

Synthesis and Structure of the Dimeric Copper(II) Complex Tetrakis[*N*-thiazol-2-yl-(4-methylphenyl)sulfonamidate]dicopper(II)

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Abstract The coordination chemistry of the ligand *N*-thiazol-2-yl-toluenesulfonamidate towards the copper(II) ion has been investigated using an electrochemical synthesis method. The X-ray structure of this complex was elucidated and is discussed. The compound crystallised in the monoclinic crystal system, $P2_1/c$ space group with $a = 17.3888(9)$, $b = 16.3003(9)$, $c = 18.3679(9)$ Å and $\beta = 114.3640(10)^\circ$. Four bidentate sulfathiazolato anions bridge two metal centers in a paddle-wheel fashion, with the nitrogen atoms as donors to give a dimeric species with a Cu...Cu distance of 2.7859(5) Å.

Keywords Copper(II) complexes · X-ray structure · *N,N'*-bidentate ligands

Introduction

Amide ligands and their metal complexes have been widely investigated due to their use as antibacterial drugs in the

field of medicine [1]. In particular, copper(II) [2] and zinc(II) [3] complexes have been used in the treatment of numerous diseases, silver(I) [4] complexes have been used for the treatment of burns, the carbonic anhydrase inhibitory properties were studied for nickel(II) complexes [5] and copper(II) complexes have been investigated as superoxide dismutase (SOD) imitators [6].

Moreover, metal complexes containing amide ligands are easily made and variation of the substituents is facile, providing the possibility of changing almost at will the ligand bite angle and steric hindrance. It is believed that the presence of bulky substituents on these ligands stabilises the metal complexes. One possibility is the introduction of a sulfonyl group as a substituent on the nitrogen atom, because this group also has an electron-withdrawing effect that increases the acid character of the NH group and makes the ligand deprotonation process easier. In addition, the presence of a heterocyclic ring with potential donor atoms would increase the coordination ability. In this respect the most widely explored system is the pyridine ring [7–14].

In the search for new systems on different sulfonamide ligands several other heterocyclic rings with potential donor atoms were investigated [5, 15] and this paper deals with the *N*-thiazol-2-yl-toluenesulfonamidatecopper(II) complex.

Experimental

Acetonitrile, dichloromethane, 2-aminothiazole, tosyl chloride, and all other reagents were commercial products and were used as supplied. Copper (Aldrich Chemie) was used as 2 × 2 cm plates.

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HTzTs: The proligand was prepared by reaction of the corresponding amine and the tosyl chloride. Tosylchloride (0.96 g, 5.0 mmol) and 2-aminothiazole (0.50 g, 5.0 mmol) were reacted together in pyridine. Evaporation of the solvent gave a white solid, which was indentified as HTzTs. Anal. C, 46.9; H, 4.5; N, 10.9; S, 24.1% Calc for $C_{10}H_{10}N_2O_2S_2$ C, 47.2; H, 4.0; N, 11.0; S, 25.0%. 1H NMR ($CDCl_3$, ppm) 2.4 ($-CH_3$); 12.9 (N–H). IR (KBr, cm^{-1}): 3136(w), 3092(w), 3062(w), 3030(w), 2904(w), 2800(w), 1566(s), 1540(s), 1329(m), 1286(m), 1147(s), 1090(s), 937(s), 851(s), 814(m), 731(m), 701(m), 670(s), 630(m), 598(w), 567(m), 547(m). The product was recrystallized from $CH_3CN/(CH_3)_2CO$ prior to use.

Synthesis of the Complex $[Cu_2(TzTs)_4]$

The complex was obtained by following an electrochemical procedure [16]. Electrolysis of an acetonitrile/dichloromethane (25 + 25 mL) solution containing HTzTs (0.240 g, 0.93 mmol) and tetraethylammonium perchlorate (*ca.* 20 mg) as a current carrier using a platinum wire as the cathode and a copper plate as the sacrificial anode at 10 mA and 11 V for 2 h dissolved 49.8 mg of copper from the anode ($E_f = 1.05 \text{ mol F}^{-1}$). During the experiment hydrogen gas was evolved at the cathode. At the end of the experiment the dark-green solid was filtered off, washed with hot acetonitrile and ether and dried in vacuo. The compound was characterised as $[Cu_2(TzTs)_4]$: Anal. Found: C, 42.5; H, 2.9; N, 9.1; S, 21.7% Calc. for $C_{20}H_{18}N_4O_4S_4Cu$ C, 42.2; H, 3.2; N, 9.8; S, 22.5%. IR (KBr, cm^{-1}): 1140(vs), 1322(s), 1598(s), 1473(s), 2921(m). Crystals suitable for X-ray diffraction studies were obtained by crystallisation from $(CH_3)_2CO/CH_3CN$.

Physical Measurements

The C, N, H and S contents of the compounds were determined on a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded as KBr mulls on a Bruker Vector-22 spectrophotometer. The 1H NMR spectrum of the ligand was recorded on a Bruker ARX-400 MHz spectrometer using $CDCl_3$ as solvent. X- (9.5 GHz) and Q-band (35 GHz) EPR measurements were carried out on polycrystalline samples using a Varian E109 spectrometer and cavities with 100-kHz field modulation. The measurements were performed at room temperature and a Cr(III) ($g = 1.9797$) sample was used for field calibration. The g -values and zero-field splitting (D and E terms) of the spin Hamiltonian were obtained from the simultaneous spectral simulation of the X- and Q-band spectra using the EasySpin program.

Crystal Structure Determination

The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo– K_α radiation. Absorption correction was carried out using SADABS [17].

The structure was solved by direct methods and refined by a full-matrix least-squares based on F^2 [18]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [19]. Details of crystal data and structural refinement are given in Table 1.

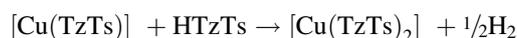
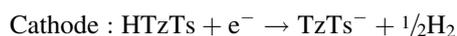
CCDC 654012 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mail.

Table 1 Summary of crystal data and structure refinement

Identification code	$Cu_2(TzTs)_2$
CCDC deposit no.	654012
Empirical formula	$C_{40}H_{36}Cu_2N_8O_8S_8$
Formula weight	1140.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 17.3888(9)$ Å $b = 16.3003(9)$ Å $c = 18.3679(9)$ Å $\beta = 114.3640(10)^\circ$
Volume	$4742.6(4)$ Å ³
Z, Calculated density	4, 1.597 mg/m ³
Absorption coefficient	1.309 mm^{-1}
$F(000)$	2328
Crystal size	$0.47 \times 0.44 \times 0.36 \text{ mm}$
θ range for data collection	$1.74\text{--}29.86^\circ$
Index ranges	$-14 \leq h \leq 24$; $-21 \leq k \leq 21$; $-22 \leq l \leq 13$
Reflections collected/unique	26,319/10,521 [$R(\text{int}) = 0.0304$]
Completeness to $2\theta = 48.0^\circ$	96.3%
Max. and min. transmission	1.00 and 0.87
Data/restraints/parameters	10521/0/599
Goodness-of-fit on F^2	0.875
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0370$, $wR_2 = 0.0751$
R indices (all data)	$R_1 = 0.0800$, $wR_2 = 0.0841$
Largest diff. peak and hole	0.277 and -0.320 e.Å^{-3}

Results and Discussion

Anodic oxidation of copper metal in a non-aqueous solution containing the weakly acidic ligand [(4-methylphenyl)sulfonyl]imino-1*H*-2-thiazole (HTzTs) yielded crystalline products of formulae $[\text{Cu}_2(\text{TzTs})_4]$. The value of the electrochemical efficiency, defined as the amount of metal dissolved per number of Faradays, was close to 1.0 mol F^{-1} . This fact, together with the formation of hydrogen gas at the cathode, is compatible with a reaction mechanism involving the anodic oxidation to copper(I) and deprotonation of the ligand at the cathode.



The oxidation of copper(I) by another HL molecule to copper(II) has been observed in another electrochemical processes involving copper as the anode [20]. The species $[\text{Cu}(\text{TzTs})_2]$ contains two anionic ligands, but the coordination polyhedron is probably incomplete due the difficulty in the ligands acting in a chelating manner [13]. As a result, the species is dimeric. This kind of dimer has been obtained previously by us (unpublished results) and by other research groups [6, 14, 15]. It is interesting to note that the clinically used sulfanilamides show similar behavior to the tosylamides, and the deprotonated form of the sulfanilamides can act in a monodentate or bidentate fashion [21].

The structure consists of dimeric units in which each copper atom is four-coordinated with a slightly distorted square-planar environment. The sulfathiazolato anions act as bridges linking to one copper(II) ion through the $\text{N}_{\text{thiazole}}$ atom and to the other copper(II) ion by means of the

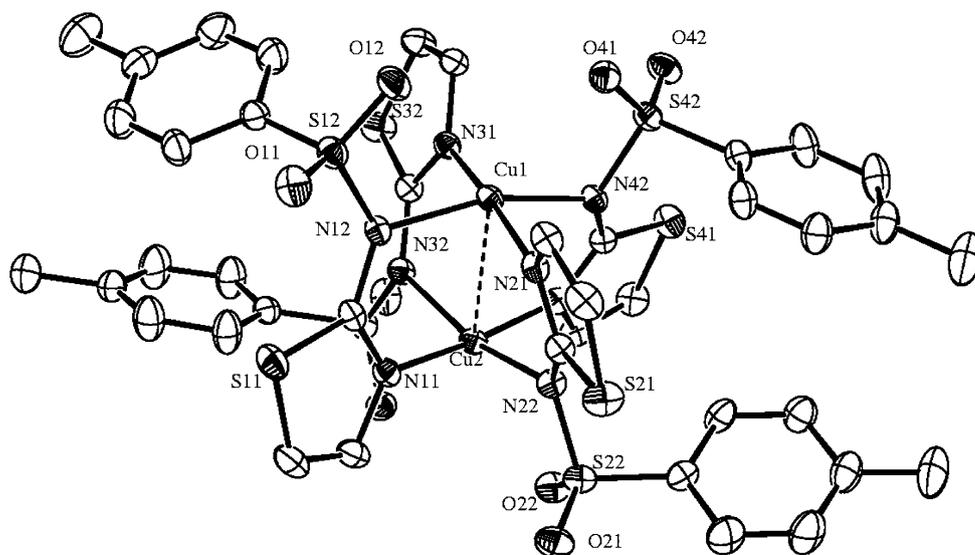
$\text{N}_{\text{sulfonamide}}$ atom. The copper atom labeled as Cu(1) is bonded to N(21) and N(31) thiazole nitrogen atoms from two molecules of sulfathiazolato ligands and N(12) and N(42) from the other two sulfathiazolato anions; the Cu(2) environment is similar, with bonding to N(11) and N(41) of the thiazole rings and N(22) and N(32) of the sulfonamido groups, in such a way that the disposition is *trans* in both cases. The internal geometry of the sulfathiazole ligand is normal and is consistent with the results from numerous studies performed previously. A selection of bond distances and angles are included in Table 2. A representation of the molecule is illustrated in Fig. 1.

It is noteworthy than Borrás et al. have already obtained another polymorph of the compound and determined its crystal structure [6], but in this case different synthetic and re-crystallization methods gave different space groups and small differences in the geometrical parameters. Firstly, the aforementioned polymorph crystallized in the monoclinic *C2/c* space group, with $a = 27.174(3)$, $b = 10.1931(10)$, $c = 20.025(2)$ Å, $\beta = 122.025(2)^\circ$. This compound has a

Table 2 Selected bond lengths [Å] and angles [°] for $[\text{Cu}_2(\text{TzTs})_4]$

Cu(1)–N(31)	1.912(2)	Cu(2)–N(11)	1.964(2)
Cu(1)–N(21)	1.921(2)	Cu(2)–N(41)	1.964(2)
Cu(1)–N(12)	1.998(2)	Cu(2)–N(32)	1.960(2)
Cu(1)–N(42)	2.003(2)	Cu(2)–N(22)	1.932(2)
Cu(1)–Cu(2)	2.7859(5)		
N(31)–Cu(1)–N(12)	95.74(9)	N(22)–Cu(2)–N(41)	93.12(9)
N(31)–Cu(1)–N(42)	84.24(9)	N(32)–Cu(2)–N(41)	86.31(9)
N(21)–Cu(1)–N(12)	84.29(9)	N(22)–Cu(2)–N(11)	86.16(9)
N(21)–Cu(1)–N(42)	93.60(9)	N(32)–Cu(2)–N(11)	92.45(9)
N(12)–Cu(1)–N(42)	162.82(9)	N(22)–Cu(2)–N(32)	162.11(9)
N(31)–Cu(1)–N(21)	172.79(10)	N(41)–Cu(2)–N(11)	173.69(9)

Fig. 1 Molecular structure of the compound. Thermal ellipsoids have been drawn with 20% probability. Hydrogen atoms have been omitted for clarity



symmetry center in the middle of the Cu–Cu bond and, consequently, both copper atoms are identical and the asymmetric unit contains only two ligands. Our polymorph is much more irregular, crystallized in the monoclinic $P2_1/c$ space group, and the asymmetric unit contains one whole dimeric molecule. The Cu–N_{thiazole} bond lengths are in the range 1.912(2)–1.964(2) Å, and the Cu–N_{sulfonamido} bond lengths are in the range 1.932(2)–2.003(2) Å, and a clear trend depending on the kinds of atoms involved in the bond is not observed—in contrast to the previously published compound. For the copper atom labeled as Cu(1) the Cu–N_{thiazole} bond lengths are about 0.08 Å shorter than the Cu–N_{sulfonamido} bond lengths, but for the copper atom labeled as Cu(2) the opposite trend is found. The *cis* bond angles in both CuN₄ chromophores are almost regular. The *trans* bond angles range from 162.11(9)° to 173.69(9)°, i.e. different to that found previously, with one *trans* angle virtually linear (178°) and the other clearly bent (155.7°) due the small bite of the bridging ligand. The distance between the two Cu centers, Cu(1)–Cu(2), is 2.7859(5) Å and this is slightly longer than that found previously.

The two CuN₄ planes are almost parallel, with a dihedral angle between the two CuN₄ mean planes of 0.4(1)°. The planes are slightly distorted, with the N_{sulfonamido} atoms 0.089(1) Å above the theoretical best plane and the N_{thiazole} atoms 0.089(1) Å below it. The Cu(1) atom is displaced 0.209(1) Å below, in the opposite direction to the other Cu(2)N₄ plane, in such a way that the distorted prism formed by the donor atoms is capped by the copper atoms (see Fig. 2). Similar values are found for the Cu(2)

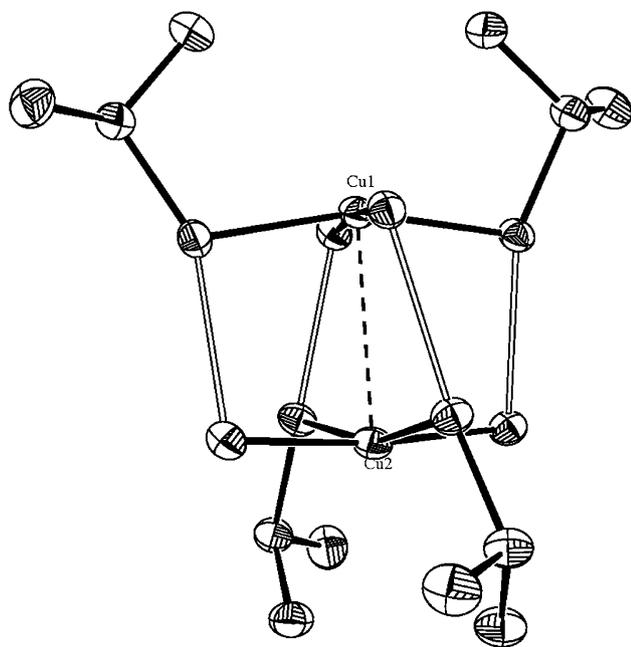


Fig. 2 View of the cage formed by the two CuN₄ chromophores

environment, with the Cu(2) atom displaced 0.205(1) Å from the best plane defined by the Cu(2)N₄ chromophore. The torsion angles N_{amido}–Cu–Cu–N_{thiazole} of 17.78(9)° are higher than those previously published, as one would expect for a more distorted structure.

Spectroscopic Properties

The IR spectrum of the complex does not contain the band observed in the ligand at 3,136 cm⁻¹, which is attributed to $\nu(\text{N–H})$ stretching. This difference in the spectra indicates that the ligand is in the anionic amidate form in the complex. The spectrum also shows weak bands in the aromatic region and these are due to $\nu(\text{C=N})$ (1,608–1,587 cm⁻¹) and $\nu(\text{C=C})$ (1,580–1,555 cm⁻¹). These bands are shifted to lower frequencies with respect to those in the free ligand as a result of coordination through the sulfonamide nitrogen atom. The band at 1,322 cm⁻¹, which is attributed to $\nu_{\text{as}}(\text{S=O})$, and band at 1,140 cm⁻¹, attributed to the $\nu_{\text{sym}}(\text{S=O})$ vibration, are also present in the spectrum along with a band at 2,921 cm⁻¹, corresponding to $\nu(\text{CH}_3)$.

The next step in our work was to study the spectroscopic properties of the complex by applying the Electron Paramagnetic Resonance (EPR) technique at the X- and Q-bands. The complex has a total electronic spin $S = 1$, and the zero-field splitting parameters, D and E , are close to 2,127 and 14 Gauss, respectively. Analysis of the EPR measurements of a crystalline sample are currently underway through the investigation of the spectral lines obtained on changing the relative angle of crystal orientation with the direction of the magnetic field.

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