Influence of tetrahedral distortion of CuN$_4$ complexes on spectroscopic properties. Synthesis, characterization and crystal structures of [Cu(*N*-(2-methylpyridyl)benzenesulfonylamidate)$_2$], [Cu(*N*-(2-methylpyridyl)toluenesulfonylamidate)$_2$] and [Cu(*N*-(2-methylpyridyl)naphthalenesulfonylamidate)$_2$] compounds

Laura Gutierrez [a], Gloria Alzuet [a], Joaquín Borrás [a,*], Malva Liu-González [b], Francisco Sanz [b], Alfonso Castiñeiras [c]

[a] *Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Valencia, 46100 Burjassot, Valencia, Spain*
[b] *Departamento de Termología, Universidad de Valencia, 46100 Burjassot, Valencia, Spain*
[c] *Departamento de Química Inorgánica, Universidad de Santiago, 15703 Santiago de Compostela, Spain*

Abstract

A series of new *N*-sulfonamide ligands and their copper(II) complexes, [Cu(*N*-(2-methylpyridyl)toluenesulfonylamidate)$_2$] (**1**), [Cu(*N*-(2-methylpyridyl)benzenesulfonylamidate)$_2$] (**2**) and [Cu(*N*-(2-methylpyridyl)naphthalenesulfonylamidate)$_2$] (**3**), have been synthesized and characterized. Single crystal X-ray analysis of the three complexes revealed that all of them present a tetracoordinate CuN$_4$ chromophore. The ligands act as bidentate, coordinating the metal ion through the pyridine and sulfonamido N atoms. The main structural difference among the compounds is the varied degree of distortion of square-planar stereochemistry. Complex **1** exhibits a regular square-planar geometry. In complexes **2** and **3** the tetrahedrality values of 50.2° and 39.0° respectively indicate a strong distortion. EHMO calculations on idealized models show the correlation between the geometrical distortion and the spectroscopic properties. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tetracoordinate copper complexes; Crystal structures; Tetrahedral distortion

1. Introduction

The importance of metal ions in biological systems is well known. One of the very interesting features of metal coordinated systems is the concerted spatial arrangement of the ligands around the metal ion. Except for special cases, the geometry exhibited by a coordinated system is often distorted. Among metal ions of biological importance, the copper(II) ion presents a high number of complexes with distortion. The range of stereochemistries which have now been characterized for copper(II) and the factors which influence them have been summarized by Hathaway [1]. The major geometries that the copper takes up are octahedral and square-pyramidal, and to a smaller extent square-planar and trigonal bipyramidal [2]. In blue copper proteins, Cu(II) shows an elongated C_{3v} distorted tetrahedral stereochemistry that gives rise to a small geometry change upon reduction that has been used to argue that the blue copper site is an entatic or rack state [3]. Tetrahedrality for any tetracoordinate complex can be characterized by the angle subtended by two planes, each encompassing the copper and two adjacent donor atoms. For strictly square-planar complexes with D_{4h} symmetry, the tetrahedrality is 0°. For tetrahedral complexes with D_{2d} symmetry, the tetrahedrality equals 90°. Battaglia et al. correlated the dihedral angle with the

* Corresponding author. Tel.: +34-96-3864530; Fax: +34-96-3864960.
E-mail address: joaquin.borras@uv.es (J. Borrás).

highest d–d transition in the electronic spectra of some tetrachlorocuprates with compressed tetrahedral D_{2d} symmetry; they showed that this variation was linear [4]. Later, a similar relationship was observed for a high number of CuN_4 complexes with the same symmetry [5].

In a previous work we reported three copper(II) complexes with the coordination polyhedron ranging from highly distorted octahedral to distorted square-pyramidal to slightly distorted square-planar geometry [6]. We compared their electronic and EPR spectra with the results obtained from molecular orbital calculations on idealized models and we found a good agreement between the theoretical results and the experimental data.

In the present paper we present three copper(II) complexes with a CuN_4 arrangement obtained from three related *N*-substituted sulfonamide ligands where the distortion of the coordination polyhedron is different. Our interest here is to uncover the structural distortion in the spectroscopic properties of these copper compounds.

2. Experimental

2.1. Materials and physical measurements

Copper nitrate trihydrate, benzenesulfonylchloride, toluenesulfonylchloride, naphthalenesulfonylchloride and 2-(aminomethyl)pyridine were reagent grade and were used without purification. Analytical data (C, H, N and S), IR, UV–Vis and EPR spectra were carried out as described previously [7].

2.2. Synthesis of the ligands

The *N*-(2-methylpyridyl)toluenesulfonylamide was obtained by condensation of 2-(aminomethyl)pyridine and toluenesulfonylchloride following the synthesis procedure previously described [8]. The other two ligands were obtained in a similar way but using benzenesulfonylchloride and naphthalenesulfonylchloride instead of toluenesulfonylchloride.

N-(2-methylpyridyl)benzenesulfonylamide (yield 0.57 g, 53%). *Anal*. Calc. for $C_{12}H_{12}N_2O_2S$: C, 58.0; H, 4.8; N, 11.2; S, 12.9. Found: C, 57.3; H, 4.7; N 11.1; S 12.7%. IR (KBr) (v_{max} (cm^{-1})): 3440 v(N–H); 1598 v(py ring); 1330, 1160 v(SO$_2$).

N-(2-methylpyridyl)naphthalenesulfonylamide (yield 0.75 g, 71%). *Anal*. Calc. for $C_{16}H_{14}N_2O_2S$: C, 64.4; H, 4.7; N, 9.4; S, 10.7. Found: C, 63.5; H, 4.8; N, 8.9; S, 10.4%. IR (KBr) (v_{max} (cm^{-1})): 3450 v(N–H); 1595 v(py ring); 1330, 1160 v(SO$_2$).

2.3. Synthesis of [Cu(N-(2-methylpyridyl)toluenesulfonylamidate)$_2$] (1), [Cu(N-(2-methylpyridyl)benzenesulfonylamidate)$_2$] (2) and [Cu(N-(2-methylpyridyl)-naphthalenesulfonylamidate)$_2$] (3)

Cu(NO$_3$)$_2$·3H$_2$O (0.24 g, 1 mmol) in 10 ml of DMF was added to 10 ml of DMF solution containing 1 mmol of the corresponding ligand. Immediately, the solution turned green. Then, 1 ml of aqueous 1 M NaOH solution was added. The resulting dark green solution was left to stand at room temperature (r.t.). After 2 or 3 days brown–green crystals (complex **1**) and blue crystals (complexes **2** and **3**) suitable for X-ray diffraction were obtained.

Anal. Calc. for $C_{26}H_{26}CuN_4O_4S_2$ (**1**) (yield 0.11 g, 44%): C, 53.3; H, 4.5; N, 9.6; S, 10.9. Found: C, 53.2; H, 4.4; N 9.5; S 11.0%. IR (KBr) (v_{max} (cm^{-1})): 1610 v(py ring); 1280, 1140 v(SO$_2$). *Anal*. Calc. for $C_{24}H_{22}CuN_4O_4S_2$ (**2**) (yield 0.098 g, 38%): C, 51.6; H, 4.0; N, 10.0; S, 11.5. Found: C, 51.7; H, 3.9; N 9.8; S 11.8%. IR (KBr) (v_{max} (cm^{-1})): 1610 v(py ring); 1290, 1145 v(SO$_2$). *Anal*. Calc. for $C_{32}H_{26}CuN_4O_4S_2$ (**3**) (yield 0.14 g, 48%): C, 58.4; H, 4.0; N, 8.5; S, 9.7. Found: C, 58.2; H, 4.1; N 8.3; S 10.0%. IR (KBr) (v_{max} (cm^{-1})): 1610 v(py ring); 1285, 1145 v(SO$_2$).

2.4. Crystallography

2.4.1. [Cu(N-(2-methylpyridyl)toluenesulfonylamidate)$_2$] (1)

A brown–green prismatic crystal was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $19.106° < \theta < 45.654°$ in an Enraf–Nonius CAD-4 automatic diffractometer [9]. Data were collected at 293 K using Cu K$_\alpha$ radiation ($\lambda = 1.54184$ Å) and the ω-scan technique, and corrected for Lorentz and polarization effects [10]. A semi-empirical absorption correction (ψ-scans) was made [11].

The structure was solved by direct methods [12], which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [13]. All hydrogen atoms were located from difference Fourier maps and were refined isotropically. Atomic scattering factors were from Ref. [14]. Molecular graphics were from PLATON-98 [15]. A summary of the crystal data, experimental details and refinement results is listed in Table 1.

2.4.2. [Cu(N-(2-methylpyridyl)benzenesulfonylamidate)$_2$] (2) and [Cu(N-(2-methylpyridyl)naphthalenesulfonylamidate)$_2$] (3)

Green crystals were of size $0.20 \times 0.25 \times 0.30$ mm (complex **2**) and $0.3 \times 0.3 \times 0.2$ mm. (complex **3**).

Throughout the experiment Mo K_{α} radiation was used with a graphite crystal monocromator on an Enraf–Nonius CAD-4 [16]. single crystal diffractometer ($\lambda = 0.7173$ Å).The unit cell dimensions were determined from the angular settings of 25 reflections with θ from 2.38 to 25.97° (complex **2**) and from 1.59 to 26.08° (complex **3**). The space group was determined to be $P2_1$ (complex **2**) from systematic absences and $P\bar{1}$ (complex **3**) from no systematic absences by ABSEN [17]. The intensity data of 2571, in *hkl* range $(0,0,-11)$ to $(11,18,10)$ and limits $(1° < \theta < 25°)$ for complex **2** and 5964 in *hkl* range $(-10,-15,-17)$ to $(0,15,17)$ and limits $(1° < \theta < 25°)$ for complex **3** were measured, using the $\omega-2\theta$ scan technique and variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. On all reflections, profile analysis was performed [18]. Lorentz and polarization corrections were applied and then data were reduced to F_0^2 values. The structure was solved using SIR-92 [19]. Isotropic least squared refinement on F^2 was made using SHELX-93 [20]. During the final stages of the refinement on F^2 the positional parameters and the anisotropic thermal parameters of the non-hygrogen atoms were refined. The hydrogen atoms were located by XHYDEX [21]. The final conventional agreement factors were $R = 0.039$ and $wR_2 = 0.076$ for 2425 'observed' reflections and 331 variables for complex **2** and $R = 0.07$ and $wR_2 = 0.15$ for 5581 'observed' reflections and 408 variables for complex **3**. The function mini-

mized was $[\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$, $\omega = 1/[\sigma^2(F_o^2) + (0.0828P)^2]$ with $\sigma(F_o^2)$ from counting statistic and $P = [(\max(F_o^2,0) + 2F_c^2)]/3$. The final difference Fourier map showed a peak of 0.600 Å^3 close to the Cu atoms, the other peaks no deeper than -0.356 Å^3 for complex **2** and a peak of 0.397 Å^3 close to the atoms of Cu, the other peaks not deeper than -0.595 Å^3 for complex **3**. The figures were drawn with ORTEP [22]. Atomic scattering factors were made with PARST [23]. A summary of the crystal data, experimental details and refinement results is collected in Table 1.

2.5. EHMO calculations

All calculations were performed using the package of Programs for Molecular Orbital Analysis by Mealli and Proserpio [24] based on CDNT (atom Cartesian coordinate calculations), ICON (extended Hückel method with the weighted H_{ij} formula) and FMO (fragment molecular orbital), included in the drawing program CACAO (computer aided composition of atomic orbitals).

The extended Hückel parameters are as follows. H_{ij} (Ev): Cu 4s, -11.40; Cu 4p, -6.06; Cu 3d, -14.00; N 2s, -26.00; N 2p, $-13.401.950$; S 3s, -20.30; S 3p, -14.00; O 2s, -32.30; O 2p, -14.80; C 2s, -21.40; C 2p, -11.40; H 1s, -13.60 eV. Orbital exponents(contraction coefficients in double-ξ expansion given in parentheses): Cu 4s, 4p, 2.20; Cu 3d, 5.95 (0.5933), 2.30 (0.5744); N 2s, 2p, 1.950; S 3s, 3p, 1.900; O 2s, 2p, 2.275; C 2s, 2p, 1.625; H 1s, 1.300.

Table 1
Crystal data and structure refinement for **1**, **2**, and **3**

	1	**2**	**3**
Formula	$C_{26}H_{26}N_4O_4S_2Cu$	$C_{24}H_{22}N_4O_4S_2Cu$	$C_{32}H_{26}N_4O_4S_2Cu$
Symmetry	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.393(7)	9.363(3)	8.890(5)
b (Å)	17.081(14)	14.798(2)	12.434(5)
c (Å)	9.950(5)	9.414(2)	14.235(5)
α (°)	90.0	90.0	114.77(5)
β (°)	99.307(6)	114.39(2)	97.072(5)
γ (°)	90.0	90.0	91.289(5)
U (Å^3)	1239.9(17)	1188(4)	1413.0(11)
Z	2	2	2
D_{calc} (g cm^{-3})	1.57	1.560	1.547
M	586.2	558.12	658.23
$F(000)$	606	574	678
μ (cm^{-1})	31.7	11.3	9.68
Goodness-of-fit	1.104	1.043	1.001
R	0.036	0.039	0.077
R_w	0.101	0.076	0.155

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **3**

1		**2**		**3**	
Bond distances					
Cu(1)–N(2)	1.9909(17)	Cu(1)–N(2A)	1.929(5)	Cu(1)–N(2)	1.925(9)
Cu(1)–N(2) #	1.9909(17)	Cu(1)–N(2)	1.932(5)	Cu(1)–N(2A)	1.953(9)
Cu(1)–N(1)	1.9984(17)	Cu(1)–N(1)	1.989(6)	Cu(1)–N(1)	1.994(9)
Cu(1)–N(1) #	1.9984(17)	Cu(1)–N(1A)	2.001(5)	Cu(1)–N(1A)	1.993(8)
Bond angles					
N(2)–Cu(1)–N(2) #	180.0	N(2A)–Cu(1)–N(2)	157.0(3)	N(2)–Cu(1)–N(2A)	161.9(4)
N(2)–Cu(1)–N(1)	83.02(7)	N(2A)–Cu(1)–N(1)	105.4(3)	N(2)–Cu(1)–N(1)	82.5(4)
N(2) # –Cu(1)–N(1)	96.98(7)	N(2)–Cu(1)–N(1)	82.5(2)	N(2A)–Cu(1)–N(1)	103.6(4)
N(2)–Cu(1)–N(1) #	96.98(7)	N(2A)–Cu(1)–N(1A))	83.3(2)	N(2)–Cu(1)–N(1A)	102.2(4)
N(2) # –Cu(1)–N(1) #	83.02(2)	N(2)–Cu(1)–N(1A)	104.9(2)	N(2A)–Cu(1)–N(1A	81.7(4)
N(1)–Cu(1)–N(1) #	180.0	N(1)–Cu(1)–N(1A)	139.4(3)	N(1)–Cu(1)–N(1A)	148.4(3)

3. Results and discussion

3.1. Crystal structures

Relevant bond distances and angles for the three complexes are given in Table 2. Figs. 1–3 show molecular drawings of the complexes **1**, **2** and **3** respectively with the atom numbering scheme.

The crystal structure of complex **1** consists of monomer units linked by stacking interactions between the aromatic rings (mean distances between rings, 3.571(4) Å), see Fig. 4. The copper(II) ion is bound centrosymmetrically by two deprotonated ligands in a square-planar environment. Each ligand coordinates the metal ion through the $N_{pyridyl}$ and the $N_{sulfonamidate}$ atoms, with mean Cu–N bond distances of 1.99 Å. These distances are similar to those reported for other *N*-(2-methylpyridyl)toluenesulfonylamide copper complexes [8] and for copper complexes with the related sulfathiazole ligand [7]. The coordination bond angles, ranging from 83.02(7)° [N(2)–Cu(1)–N(1)] to 96.98(7)° [N(2)–Cu(1)–N(1) #], deviate slightly from those of a regular square-planar geometry. The Cu(II) ion is in the plane formed by the four N atoms; the dihedral angle between the planes Cu(1)N(1)N(2) and Cu(1)N(1) # N(2) # equal to 0° confirms the square-planar arrangement of the CuN_4 chromophore. The coordination behavior of the ligand as bidentate gives rise to a planar five-membered chelate ring that probably stabilizes the complex.

The crystal structure of complex **2** shows the Cu(II) ion surrounded by four N atoms from two deprotonated *N*-(2-methylpyridyl)benzenesulfonylamide ligands in a very distorted square-planar arrangement. The ligand presents the same bidentate behavior of the *N*-(2-methylpyridyl)toluenesulfonylamide ligand in complex **1**. The Cu–$N_{pyridyl}$ bond distances [1.989(6) and 2.001(5) Å] are similar to the corresponding distances in complex **1** however, the Cu–$N_{sulfonamidate}$ dis-

tances are slightly lower [1.929(5) and 1.932(5) Å]. The main structural differences between complexes **1** and **2** can be observed in the bond angles of the CuN_4 chromophore. While in complex **1** the diagonal angles N(1)–Cu(1)–N(1) # and N(2)–Cu(1)–N(2) # are 180°, in complex **2** these angles are 139.4(3)° and 157.0(3)° respectively. The strong distortion from the square-planar geometry of complex **2** is indicated by the tetrahedrality value of 50.2°.

In complex **3** (Fig. 3) the Cu(II) ion resides in a distorted square-planar environment that consists of four nitrogen atoms of two deprotonated ligands. Each ligand, acting as bidentate, links the metal ion through its pyridyl and sulfonamidate nitrogen atoms. The Cu–$N_{sulfonamidate}$ bond distances are 1.925(9) and 1.953(9) Å and the Cu–$N_{pyridyl}$ distances are 1.993(8) and 1.994(9) Å. The tetrahedrality of the CuN_4 chromophore is 39.0°, this value is intermediate between that observed in complex **1** and complex **2**.

The most striking difference among the complexes **1**, **2** and **3** is the varied degree of square-planar distortion.
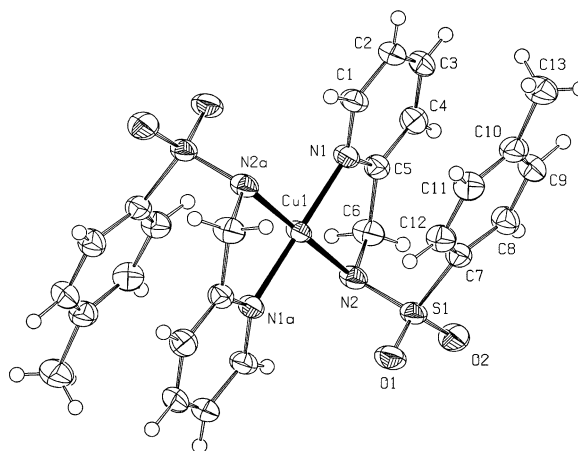

Fig. 1. Molecular drawing of [Cu(*N*-(2-methylpyridyl)toluenesulfonylamidate)$_2$] (**1**) with the atom numbering scheme.
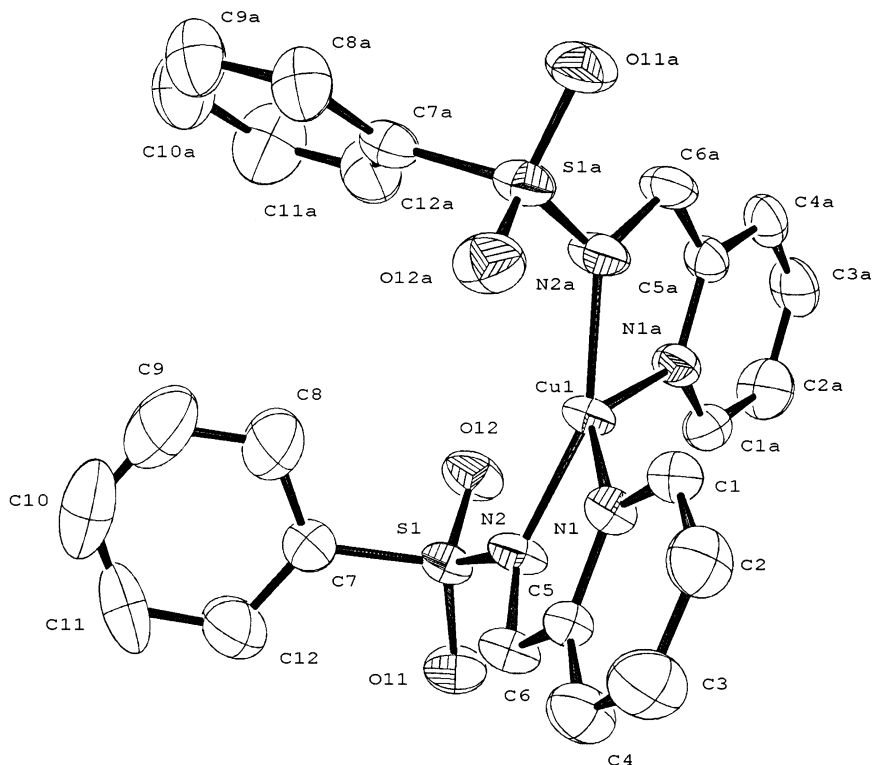
Fig. 2. Molecular drawing of [Cu(*N*-(2-methylpyridyl)benzenesulfonylamidate)$_2$] (**2**) with the atom numbering scheme.

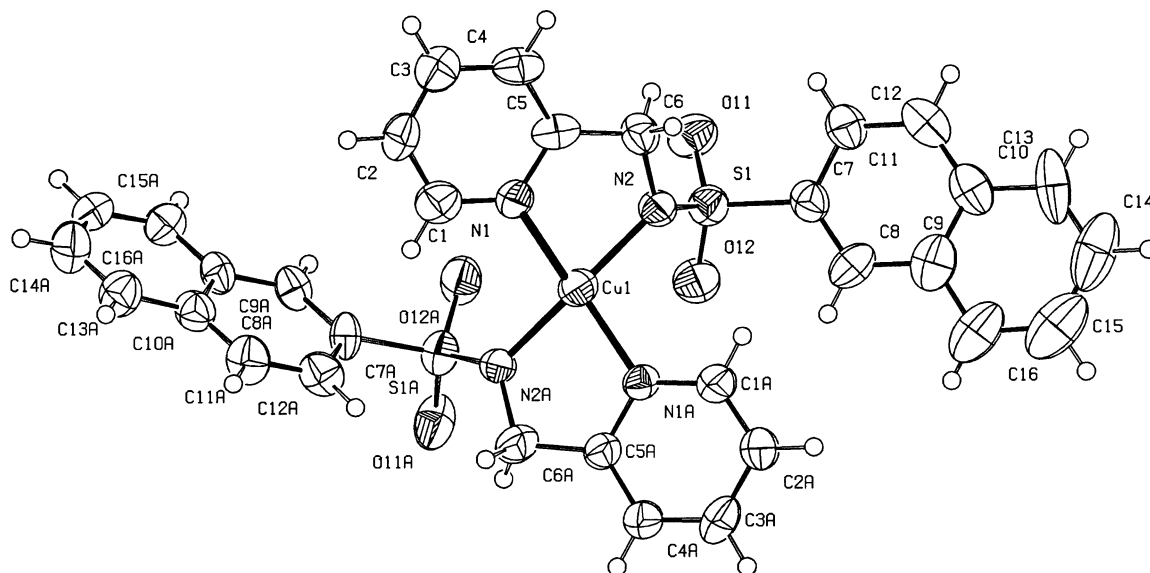Fig. 3. Molecular drawing of [Cu(*N*-(2-methylpyridyl)naphtalenesulfonylamidate)$_2$] (**3**) with the atom numbering scheme.

The three ligands in the compounds differ only in the aromatic ring on the sulfur atom of the sulfonamide group. At first, it could be suggested that the size of the rings and therefore the steric effect afforded by them would be a determining factor governing the degree of the distortion of the coordination polyhedra. In this sense, the distortion might increase in the order **2** < **1** <

3. However, in our complexes the increment is found to be in the order **1** < **3** < **2** and hence the dissimilarity in the spatial arrangement around copper cannot arise only as a result of steric effects of the ligand. In the particular case of complex **1**, the almost regular geometry of its coordination polyhedron could be determined by the stacking interactions in the molecular structure.
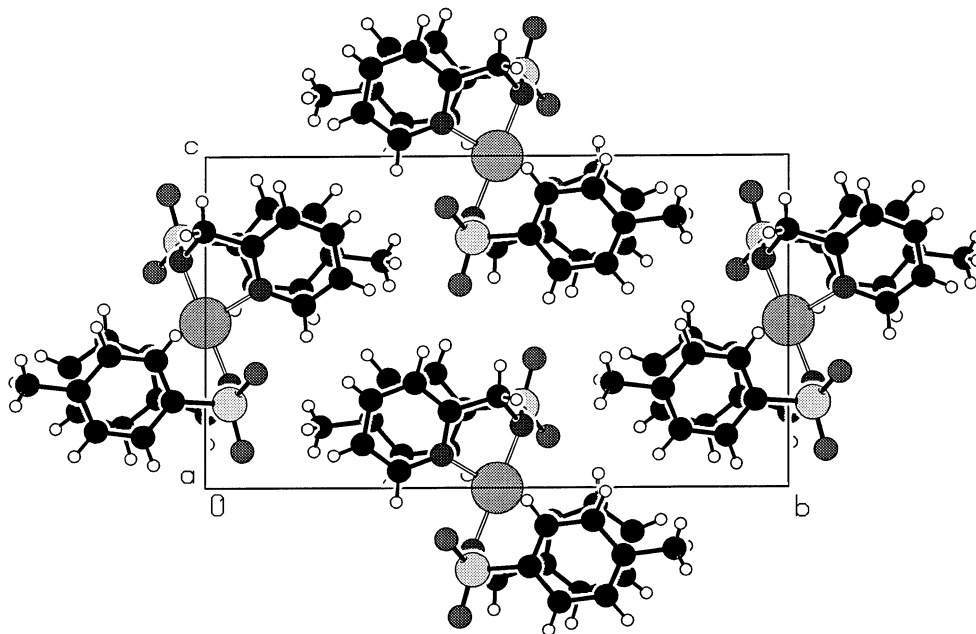
Fig. 4. Crystal packing of [Cu(*N*-(2-methylpyridyl)toluenesulfonylamidate)₂] (**1**).

3.2. Spectroscopic properties

In the IR spectra of the three complexes the stretching vibrations of the pyridine ring and the SO_2 group are shifted (approximately 12–50 cm^{-1}) from those of the free ligands due to their involvement in coordination and to the deprotonation of the sulfonamido moiety.

The solid electronic spectra of the three complexes display a band near 25000 cm^{-1} assigned to a LMCT transition. Furthermore, complex **1** exhibits a d–d broad band at about 20000 cm^{-1} and the other two complexes show a broad and weak band at about 16000 cm^{-1}. These electronic spectra are consistent with the degree of distortion from the square-planar geometry found in the X-ray structural analysis.

The X-band EPR spectra at room temperature of polycrystalline samples of compounds **1** and **2** are rhombic with *g* parameters, obtained by simulation [25], $g_x = 2.035$, $g_y = 2.070$ and $g_z = 2.140$ (complex **1**) and $g_x = 2.045$, $g_y = 2.095$ and $g_z = 2.200$ (complex **2**). Complex **3** shows an axial spectrum with $g_\perp = 2.054$ and $g_\parallel = 2.226$. In good agreement with the most regular square-planar polyhedron of complex **1**, its g_z value is the lowest [26].

3.3. Molecular orbital calculations

In order to investigate the electronic structure of the three complexes we carried out extended Hückel molecular orbital (EHMO) calculations by means of the CACAO program [24]. As the systems are so complicated it is difficult to obtain results that can be correlated to

the electronic structures of the compounds, so we have designed three idealized models substituting the four N atoms of the ligands by ammonia molecules using the coordinates of the ligand N donor atoms obtained from the crystallographic data. In this way, the copper ion and the N atoms retain the sites found in the crystal structures and the distortion of coordination polyhedron remains.

From the EHMO calculations several interesting aspects can be deduced. (i) The SOMOs (semioccupied molecular orbital) are antibonding orbitals. In all the complexes, the d_{xy} orbital of the Cu(II) has a contribution to SOMO formation of 43%. Moreover, in the complexes **2** and **3** there is a small involvement (4%) of the $4p_z$ orbitals. The $2p_x$ and $2p_y$ orbitals of the nitrogen atoms of the ligands are involved in all the SOMOs with a participation of 7%. The energy of the SOMO orbital for complex **1** is -10.086 eV; for the complexes **2** and **3** it is -11.036 and -11.004 eV, respectively. Hence, it seems that there is a correlation between the degree of tetrahedral distortion and the stability of the SOMO, higher tetrahedral distortion leading to higher stability of the SOMO. (ii) In complex **1** the four following molecular orbitals present the only contribution of the d orbitals of the Cu(II) ion while in the more distorted complexes **2** and **3** the HOMO and HOMO-1 exhibit participation of the $2p_x$ and $2p_y$ orbitals of the nitrogen atoms of the ligands. (iii) The energy difference between SOMO and HOMO for the square-planar complex **1** is 3.710 eV, this difference for the complexes **2** and **3** is 2.345 and 2.475 eV, respectively. Thus, it can be deduced that the electronic transition in complex **1** must be more energetic than in the complexes **2** and **3**.

These results are consistent with the electronic spectra where the d–d band of complex **1** appears near 20 000 cm^{-1} while in compounds **2** and **3** it is found at about 16 000 cm^{-1}.

4. Supplementary material

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 150109, CCDC 150110, CCDC 150111. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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