/^\circ$	97.26(3)	68.52(1)
$\gamma/^\circ$	97.01(4)	62.53(1)
$V/\text{\AA}^3$	1026.2(8)	1017.5(3)
Z	2	2
$\rho(\text{calcd})/\text{g cm}^{-3}$	1.721	1.736
$\lambda/\text{\AA}$	0.71073	0.71073
μ/cm^{-1}	12.299	12.308
Max–min transmission (%) ^b	99.81–95.47	99.97–88.25
T/K	95	103
Max. $2\theta/^\circ$	50	50
No. of unique reflections	3499	3571
No. of reflections in refinement, N_0	3019 ($I > 2\sigma$)	2595 ($I > 2\sigma$)
Parameters refined, N_v	370	379
Extinction coefficient	$4.29 \cdot 10^{-8}$	
$R = (\sum F_o - F_c / \sum F_o)$	0.029	0.034
$R_w = ((\sum w(F_o - F_c)^2) / \sum w F_o ^2)^{1/2}$	0.036	0.035
$S = ((\sum w(F_o - F_c)^2) / (N_0 - N_v))^{1/2}$	1.299	1.194
k in weighting scheme ^c	0.04	0.03

^a Cell dimensions based on setting angles of 25 reflections ($17 < 2\theta < 42^\circ$). ^b Empirical absorption correction based on Ψ scans of six reflections. ^c Function minimized $\sum (w(|F_o| - |F_c|)^2)$, $w = 4F_o^2 / (\sigma_c^2 + (kF_o^2)^2)$, where σ_c is the standard deviation in F^2 based on counting statistics alone.

Table 2. Positional parameters of non-hydrogen atoms, compound 1.

Atom	X/a	Y/b	Z/c
Cu	0.11983(4)	0.47979(2)	0.33007(2)
S	0.23682(9)	0.44554(5)	0.49838(5)
O(1)	0.3687(3)	0.1814(2)	0.2260(2)
O(2)	0.6312(3)	0.1272(2)	0.1881(2)
O(3)	0.6091(3)	0.3113(1)	0.2419(2)
O(4)	0.4655(3)	0.7561(2)	0.1661(1)
O(5)	0.5808(3)	0.6952(2)	0.3021(1)
O(6)	0.6760(3)	0.8720(2)	0.3091(2)
O(7)	0.3603(2)	0.4653(1)	0.2331(1)
O(8)	0.0309(3)	0.1619(2)	0.0521(2)
O(9)	0.2340(3)	0.9309(2)	0.1466(2)
O(10)	0.3413(3)	0.1054(2)	-0.0455(2)
N(1)	0.0007(3)	0.3087(2)	0.2619(2)
N(2)	0.0503(3)	0.2450(2)	0.3348(2)
N(3)	0.0966(3)	0.1045(2)	0.4038(2)
N(4)	0.1811(3)	0.2132(2)	0.4807(2)
N(5)	0.1989(3)	0.6531(2)	0.3962(2)
N(6)	-0.0360(3)	0.5239(2)	0.2076(2)
N(7)	0.5341(3)	0.2054(2)	0.2165(2)
N(8)	0.5733(3)	0.7758(2)	0.2591(2)
C(1)	0.0191(4)	0.1271(2)	0.3153(2)
C(2)	0.1568(3)	0.2996(2)	0.4404(2)
C(3)	0.3207(3)	0.7134(2)	0.4944(2)
C(4)	0.3663(4)	0.8339(2)	0.5336(2)
C(5)	0.2843(4)	0.8950(2)	0.4702(2)
C(6)	0.1623(4)	0.8344(2)	0.3678(2)
C(7)	0.1236(3)	0.7131(2)	0.3320(2)
C(8)	-0.0029(3)	0.6400(2)	0.2238(2)
C(9)	-0.0811(4)	0.6856(2)	0.1438(2)
C(10)	-0.2017(4)	0.6106(2)	0.0455(2)
C(11)	-0.2380(3)	0.4924(2)	0.0297(2)
C(12)	-0.1520(3)	0.4519(2)	0.1115(2)

Table 3. Positional parameters of non-hydrogen atoms, compound 2.

Atom	X/a	Y/b	Z/c
Cu	0.70445(4)	0.02138(4)	0.17597(3)
S	0.91947(9)	-0.09892(9)	0.26596(7)
O(1)	0.2001(3)	0.4882(3)	0.6616(2)
O(2)	0.0734(3)	0.7251(3)	0.6532(2)
O(3)	0.0738(3)	0.6347(3)	0.5234(2)
O(4)	0.5310(3)	0.3874(2)	-0.0823(2)
O(5)	0.6825(2)	0.2245(2)	0.0370(2)
O(6)	0.4394(3)	0.2427(3)	0.0739(2)
O(10)	0.2124(3)	0.4718(3)	0.8847(2)
N(1)	0.8090(3)	-0.0931(3)	0.0592(2)
N(2)	0.9876(3)	-0.2512(3)	-0.0535(2)
N(3)	1.0222(3)	-0.3012(3)	0.1343(2)
N(4)	1.1173(3)	-0.3830(3)	0.2895(2)
N(5)	0.5842(3)	0.1474(3)	0.2910(2)
N(6)	0.5181(3)	-0.0549(3)	0.2649(2)
N(10)	0.1164(3)	0.6168(3)	0.6126(2)
N(20)	0.5483(3)	0.2864(3)	0.0095(2)
C(1)	0.7596(4)	-0.0363(3)	-0.0535(3)
C(2)	0.8645(4)	-0.1603(3)	-0.1188(3)
C(3)	0.9383(3)	-0.2128(3)	0.0488(3)
C(4)	1.1431(4)	-0.4534(3)	0.1256(3)
C(5)	1.1945(4)	-0.5137(3)	0.2408(3)
C(6)	1.0203(3)	-0.2651(3)	0.2289(3)
C(7)	0.6306(4)	0.2450(3)	0.2992(3)
C(8)	0.5447(4)	0.3303(4)	0.3815(3)
C(9)	0.4088(4)	0.3107(4)	0.4579(3)
C(10)	0.3597(4)	0.2108(4)	0.4501(3)
C(11)	0.4489(4)	0.1295(3)	0.3645(3)
C(12)	0.4084(4)	0.0203(3)	0.3465(3)
C(13)	0.2700(4)	-0.0066(4)	0.4074(3)
C(14)	0.2456(4)	-0.1155(4)	0.3864(3)
C(15)	0.3604(4)	-0.1940(4)	0.3053(3)
C(16)	0.4952(4)	-0.1603(3)	0.2454(3)

[Cu(bpy)(atth)(H₂O)]²⁺ complex ions, nitrate counterions and water of hydration. The copper coordination geometry may best be described as distorted square pyramidal, with sulfur and amino nitrogen of the atth ligand [Cu-S=2.340(1) Å, Cu-N(1)=2.022(2) Å] and the two bpy nitrogen atoms [Cu-N(5)=1.992(2) Å, Cu-N(6)=2.033(2) Å] in the equatorial plane, and a water oxygen in the apical position [Cu-O(7)=

2.244(2) Å], cf. Fig 1. The atomic deviations from the mean equatorial plane are -0.069, 0.075, 0.081 and -0.086 Å for S, N(1), N(5) and N(6), respectively, with Cu displaced towards O(7) by 0.204 Å from the mean plane. The bipyridyl ligand shows a slight twist around the C(7)-C(8) bond, the dihedral angle between

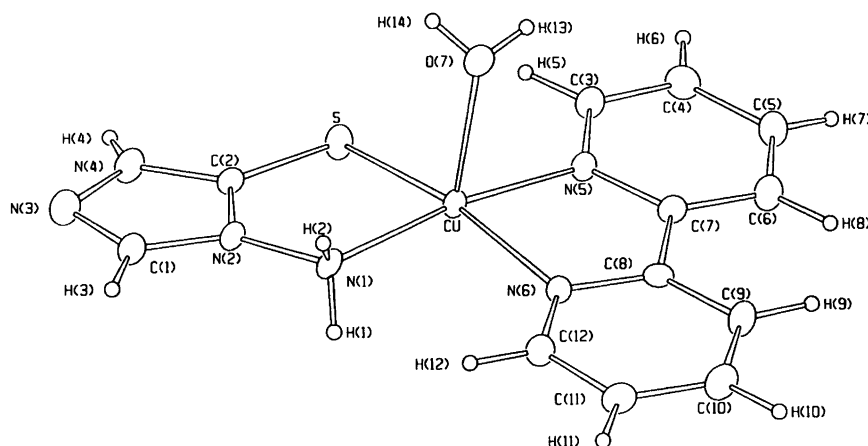


Fig. 1. The complex unit [Cu(bpy)(atth)(H₂O)]²⁺ (1) with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

Table 4. Bond lengths (in Å) and angles (in °) in compound 1.

Atoms	Distance	Atoms	Distance	Atoms	Distance
Cu–S	2.3395(7)	O(6)–N(8)	1.238(3)	C(3)–C(4)	1.378(4)
Cu–O(7)	2.244(2)	N(1)–N(2)	1.411(3)	C(4)–C(5)	1.379(4)
Cu–N(1)	2.022(2)	N(2)–C(1)	1.367(3)	C(5)–C(6)	1.384(4)
Cu–N(5)	1.992(2)	N(2)–C(2)	1.353(3)	C(6)–C(7)	1.386(4)
Cu–N(6)	2.033(2)	N(3)–C(4)	1.378(3)	C(7)–C(8)	1.476(3)
S–C(2)	1.692(3)	N(3)–C(1)	1.296(3)	C(8)–C(9)	1.382(4)
O(1)–N(7)	1.236(3)	N(4)–C(2)	1.327(3)	C(9)–C(10)	1.387(4)
O(2)–N(7)	1.246(3)	N(5)–C(3)	1.348(3)	C(10)–C(11)	1.382(4)
O(3)–N(7)	1.263(3)	N(5)–C(7)	1.354(3)	C(11)–C(12)	1.381(4)
O(4)–N(8)	1.249(3)	N(6)–C(8)	1.354(3)		
O(5)–N(8)	1.264(3)	N(6)–C(12)	1.345(3)		
Atoms	Angle	Atoms	Angle	Atoms	Angle
S–Cu–O(7)	103.43(5)	N(3)–N(4)–C(2)	113.0(2)	N(2)–C(2)–N(4)	104.0(2)
S–Cu–N(1)	88.34(6)	Cu–N(5)–C(3)	126.5(2)	N(5)–C(3)–C(4)	122.3(2)
S–Cu–N(5)	95.06(6)	Cu–N(5)–C(7)	114.8(5)	C(3)–C(4)–C(5)	118.9(2)
S–Cu–N(6)	164.84(6)	C(3)–N(5)–C(7)	118.7(2)	C(4)–C(5)–C(6)	119.5(3)
O(7)–Cu–N(1)	96.3(1)	Cu–N(6)–C(8)	113.4(2)	C(5)–C(6)–C(7)	119.0(2)
O(7)–Cu–N(5)	90.38(8)	Cu–N(6)–C(12)	127.9(2)	N(5)–C(7)–C(6)	121.6(2)
O(7)–Cu–N(6)	91.37(8)	C(8)–N(6)–C(12)	118.4(2)	N(5)–C(7)–C(8)	115.1(2)
N(1)–Cu–N(5)	171.6(5)	O(1)–N(7)–O(2)	121.0(2)	C(6)–C(7)–C(8)	123.3(2)
N(1)–Cu–N(6)	93.37(8)	O(1)–N(7)–O(3)	119.6(2)	N(6)–C(8)–C(7)	115.0(2)
N(5)–Cu–N(6)	81.36(8)	O(2)–N(7)–O(3)	119.4(2)	N(6)–C(8)–C(9)	122.1(2)
Cu–S–C(2)	93.22(9)	O(4)–N(8)–O(5)	119.4(2)	C(7)–C(8)–C(9)	123.0(2)
Cu–N(1)–N(2)	112.4(2)	O(4)–N(8)–O(6)	121.3(2)	C(8)–C(9)–C(10)	119.0(2)
N(1)–N(2)–C(1)	130.5(2)	O(5)–N(8)–O(6)	119.3(2)	C(9)–C(10)–C(11)	119.0(2)
N(1)–N(2)–C(2)	120.9(2)	N(2)–C(1)–N(3)	110.7(2)	C(10)–C(11)–C(12)	119.2(2)
C(1)–N(2)–C(2)	108.5(2)	S–C(2)–N(2)	124.8(2)	N(6)–C(12)–C(11)	122.3(2)
N(4)–N(3)–C(1)	103.9(2)	S–C(2)–N(4)	131.2(2)		

the two pyridyl rings being 5.4(5)°. The atth ligand is essentially planar.

Between pairs of complex ions, related by a centre of symmetry, there are weak Cu...S interactions of 3.590(1) Å, the sulfur atom screening the sixth position around copper, the angle O(7)–Cu...S is 170.5°. The Cu...Cu distance within this dinuclear moiety is 4.679 Å. The complex ions, nitrate ions and water molecules are connected through an extensive network of hydrogen bonding. A stereo drawing of the crystal structure is shown in Fig. 2.

Description of the structure of [Cu(bpy)(imthim)-(NO₃)](NO₃)·H₂O (2). The structure is built of [Cu(bpy)(imthim)(NO₃)]⁺ complex ions, nitrate counter-ions and water of hydration. The copper coordination geometry is slightly distorted trigonal bipyramidal, with sulfur, one bpy nitrogen atom and one nitrate oxygen atom in the equatorial plane [Cu–S = 2.347(1) Å, Cu–N(6) = 2.087(3) Å, Cu–O(5) = 2.159(2) Å; bond angles in this plane ranging from 114 to 123°], and the second bpy nitrogen atom and an imthim imino nitrogen in the axial positions [Cu–N(5) = 1.981(3) Å, Cu–N(1) = 1.921(3) Å], cf. Fig 3. The Cu atom is displaced by 0.148 Å from the mean equatorial plane towards N(1). The bipyridyl ligand shows a slight twist around the C(11)–C(12) bond, the dihedral angle

between the two pyridyl rings being 5.3(1.0)°. Each five-membered ring of the imthim ligand deviates, as expected, significantly from planarity; the dihedral angle C(4)N(3)C(6)/N(2)C(3)N(1) of 16.7(9)° gives a measure of the twist around the inter-ring bond. The coordinated nitrate ion is considered monodentate in the description given. However, it may be noted that O(6) is situated at a Cu–O distance of 2.891(2) Å, at the limit of what may be considered semi-coordination to copper.¹²

Hydrogen bonds occur between water of hydration, nitrate ions and imthim amide groups. A stereo drawing of the crystal structure is shown in Fig. 4.

Discussion

Preparations. The synthesis of compound 2 was aimed at producing a heteroleptic copper(II) complex with imidazolidine-2-thione (imth) as one of the ligands. It is well known that imth reduces simple copper(II) salts [e.g. Cu(NO₃)₂, CuCl₂, Cu(ClO₄)₂]. Such reactions have given a number of different copper(I) complexes which have been isolated and characterized.^{13a,b} In the present work the reaction of imth with an excess of Cu(bpy)²⁺ allowed the isolation of a copper(II)–thione complex. However, a ligand-centered reaction had taken place. The imthim ligand in the isolated complex results from

Table 5. Bond lengths (in Å) and angles (in °) in compound 2.

Atoms	Distance	Atoms	Distance	Atoms	Distance
Cu-S	2.347(1)	N(1)-C(1)	1.485(5)	N(6)-C(16)	1.329(6)
Cu-O(5)	2.159(2)	N(1)-C(3)	1.305(3)	C(1)-C(2)	1.526(5)
Cu-N(1)	1.921(3)	N(2)-C(2)	1.451(4)	C(4)-C(5)	1.520(5)
Cu-N(5)	1.981(3)	N(2)-C(3)	1.340(5)	C(7)-C(8)	1.384(5)
Cu-N(6)	2.087(3)	N(3)-C(3)	1.374(4)	C(8)-C(9)	1.374(5)
S-C(6)	1.688(3)	N(3)-C(4)	1.486(3)	C(9)-C(10)	1.371(7)
O(1)-N(10)	1.256(3)	N(3)-C(6)	1.366(5)	C(10)-C(11)	1.392(5)
O(2)-N(10)	1.238(5)	N(4)-C(5)	1.455(5)	C(11)-C(12)	1.469(6)
O(3)-N(10)	1.258(5)	N(4)-C(6)	1.319(3)	C(12)-C(13)	1.384(5)
O(4)-N(20)	1.242(3)	N(5)-C(7)	1.332(6)	C(13)-C(14)	1.385(7)
O(5)-N(20)	1.278(4)	N(5)-C(11)	1.354(4)	C(14)-C(15)	1.377(5)
O(6)-N(20)	1.237(4)	N(6)-C(12)	1.352(4)	C(15)-C(16)	1.385(5)

Atoms	Angle	Atoms	Angle	Atoms	Angle
S-Cu-O(15)	121.29(7)	C(5)-N(4)-C(6)	113.9(3)	N(4)-C(5)-C(4)	102.9(3)
S-Cu-N(1)	93.86(9)	Cu-N(5)-C(7)	123.5(3)	S-C(6)-N(3)	128.3(3)
S-Cu-N(5)	90.09(9)	Cu-N(5)-C(11)	116.5(2)	S-C(6)-N(4)	123.0(3)
S-Cu-N(6)	114.31(8)	C(7)-N(5)-C(11)	119.9(3)	N(3)-C(6)-N(4)	108.7(3)
O(5)-Cu-N(1)	89.5(1)	Cu-N(6)-C(12)	113.2(2)	N(5)-C(7)-C(8)	122.1(4)
O(5)-Cu-N(5)	88.3(1)	Cu-N(6)-C(16)	127.3(3)	C(7)-C(8)-C(9)	118.4(4)
O(5)-Cu-N(6)	123.0(1)	C(12)-N(6)-C(16)	119.4(3)	C(8)-C(9)-C(10)	120.1(4)
N(1)-Cu-N(5)	176.0(1)	O(1)-N(10)-O(2)	120.2(3)	C(9)-C(10)-C(11)	119.4(4)
N(1)-Cu-N(6)	98.6(1)	O(1)-N(10)-O(3)	119.7(3)	N(5)-C(11)-C(10)	120.2(3)
N(5)-Cu-N(6)	80.0(1)	O(2)-N(10)-O(3)	120.0(3)	N(5)-C(11)-C(12)	115.2(3)
Cu-S-C(6)	104.5(1)	O(4)-N(20)-O(5)	119.3(3)	C(10)-C(11)-C(12)	124.6(3)
Cu-O(5)-N(20)	113.0(2)	O(4)-N(20)-O(6)	121.4(3)	N(6)-C(12)-C(11)	114.8(3)
Cu-N(1)-C(1)	120.9(2)	O(5)-N(20)-O(6)	119.3(3)	N(6)-C(12)-C(13)	121.3(4)
Cu-N(1)-C(3)	132.2(2)	N(1)-C(1)-C(2)	105.1(3)	C(11)-C(12)-C(13)	123.9(3)
C(1)-N(1)-C(3)	106.2(3)	N(2)-C(2)-C(1)	101.7(3)	C(12)-C(13)-C(14)	119.3(4)
C(2)-N(2)-C(3)	108.8(3)	N(1)-C(3)-N(2)	115.7(3)	C(13)-C(14)-C(15)	118.7(4)
C(3)-N(3)-C(4)	120.6(3)	N(1)-C(3)-N(3)	125.2(3)	C(14)-C(15)-C(16)	119.4(4)
C(3)-N(3)-C(6)	128.3(3)	N(2)-C(3)-N(3)	119.1(3)	N(6)-C(16)-C(15)	121.9(4)
C(4)-N(3)-C(6)	110.9(3)	N(3)-C(4)-C(5)	102.7(3)		

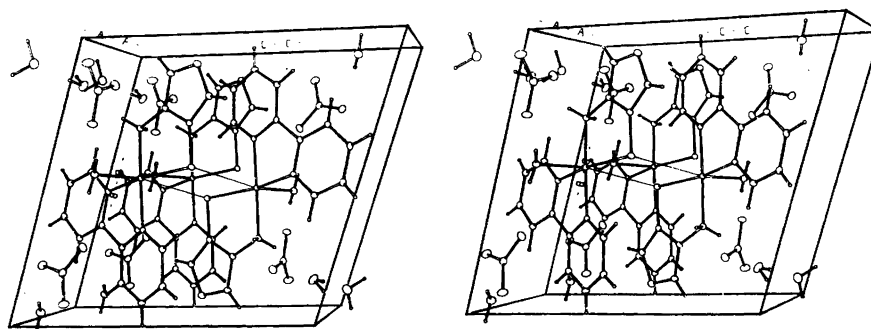


Fig. 2. Stereo drawing showing the crystal packing of $[\text{Cu}(\text{bpy})(\text{atth})(\text{H}_2\text{O})](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (**1**). The weak Cu...S interactions are indicated by single lines.

ring fusion of two imth molecules by the formation of a new C-N bond and the simultaneous loss of H_2S . The same product (imthim) has been obtained in an I_2 -catalyzed reaction.¹⁴ Also, an analogous reaction, promoted by copper(II), has been described for thiazolidine-2-thione.¹⁵ The direct synthesis of compound **1** only succeeded when $\text{Cu}(\text{bpy})^{2+}$ was in excess relative to atth. For stoichiometric mixtures redox reactions

became prominent. Attempts at isolating analogous complexes with the deprotonated ligands did not succeed.

Structural aspects.

Thione vs. thiolate form of atth and imthim ligands. Various uncomplexed derivatives of atth are structurally characterized; the S-C distance varies in the range

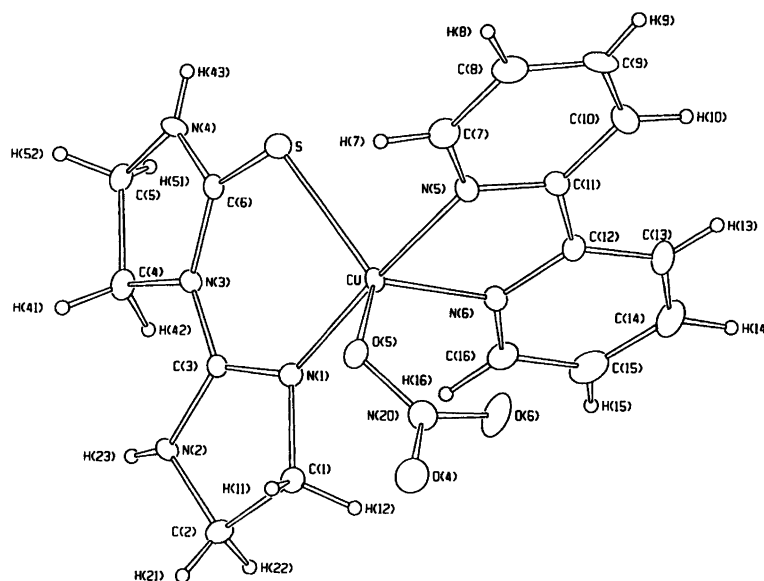


Fig. 3. The complex unit $[\text{Cu}(\text{bpy})(\text{imthim})(\text{NO}_3)]^+$ (**2**) with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

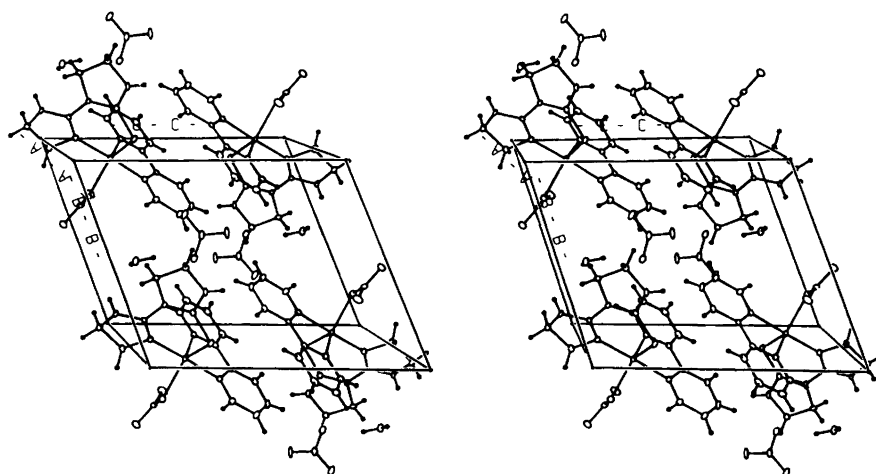


Fig. 4. Stereo drawing showing the crystal packing of $[\text{Cu}(\text{bpy})(\text{imthim})(\text{NO}_3)](\text{NO}_3) \cdot \text{H}_2\text{O}$ (**2**).

1.667–1.681 Å [3-methyl derivative 1.674(6) Å,¹⁶ 3-benzoylhydrazino derivative 1.668(3) Å,^{17a} 4-benzylideneamino derivative 1.673(2) Å,^{17b} 4-formylamino derivative 1.667(15) Å,¹⁸ 3-hydrazino derivative 1.681(5) Å].¹⁹ By comparison, the S–C bond in the uncomplexed atth^- anion is lengthened to 1.724(4) Å.²⁰ In compound **1** the S–C distance in the atth ligand [1.692(3) Å] lies between that found in the uncomplexed neutral molecules and the atth^- anion. In Cu^{II} complexes of the atth -3-methyl derivative similar S–C bond lengths are found (1.687–1.694 Å, σ in the range 0.003–0.006 Å).^{16,21} Also, in the Cu^{II} complex of 9-methyl-6-thiopurine a S–C distance [1.692(4) Å] slightly longer than that of the parent 6-thiopurine molecule [1.676(2) Å] is found.^{22,23} The marginal S–C lengthening occurring upon complexation is associated with a simultaneous small shortening of the adjacent bonds, indicating a small change towards more thiolate

character in these compounds, where the mesoionic form is stabilized by the aromaticity of the ring.

In the imthim ligand no ring aromaticity is present to give extra stability to the mesoionic form, and one might expect this to affect the degree of thione/thiolate character. Although the S–C bond length in compound **2** [1.688(3) Å] is not significantly different from that in compound **1**, it may be seen, when comparing with the S–C bond length reported in uncomplexed imidazolidine-2-thione [1.692(1) Å],²⁴ that in this particular case, there is no evidence of S–C bond lengthening upon complexation.

Three copper(II) complexes where the heterocyclic thione ligands have been deprotonated (NH or OH groups), have been characterized by X-ray crystallographic methods.^{25–27} In these complexes the thiolate character would be expected to be more pronounced. Indeed the S–C bonds in these complexes [1.705(7) Å,

1.716(6) Å, 1.712(4) and 1.716(4) Å] are slightly longer than those of the similar neutral thione ligands.

One may conclude that the sulfur ligands in the present two compounds remain essentially in their thione form, although there may be a slight displacement towards the mesoionic form upon complexation of the ligand with ring aromaticity.

The Cu–S bonds. Surprisingly, the Cu–S bond lengths in **1** and **2** [2.340(1) Å] and 2.347(1) Å are almost identical. One might have expected the equatorial bond in the trigonal bipyramid of **2** to be appreciably longer than the equatorial bond in the square pyramidal coordination of **1**. The bond lengths fall within the region observed in the other Cu^{II}–thione complexes: the bonds in the complexes of the atth-3-methyl derivative range from 2.284(3) to 2.320(3) Å,^{16,21} and the bond in the 9-methyl-6-thiopurine complex is 2.424(1) Å.²² In all these latter cases the bonds are equatorial in complexes of square pyramidal or square planar coordination geometries.

In the complexes where the heterocyclic thione ligands have been deprotonated the Cu–S bonds are 2.308(3),²⁵ 2.292(2),²⁶ 2.209(1) and 2.227(1) Å.²⁷ Only in the latter case, where the geometric requirements of the ligand impose a near tetrahedral coordination geometry on the copper(II) ion, do the Cu–S distances decrease to close to 2.20 Å, approaching the distance quoted for Cu(II)–S(cys) in the oxidized form of plastocyanin [2.13(2) Å].²⁸

References

- Addison, A. W., Rao, T. N. and Sinn, E. *Inorg. Chem.* **23** (1984) 1957.
- Toftlund, H., Becher, J., Olesen, P. H. and Pedersen, J. Z. *Isr. J. Chem.* (1985) 56.
- Bouwman, E., Driessen, W. L. and Reedijk, J. *Coord. Chem. Rev.* **104** (1990) 143.
- Casella, L. *Inorg. Chem.* **23** (1984) 2781.
- Casella, L., Gullotti, M., Pintar, A., Pinciroli, F., Vigano, R. and Zanello, P. *J. Chem. Soc., Dalton Trans.* (1989) 1161.
- Castro, I., Julve, M., Muñoz, M. C. and Diaz, W. *Inorg. Chim. Acta* **179** (1991) 59.
- Beyer, H. and Kröger, C.-F. *Ann. Chem. (Warsaw)* **637** (1960) 135.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L. Germain, G., DeClerq, J. P. and Woolfson, W. W. *MULTAN80, A System Of Computer Programs For The Automatic Solution Of Crystal Structures From X-ray Diffraction Data*. University of York, UK, 1980.
- MolEN, An Interactive Structure Solution Procedure*. Enraf-Nonius, Delft, The Netherlands 1990.
- (a) Cromer, D. T. and Waber, J. T. *International Tables for X-Ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, UK, 1974, Table 2.2B; (b) Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A24* (1968) 321.
- Cromer, D. T. *International Tables for X-Ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, UK, 1974, Table 2.3.1.
- Procter, I. M., Hathaway, B. J. and Nicholls, P. *J. Chem. Soc. A* (1968) 1678.
- (a) Raper, E. S., Wilson, J. D. and Clegg, W. *Inorg. Chim. Acta* **194** (1992) 51; (b) Devillanova, F. A., Verani, G., Battaglia, L. P. and Corriadi, A. B. *Transition Met. Chem.* **5** (1980) 362, and references therein.
- Herbstein, F. H. and Schwotzer, W. *J. Am. Chem. Soc.* **106** (1984) 2367.
- Ainscough, E. W., Anderson, B. F., Baker, E. N., Bingham, A. G., Brader, M. L., Brodie, A. M. and Gainsford, G. J. *Inorg. Chim. Acta* **105** (1985) L5.
- Bigoli, F., Lanfranchi, M. and Pellinghelli, M. A. *J. Chem. Res. (M)* (1990) 1712.
- Secombe, R. C. and Kennard, C. H. L. *J. Chem. Soc., Perkin Trans. 2* (1973) (a) 4; (b) 9.
- Gors, C., Baert, F. and Foulon, M. *Acta Crystallogr., Sect. B* **35** (1979) 489.
- Isaacs, N. W. and Kennard, C. H. L. *J. Chem. Soc. B* (1971) 1270.
- Secombe, R. C., Tillack, J. V. and Kennard, C. H. L. *J. Chem. Soc., Perkin Trans. 2* (1973) 6.
- Cingi, M. B., Bigoli, F., Lanfranchi, M., Pellinghelli, M. A., Vera, A. and Buluggiu, E. *J. Chem. Soc., Dalton Trans.* (1992) 3145.
- Sletten, E. and Apeland, A. *Acta Crystallogr., Sect. B* **31** (1975) 2019.
- Sletten, E., Sletten, J. and Jensen, L. H. *Acta Crystallogr., Sect. B* **25** (1969) 1330.
- Mak, T. C. W., Jasim, K. S. and Chiek, C. *Can. J. Chem.* **62** (1984) 808.
- Tokii, T., Nakashima, M., Furuhashi, T., Muto, Y. and Lintvedt, R. L. *Chem. Lett.* (1990) 363.
- Boyko, J. A., Furey, W. F. Jr., Lalanchette, R. A. *Acta Crystallogr., Sect. C* **48** (1992) 1606.
- Henning, L., Kirmse, R., Hammerich, O., Larsen, S., Frydendahl, H., Toftlund, H. and Becher, J. *Inorg. Chim. Acta* **234** (1995) 67.
- Guss, J. M., Bartunk, H. D., Freeman, H. C. *Acta Crystallogr., Sect. B* **48** (1992) 790.

Received October 19, 1995.