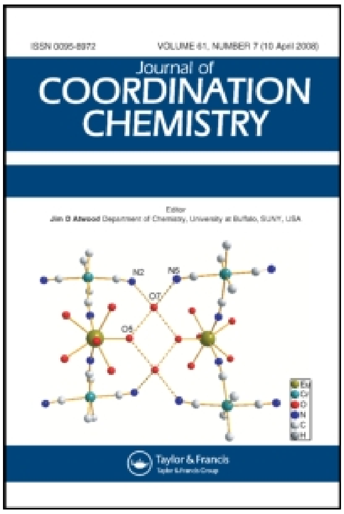

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# Synthesis and characterization of a Cu(II) complex of 2-benzylmercapto-5-methyl-1,3,4-thiadiazole ($C_{10}H_{10}N_2S_2$)

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# Synthesis and characterization of a Cu(II) complex of 2-benzylmercapto-5-methyl-1,3,4-thiadiazole ($C_{10}H_{10}N_2S_2$)

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A Cu(II) complex of 2-benzylmercapto-5-methyl-1,3,4-thiadiazole was synthesized and characterized. The crystal structure of the copper complex and the free ligand were determined by single-crystal X-ray diffraction at room temperature: {$[Cu(C_{10}H_{10}N_2S_2)_2(Cl)_2]$, $P\bar{1}$ triclinic, $a = 8.1450(2)$ Å, $b = 8.1690(2)$ Å, $c = 10.8180(3)$ Å, $\alpha = 97.4040(12)^\circ$, $\beta = 101.6270(11)^\circ$, $\gamma = 116.1431(14)^\circ$; $C_{10}H_{10}N_2S_2$ ligand, *P*bca orthorhombic, $a = 8.7938(7)$ Å, $b = 9.6491(7)$ Å, $c = 25.3552(18)$ Å}. The metal complex framework consists of discrete units that provide crystalline stability through a network of van der Waals contacts. The Cu(II) is coordinated by two chloride ions and two 2-benzylmercapto-5-methyl-1,3,4-thiadiazole monodentate ligands showing a distorted square planar configuration. Both thiadiazole ligands coordinate through the N atom bonded to the benzylthio substituted C atom.

The FTIR spectroscopic data are consistent with this structural model. Analysis of the magnetic susceptibility from 5 K to room temperature indicates the presence of paramagnetic Cu(II), confirmed by the EPR spectrum.

*Keywords*: 2-Benzylmercapto-5-methyl-1,3,4-thiadiazole; Cu(II) complexes; Crystal structure; Spectroscopic behavior; Magnetic behavior

## 1. Introduction

The 1,3,4-thiadiazole ring allows different substituents at positions 2 and 5. The structural and electronic modifications of its derivatives with diverse substituents and their metal complexes are particularly interesting due to their influence on the

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pharmacological and biological properties, such as inhibitory activity on carbonic anhydrase enzyme [1–3]. In the last years the crystal structures and the spectroscopic behaviors of some 1,3,4-thiadiazole ligands containing –$SO_2NH_2$ (sulfonamide) and –SH (thiol) groups, and their metal complexes were examined in our laboratory [4–12]. Interactions of these ligands with metal ions have been widely studied [13–20] and the coordination geometries around the metal ion were found to be square pyramidal, octahedral and square-planar in the 33, 47 and 20% of the cases, respectively.

Low molecular weight 1,3,4-thiadiazole derivative thioethers (–S–$CH_2$–R) and their metal complexes can be considered as models for studying the coordination behavior of resins based on poly(styrene-codivinylbenzene) that incorporate 2-amino-1,3,4-thiadiazole-5-thiol in its structure, used as efficient uptake agents for toxic metal ions.

The versatility exhibited by these thioethers as ligands in metal complexes has not received enough attention. Information on the structural and spectroscopic behavior is very scarce and as far as we know, restricted to the crystal structure of 2-amino-5-benzylmercapto-1,3,4-thiadiazole ($C_9H_9N_3S_2$) [21] and our previous work dealing with some of its complexes [22]. After investigating the coordination behavior of $C_9H_9N_3S_2$, particularly towards Cu(II), we wonder how the substitution of resonance donor amino group by an inductive donor group such as methyl affect versatility, crystal packing and H–bond strength in the lattice and ligand coordination sites for 1,3,4-thiadiazole derivative thioethers. In the present work we report the synthesis and characterization of $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$. The coordination behavior, crystal structure, spectroscopic and magnetic properties are analyzed. Crystal data at room temperature for the free ligand $C_{10}H_{10}N_2S_2$ are also reported. Bond distances and angles of the 1,3,4-thiadiazole ring in the metal complex are compared to those in the free ligand.

## 2. Experimental

### 2.1. *Syntheses*

The syntheses were performed using analytical grade reagents according to the following procedures. The ligand, 2-benzylmercapto-5-methyl-1,3,4-thiadiazole ($C_{10}H_{10}N_2S_2$) was obtained by complete reaction of 0.40 g (17.38 mmol) of $Na^\circ$ dissolved in 100 mL absolute ethanol, with 2.00 g (15.04 mmol) of 5-methyl-1,3,4-thiadiazole-2-thiol and 1.80 mL (15.32 mmol) of benzyl bromide. The reaction was performed at room temperature (r.t.) with stirring under Ar and monitored by TLC. After 18 h, the obtained precipitate was filtered and washed with distilled water. The filtrate was hydrolyzed with distilled water. The resulting solid was filtered and dried with $P_4O_{10}$ in a dessicator. Thus, $C_{10}H_{10}N_2S_2$ (97% yield) was obtained as a white solid (m.p. $= 63 \pm 1^\circ C$) which was crystallized using absolute ethanol. The product was characterized by FTIR (see table 3), microanalysis, NMR, MS, HR-EIMS and the structure was determined by single crystal X-ray diffraction.

Microanalysis: Anal. Calcd for $C_{10}H_{10}N_2S_2$ (%): C, 54.0; H, 4.5; N, 12.6; S, 28.8. Found: C, 53.7; H, 4.2; N, 12.2; S, 28.4. $^1$H-NMR (250 MHz) ($CDCl_3$): $\delta$ 2.61 (s, 3H, $CH_3$); 4.42 (s, 2H, $CH_2$); 7.20–7.32 (m, 5H, phenyl group). $^{13}$C–NMR (100 MHz) ($CDCl_3$): $\delta$ 15.77 ($CH_3$); 38.59 ($CH_2$); 128.41, 129.09, 129.57, 136.35 (phenyl group);

165.28 and 165.55 thiadiazole quaternary carbons. MS (FAB+) $m/z$ 223 (100%) $[M+1]^+$; $m/z$ 222 (16%) $[M]^+$; $m/z$ 195 (5%). HR-EIMS: $m/z$ 223.0359 $[M+1]^+$ (ca 223.03636).

The complex was obtained by the following procedure: 0.17 g (1.00 mmol) of Cu(II) chloride dihydrate and 0.44 g (2.00 mmol) of the ligand were dissolved in 50.00 mL absolute ethanol, with magnetic stirring until total dissolution at r.t. for 2 h. Green prismatic crystals of the $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$ (0.37 g) (64% yield) were obtained by solvent evaporation at r.t. after two weeks. Suitable crystals for characterization and DRX study were separated from the mother liquor. Microanalysis: Anal. Calcd for $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$ (%): Cu, 11.0; C, 41.5; H, 3.5; N, 9.7; S, 22.2. Found: Cu, 10.2; C, 41.1; H, 3.1; N, 9.4; S, 21.6.

## 2.2. *X-ray crystal structure determinations*

A single crystal of $C_{10}H_{10}N_2S_2$ suitable for X-ray diffraction was mounted on a glass fiber and transferred to the Nonius CAD-4 diffractometer using Mo-K$\alpha$ radiation. The structure was solved by direct methods and refined anisotropically on $F^2$ (SHELXS-97 and SHELXL-97, G.M. Sheldrick, University of Göttingen, 1997). All hydrogen atoms were refined using a *riding* model. The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from the International Tables for Crystallography [23]. The crystallographic plot was made with SHELXTL.

Data collection for a single crystal of $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$ was performed on a Nonius Kappa-CCD diffractometer using Mo-K$\alpha$ radiation. Crystal-detector distance was fixed at 30 mm, and a total of 210 images were collected using the oscillation method, with scan angle per frame (2°) oscillation and 35 seconds exposure time per image. Data collection strategy was calculated with the Collect program [24]. Data reduction and cell refinement were performed with the HKL Denzo and Scalepack programs [25]. The structure was solved by direct methods using the SIR-97 program [26]. Least squares refinement was carried out with SHELXL-97 [27]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in geometric positions. Geometrical calculations were made with PARST [28]. The crystallographic plot was made with ORTEP [29]. The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from the International Tables for Crystallography [23]. Crystal data and experimental details for both compounds are given in table 1.

## 2.3. *Instruments and techniques*

FTIR spectra were recorded on a Nicolet Protégé 460 spectrometer provided with a CsI beamsplitter in the 4000 to 225 $cm^{-1}$ range using KBr pellets for the solid samples. Spectral resolution was better than 4 $cm^{-1}$ between 4000 and 2000 $cm^{-1}$, and better than 2 $cm^{-1}$ in the remaining ranges.

Magnetization measurements at different temperatures and magnetic fields were carried out from r.t. to 5 K with a superconducting quantum interference device (SQUID) and from 200 K to 80 K with vibrating sample commercial magnetometers (VSM). In both cases, the magnetic susceptibility ($\chi = M/H$) was computed as the ratio between the magnetization ($M$) and the magnetic field ($H$). EPR spectra were taken at 9.44 GHz (X-Band) with a Bruker ESP-300 spectrometer.

Table 1. Crystallographic data for $C_{10}H_{10}N_2S_2$ and $[Cu(C_{10}H_{10}N_2S_2)_2(Cl)_2]$.

| Crystallographic data | $C_{10}H_{10}N_2S_2$ | $[Cu(C_{10}H_{10}N_2S_2)_2(Cl)_2]$ |
|---|---|---|
| Empirical formula | $C_{10}H_{10}N_2S_2$ | $C_{20}H_{20}N_4S_4Cl_2Cu$ |
| Molecular weight | 222.32 | 579.08 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | *P*bca | $P\bar{1}$ |
| Unit cell parameters (Å, °) | | |
| $a$ | 8.7938(7) | 8.1450(2) |
| $b$ | 9.6491(7) | 8.1690(2) |
| $c$ | 25.3552(18) | 10.8180(3) |
| $\alpha$ | 90 | 97.4040(12) |
| $\beta$ | 90 | 101.6270(11) |
| $\gamma$ | 90 | 116.1431(14) |
| $T$ ($K$) | 293(2) | 293(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $V$ (Å$^3$) | 2151.4(3) | 613.20(3) |
| $Z$ | 4 | 2 |
| $D_{\text{Calcd}}$ (g cm$^{-3}$) | 1.373 | 1.568 |
| $F(000)$ | 928 | 295 |
| Crystal size (mm$^3$) | $0.68 \times 0.60 \times 0.18$ | $0.15 \times 0.28 \times 0.32$ |
| $\theta_{\min}$, $\theta_{\max}$ (°) | 3.21, 24.98 | 1.98, 35.60 |
| Reflections collected | 6081 | 7665 |
| Independent reflections | 1890 | 5429 |
| Limiting indices | $-10 \le h \le 6$, $-11 \le k \le 11$, $0 \le l \le 30$ | $-12 \le h \le 13$, $-13 \le k \le 13$, $-17 \le l \le 12$ |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1890/0/127 | 5429/0/136 |
| Final $R_1$, $wR_2$ $[I>2\sigma(I)]$ | 0.0427, 0.0988 | 0.0419, 0.1092 |
| Goodness-of-fit on $F^2$ | 1.065 | 1.004 |
| Minimum and maximum residual (e Å$^{-3}$) | 0.245 and −0.202 | 0.661 and −0.575 |

Elemental analyses (C, H, N, S) were made with a Carlo Erba EA 1108 microanalyzer belonging to the Instituto de Química Física de Materiales, Medio Ambiente y Energía (INQUIMAE), Universidad de Buenos Aires, Argentine; sulfanylamide was used as standard. Copper elemental analysis was performed with a Shimadzu Model AA-6800 atomic absorption spectrometer equipped with a deuterium background corrector; a copper hollow cathode lamp was employed as the radiation source.

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AC-250, with $CDCl_3$ as dissolvent and TMS as internal reference. The equipment belongs to the Universidad de Valencia, Spain.

The MS and HR-EIMS were recorded on a VG AUTOSPEC. The values were expressed in $m/z$ units. The equipment belongs to the Universidad de Valencia, Spain.

## 3. Results and discussion

The ligand has been previously reported but full physical data are lacking [30], so the present manuscript represents the first published description of the X-ray crystal data. The molecular structure of the ligand displaying a planar heterocyclic ring (mean deviation 0.009(2) Å) is shown in figure 1. In the heterocyclic ring, bond lengths and angles correspond to a 1,3,4-thiadiazole aromatic ring (see table 2).

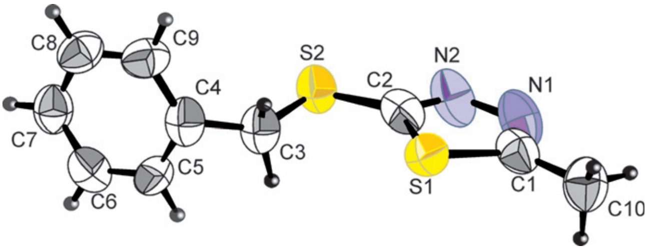

Figure 1. Ellipsoid plot (50% probability level) of 2-benzylmercapto-5-methyl-1,3,4-thiadiazole.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu(C_{10}H_{10}N_2S_2)_2(Cl)_2]$ in comparison with $C_{10}H_{10}N_2S_2$.

| | $C_{10}H_{10}N_2S_2$ (Å) | $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$ (Å) |
|---|---|---|
| Copper bonds | | |
| Cu–N2(A) | – | 1.9888(13) |
| Cu–N2(B) | – | 1.9888(13) |
| Cu–Cl1(A) | – | 2.2433(5) |
| Cu–Cl1(B) | – | 2.2433(5) |
| 1,3,4-thiadiazole ring | | |
| C1–N1 | 1.291(4) | 1.298(2) |
| N1–N2 | 1.384(4) | 1.382(2) |
| N2–C2 | 1.297(4) | 1.301(2) |
| C1–S1 | 1.722(3) | 1.738(2) |
| C2–S1 | 1.724(3) | 1.7240(17) |
| N2(A)–Cu–Cl1(A) | – | 89.99(5) |
| N2(B)–Cu–Cl1(A) | – | 90.01(5) |
| N2(A)–Cu–Cl1(B) | – | 90.01(5) |
| N2(B)–Cu–Cl1(B) | – | 89.99(5) |
| Cl1(B)–Cu–N1(A) | – | 96.39(3) |
| Cl1(B)–Cu–N1(B) | – | 83.61(3) |
| Cl1(A)–Cu–N1(A) | – | 83.61(3) |
| Cl1(A)–Cu–N1(B) | – | 96.39(3) |
| N1(A)–Cu–N1(B) | – | 155.11(6) |

Note: (A) and (B) are each thioether and chlorine ligands.

The heterocyclic bond distances and angles are similar to those found for other 1,3,4-thiadiazole structures [see for example 2,2′-(1,2-phenylenebis(methylenethio))-*bis*(5-methyl-1,3,4-thiadiazole), 2-(4′-cyanophenylthio)-5-methylthiadiazole, 2-(benzylthio)-5-phenyl-1,3,4-thiadiazole or 2,2′-(1,4-butanediyldithio)*bis*(1,3,4-thiadiazole)] [31]. In 2-benzylmercapto-5-methyl-1,3,4-thiadiazole, the phenyl ring is almost perpendicular to the heterocyclic ring (dihedral angle 84.69(8)°).

The molecular structure and relevant bond distances and angles for $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$ are shown in figure 2 and table 2. The structure consists of discrete $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$ centrosymmetric units, with two molecules per unit cell. Each Cu(II) is coordinated by two chloride ions and two 1,3,4-thiadiazole ligands. The geometry around the Cu(II) ion is best described as distorted square-planar with the two chlorides in *trans* position. Both 2-benzylmercapto-5-methyl-1,3,4-thiadiazole ligands coordinate through the N2 atom with a Cu–N2 distance of 1.9888(13) Å. The Cu–N bond lengths are comparable to those reported in the literature for

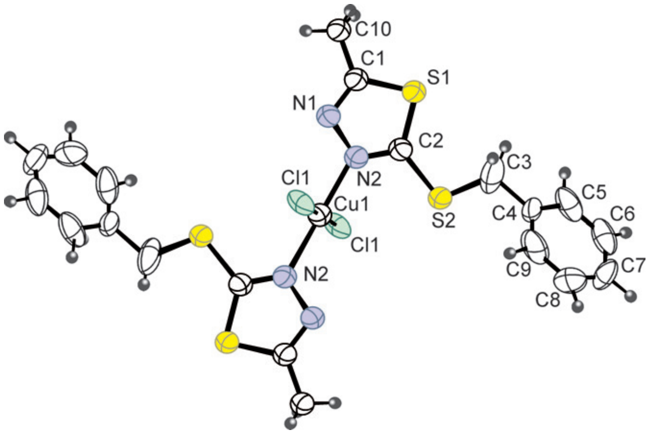

Figure 2. ORTEP drawing of $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$.

complexes with basal plane around Cu(II) [14, 15]. The Cu–Cl distance [2.2433(5) Å] is similar to that found in other similar complexes [32, 33].

The square-planar geometry around Cu(II) is less frequent for Cu(II) complexes with similar ligands. Most of the copper(II) structures (80%) (see for example [13–15, 34]) and in which the metal is coordinated directly by the thiadiazole group are octahedral or distorted square pyramidal geometry while only 20% are square planar (see for example [35, 36]). Thus, it seems that the steric effect of the bulky benzyl substituent and the absence of electronic delocalization through the thiadiazole substituent force Cu(II) into a *quasi* square-planar coordination environment. These facts correlate with coordination occurring through the N2 thiadiazole atom in the complex. Six other structures of copper complexes containing a ligand derived from the 1,3,4-thiadiazole ring coordinating through N in a monodentate fashion have been found in the CSD [37]. Two of them present a symmetric substituted 1,3,4-thiadiazole ligand: *bis*(4,7,10-trioxa-1,13-dithia(13)(2,5)-1,3,4-thiadiazolophane-N)-dibromocopper(II), and catena-(($\mu_2$-4,16-dioxa-1,7,13,19-tetrathia(7.7)(2,5)-1,3,4-thiadiazolophane-N,N′)-*bis*(nitrato-O)-copper) [36, 38]. In the other three, tetrakis(2-amino-5-methyl-1,3,4-thiadiazole-N)-chloro-copper(II) chloride, tetrakis(2-amino-5-ethyl-1,3,4-thiadiazole-N)-chloro-copper(II) chloride and trans-*bis*(2-amino-5-methyl-1,3,4-thiadiazole-N)-*bis*(3,5-dicarboxybenzoato-O)-copper(II) dehydrate, the 2-amino-5-alkyl-1,3,4-thiadiazole ligand is coordinated through the N bonded to the amino substituted C atom (N1 in our case) [39, 40]. For the remaining CSD reported complex, catena(diammino-*bis*($\mu_2$-2-(aminobenzenesulfonamido)-5-ethyl-1,3,4-thiadiazole-N,N″)-copper(II)) the 1,3,4-thiadiazole ligand is coordinated through N bonded to the *p*-aminobenzenesulfonamido substituted C atom [41]. Therefore in all reported Cu(II) complexes containing a monocoordinated 1,3,4-thiadiazole ligand the N bonded to the alkylthio substituted C atom group (N2 in our case) remains non-coordinated.

We report herein a ligand derived from the 1,3,4-thiadiazole ring coordinating through the N bonded monodentate to the alkylthio substituted C atom. Clearly, this particular behavior is due to the presence of the 5-methyl substituent with no electron delocalization. In some 1,3,4-thiadiazole sulfonamides with substituted amino groups,

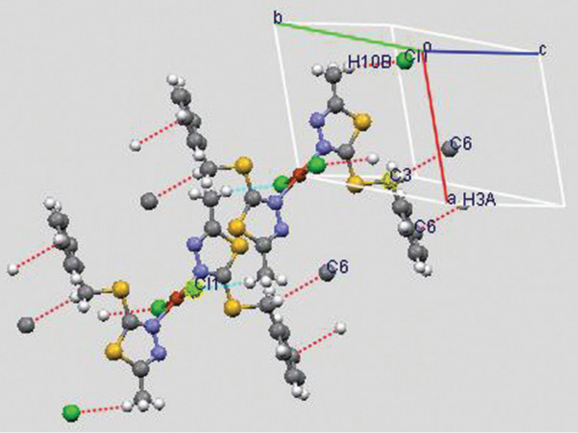

Figure 3. Molecular interactions and unit cell of $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$.

the N1 is the best donor atom because there is a significant interaction between the 1,3,4-thiadiazole ring and the substituted amino group; the negative differential charge on $N_{amino}$ is able to move through the $N_{amino}$-C1–N1 bonds and stabilize the decrease of negative charge in N1 generated upon coordination [22].

The most remarkable intermolecular distances for $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$ are $C(10)–H(10B)\cdots Cl(1)_i$ (i: $-x+1$, $-y+1$, $-z$) (2.8796(6) Å) and $C(3)–H(3A)\cdots C(6)_{ii}$ (ii: $-x+2$, $-y+1$, $-z+1$) (2.8673(25) Å), <4 Å indicating that molecules are held together by van der Waals forces (see figure 3).

No significant changes are observed in bond distances and angles in the 1,3,4-thiadiazole ring of the copper complex compared to those in the free ligand. It is evident that coordination has little influence on the ring structure, a situation clearly different from that found in the 2-amino-1,3,4-thiadiazole derivative thioether copper(II) [22].

In general, the distances and angles of the ligand under study are similar to those found for its analogue amino-thioether previously investigated [22]. However, the coordination toward Cu(II) is different. While the amino-thioether coordinates through the N1 of the ring, the methyl-thioether coordinates through N2, both as monodentate ligands. This dissimilar behavior cannot be attributed to the presence of different counteranions or solvents since both copper complexes were synthesized in the same medium and using copper(II) chloride. Nevertheless, the thiadiazolic methyl thioether does not have the slight electron density delocalization on C1–N1 that is found in thiadiazolic amino thioether and similar compounds with basic groups as substituents (amino, acetamido, tertbutyloxycarbonylamino), indicating electronic modification on the ring because of the methyl group. Thus, both steric and electronic effects of the ligands play important roles in affecting the structural topologies of such metal organic coordination architectures [42].

### 3.1. *Infrared spectra*

The FTIR spectra of the free ligand and its copper complex $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$ show the characteristic modes, in agreement with previous data [7, 8, 43].

Table 3. FTIR assignment for $C_{10}H_{10}N_2S_2$ and $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$.

| Mode | $C_{10}H_{10}N_2S_2$ | $[Cu(C_{10}H_{10}N_2S_2)_2Cl_2]$ |
|---|---|---|
| $\nu$C–H | 3058 (w) | 3053 (w) |
| | 3046 (w) | 3029 (w) |
| | 3033 (w) | 3006 (w) |
| | 2954 (w) | 2925 (w) |
| | 2920 (w) | 2761 (w) |
| | 2846 (w) | |
| | 2724 (w) | |
| $\nu$C–N | 1585–1496 (d, m) | 1494 (m) |
| | | 1454 (m) |
| $\delta$C–H | 1457 (m) | 1424 (m) |
| | | 1393 (s) |
| | | 1372 (m) |
| | | 1297 (w) |
| $\nu$C–C | 1245 (m) | 1239 (m) |
| $\delta$C–H | 1209 (w) | 1191 (m) |
| | | 1131 (s) |
| $\nu$N–N | 1050 (s) | 1058 (m) |
| | | 1027 (w) |
| $\delta$C–H | 992 (m) | 1002 (w) |
| | 972 (w) | 995 (w) |
| | 929 (w) | 978 (w) |
| | 901 (w) | 921 (w) |
| | 807 (m) | 886 (w) |
| | | 848 (w) |
| | | 822 (m) |
| | | 801 (m) |
| $\nu$C–S | 762 (w) | 773 (m) |
| | 716 (s) | 709 (s) |
| | 700 (sh) | 692 (sh) |
| Lattice modes | – | 566 (w) |
| | | 538 (w) |
| | | 477 (m) |
| | | 428 (m) |
| | | 368 (w) |
| | | 332 (s) |
| | | 286 (s) |

Note: (s) strong (m) medium (w) weak (sh) shoulder.

Table 3 presents the assignment of the most significant FTIR bands. Due to the rigidity of the 1,3,4-thiadiazole ring, the spectra cannot be interpreted in terms of localized vibrations because many atoms of the ring are involved in several modes [44]. However, an assignment for the bands with a major contribution of the 1,3,4-thiadiazole ring modes was possible on the basis of that performed by Edwards and co-workers [45] and our previous theoretical studies [10]. In the spectrum of the copper complex, the $\nu$C=N and $\nu$N–N modes are only slightly modified with respect to the free ligand, in contrast to that observed on the IR spectrum of the complex with the aminothioether in which those modes were shifted to lower frequencies by metal chelation [22]. This is consistent with a different coordination site for the complex under study, the $N2_{\text{thiadiazole}}$ (instead of the N1 found for the complex with the aminothioether). Also, the C–H vibrational modes were modified in the spectrum of the complex with respect to the free ligand, attributed to different crystal packing.

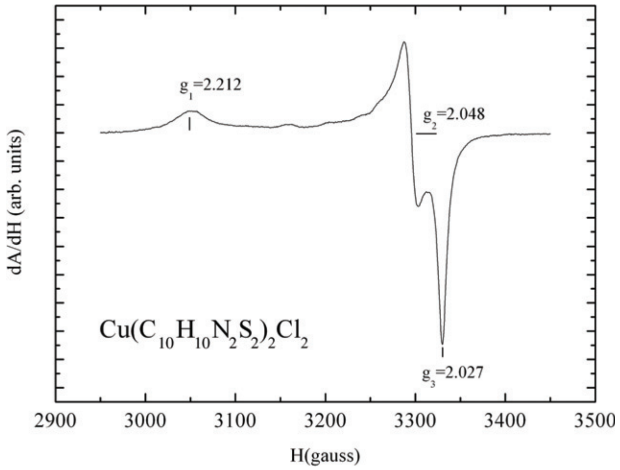

Figure 4. EPR spectrum in X-band at room temperature of $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$.

The $\nu$Cu–N and $\nu$Cu–Cl modes, expected at low-frequencies, could not be identified due to overlapping effects with lattice modes.

### 3.2. *Magnetic properties of $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$*

The Electron Paramagnetic Resonance (EPR) spectrum at room temperature was performed on a powdered sample. The obtained line is shown in figure 4 where three different spectroscopic splitting factors ($g_i$) can be identified, $g_1=2.212$, $g_2=2.048$ and $g_3=2.027$. These values are within expected $g$-values for $Cu^{2+}$ ($S=1/2$) paramagnetic ions [46] and the line can be satisfactorily reproduced for a powder spectrum. The anisotropy can be due to Cu in a planar array of two N and two Cl atoms. The total anisotropic $g$-value, computed from $<g>^2=(g_1^2+g_2^2+g_3^2)/3$, is $<g>=2.097$, gives a Curie constant $C=0.413$ emu/mol K or the effective magnetic moment of $1.82\,\mu_B$.

The magnetization was measured at 1000 Oe between 5 K and 310 K. The increase of $\chi$ when the temperature is diminished suggests paramagnetic behavior of the thioether copper(II) complex. We subtract from the magnetization data, the diamagnetic contribution ($M_d=-77.1\times10^{-3}$ emu/mole) of $[Cu(C_{10}H_{10}N_2S_2)Cl_2]$, which can be calculated adding each ion contribution [47].

The inverse of susceptibility was computed as H/M, where M is now the corrected values, and the data are represented in figure 5 with open circles. The line is the linear fit of the experimental data at low temperature using the inverse of a Curie–Weiss law ($\chi^{-1}=(T-\theta)/C$ between 5 K and 300 K. From the slope ($1/C$) we obtain the Curie constant ($C=0.415(2)$ emu/mol K) value, which gives an effective magnetic moment of $1.82(1)\ \mu_B$. This value is in good agreement with those from the EPR experiment and also with that expected for isolated paramagnetic $Cu^{2+}$ with spin and orbital contributions. The $\theta$ value obtained from the fit is $-2.2(3)$ K, suggesting the presence of small antiferromagnetic correlation between $Cu^{2+}$ neighbors.

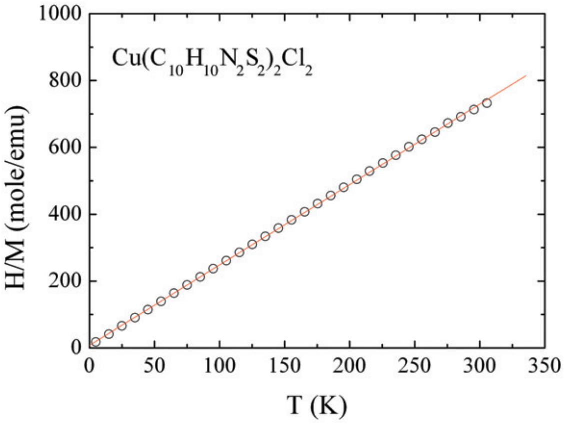

Figure 5. Inverse of magnetic susceptibility ($\chi^{-1}$) *vs.* T for [$Cu(C_{10}H_{10}N_2S_2)_2Cl_2$]. The linear fit is with a paramagnetic Curie–Weiss law.

## 4. Conclusions

Single-crystal X-ray diffraction data, FTIR spectrum and magnetic behavior of the Cu(II) complex of 2-benzylmercapto-5-methyl-1,3,4-thiadiazole are reported. In the copper(II) complex the ligand coordinates through the thiadiazole ring N2 atom yielding a copper(II) monomer. This is the only one example of a Cu(II) complex using a 1,3,4-thiadiazole derived ligand that coordinates this way and exhibits square-planar geometry. The conformation of the bulky benzyl substituent at position 2 of the 1,3,4-thiadiazole ring is not modified upon metal-ligand coordination. This fact, together with the fact that the coordination geometry around the Cu(II) is best described as distorted square-planar, similar to Pt(II) and Au(I) complexes [16], makes this copper(II) complex an appropriate low weight model for protonated copolymer resins based on poly(styrene-codivinylbenzene) and linked to 2-amino-1,3,4-thiadiazole-5-thiol generally used for extraction of gold and platinum.

## Supplementary material

CCDC 199762 and CCDC 611439 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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