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X-ray structure and EPR behavior of a new dimeric copper(II) complex with 4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide

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Abstract

A new complex, $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$ (sulfameter = 4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide), has been synthesized. Its structure has been determined by single-crystal X-ray diffraction and its spectroscopic properties (EPR, IR, Raman, UV–Vis) have been analyzed. The structure presented three different dimeric units in the unit cell and the EPR spectra, characteristic of antiferromagnetically coupled dimers, revealed two magnetically different dimeric environments.

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1. Introduction

There are many topics of considerable importance in sulfonamide coordination chemistry. In the analytical area, sulfonamides have been investigated as reagents for the separation, concentration, and selective determination of many of the first-row transition metal cations [1–3]. As a result, analytical tests using reactions with sulfonamides, have been included in modern pharmacopoeias (Ph.Eur, BP, USP). Moreover, some sulfonamide complexes have proved to be relevant catalysts in chemical reactions, such as Zn-sulfonamide complexes that catalyzes enantioselective cyclopropanations [4] and also as reagents for the cleavage of nucleic acids [5–7]. On the other hand, numerous sulfonamide complexes have been studied as simple models of metal–protein interactions [8–11].

In addition, some metal sulfonamides have drawn much attention due to the fact that they are used in medicine especially as antibacterial drugs. It is known that coordination with metals can modify the toxicological and pharmacological properties of free sulfonamides [12–17].

In all the above reported areas knowledge of the structure of the involucrate sulfonamide complexes is extremely useful for understanding their activity.

Due to their versatility, these ligands can act as monodentate, bidentate or polydentate coordinating groups, providing monomeric structures, dimeric, and polymeric arrangements [8,18–21]. Sulfameter (4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide), a well-known antibacterial sulfadrug, has several groups with donor atoms that can interact with metal ions, such as the ⁴N from aryl amine, the ¹N and O from the sulfonamide group, and heterocyclic N (N_h) as shown in Fig. 1. In spite of the fact that a copper complex with sulfameter is reported [22] until now no single-crystal X-ray diffraction studies have been performed.

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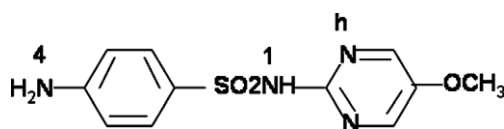


Fig. 1. Sulfameter (4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide) scheme.

As a part of our work on biologically interesting copper complexes [21,23–25] and with the aim to contribute with structural information useful for the general understanding of the microbiological behavior of metal–sulfonamide complexes, the synthesis and structural characterization of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$ were reported. Its structure was analyzed and compared with spectroscopic results. Although there are different molecules with sulfonamides reported with similar dimeric Cu–Cu interactions [26–31], this structure presented three dimeric units in the unit cell and the EPR spectra revealed two magnetically different dimeric environments.

2. Experimental

2.1. Materials and methods

Sulfameter and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were provided by SIGMA and Fluka, respectively, and all reagents were of analytical grade.

The decomposition point was measured with a Gallenkamp apparatus.

The elemental analysis was performed with a Carlo Erba EA1108 elemental analyzer. The copper content was determined by iodometric method.

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.

IR spectra, in the range between 4000 and 200 cm^{-1} , were recorded on a BOMEM M 102 FTIR spectrophotometer using the KBr pellet technique.

Raman spectra were scanned on a Brucker FRA 106 instrument mounted on an IFS 66 Fourier transform optical bench. A Nd/YAG laser (power = 100 mW) was used for excitation.

Electronic spectra were registered on a Beckman DU 70 spectrophotometer using a suspension in Nujol.

2.2. Synthesis of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$

The complex was synthesized according to the procedure described by Bult et al. [32]. A solution of NaOH 1 M was added drop wise over a suspension of sulfameter

(2.8 g, 10 mmol) in 100 mL of water until total dissolution (pH 9–10). To the resulting solution 50 mL of 0.5 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added with stirring. After half an hour the brown precipitate formed was filtered, washed with water, dried at room temperature and protected from light. The complex was recrystallized from acetone. Yield (4.6 g, 73%). The decomposition point was 226°C . The results of the elemental analysis were: *Anal.* Calc. for $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$ ($\text{C}_{132}\text{H}_{137}\text{N}_{48}\text{O}_{38.5}\text{S}_{12}\text{Cu}_6$): C, 41.97; N, 17.81; H, 3.63; S, 10.17; Cu, 10.10. Found: C, 41.86; N, 17.70; H, 3.70; S, 9.93; Cu, 10.22%.

2.3. Crystal structure determination

Low temperature X-ray diffraction data collection was performed at 150(2) K, on an Enraf-Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated $\text{MoK}\alpha$ radiation (0.71073 \AA). Data were collected up to 50.8° in 2θ , with a redundancy of 4 in the ϕ scans mode. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [33]. Integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [34]. Multi-scan absorption correction was applied [35].

The structures were solved by direct methods with SHELXS-97 [36]. The models were refined by full-matrix least squares on F^2 with SHELXL-97 [37]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [37]. Hydrogen atoms of the CH and CH_2 groups were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom to which each one was bonded. This percentage was set to 50% for the hydrogen atoms of the CH_3 groups and the water molecules. Data collections and experimental details for the complexes are summarized in Table 1. The programs SHELXL-97 and ORTEP-3 [38] were used within WinGX [39] to prepare materials for publication. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The synthesis of the complex was performed in an alkaline medium where the deprotonation of the amide group took place, additionally favored by the coordination through this group. Consequently, the copper complex was neutral.

The experimental elementary analysis values are in reasonable agreement with the calculated ones.

3.1. Crystal structure determination of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$

The unit cell comprises three slightly different dimeric units. Fig. 2 presents an ORTEP diagram of one of these

Table 1
Crystal data and structure refinement of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$

Empirical formula	$[\text{C}_{44}\text{H}_{44}\text{N}_{16}\text{O}_{12}\text{S}_4\text{Cu}_2]_3 \cdot 2.5\text{H}_2\text{O}$
Formula weight	3777.86
Crystal system	monoclinic
Space group	$P2_1/c$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	19.567(1)
<i>b</i> (Å)	43.197(2)
<i>c</i> (Å)	18.885(1)
β (°)	97.494(2)
Volume (Å ³)	15825.9(14)
<i>Z</i>	4
<i>D</i> _{calc} (Mg/m ³)	1.586
Absorption coefficient (mm ^{−1})	1.043
<i>F</i> (000)	7756
Crystal size (mm)	0.20 × 0.12 × 0.04
θ Range for data collection (°)	2.92–25.40
Index ranges	$-23 \leq h \leq 23$, $-50 \leq k \leq 52$, $-22 \leq l \leq 22$
Reflections collected	55826
Independent reflections [<i>R</i> (int)]	28930 [0.2094]
Completeness to $\theta = 25.4^\circ$	99.5%
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.9403 and 0.8022
Data/restraints/parameters	28930/1/2146
Goodness-of-fit on <i>F</i> ²	1.020
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0793, <i>wR</i> ₂ = 0.0949
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2604, <i>wR</i> ₂ = 0.1276
Largest difference in peak and hole (e Å ^{−3})	0.561 and −0.455

dimeric units, showing the atoms labeling and the 30% probability ellipsoids.

Each copper atom of the dinuclear unit is four-coordinated with a slightly distorted square planar environment. It is bonded to four sulfameter ligands through two *N*_h

pyridazine atoms from two sulfameter molecules and two ¹N atoms from the other sulfameter ligands as scheme in Fig. 3 shows. In the coordination polyhedra both *N*_h atoms are in trans position and consequently the ¹N atoms show the same disposition.

In addition, each copper interacts with two sulfonamide O atoms, as Fig. 3 shows and as it can be inferred from the IR spectrum. This coordination environment is different from that previously suggested for a similar copper complex $[\text{Cu}(\text{sulfameter})_2] \cdot 3\text{H}_2\text{O}$ where the spectroscopic data indicated the coordination through the sulfonyl oxygen and sulfonamide nitrogen [22]. The two copper ions of each unit are bridged by four-triatomic ¹N–C–*N*_h chemical path (see Fig. 3).

Fig. 4 shows the disposition of the three slightly different dimeric units in the unit cell.

Selected bond distances and angles around the copper atoms for the three dimeric units are presented in Table 2. For the sake of clarity the N atoms are labeled with the nomenclature noted in Fig. 1 and not to the ORTEP diagram.

As shown in Table 2, in some copper centers the Cu–*N*_h bond distances are shorter than the Cu–*N*¹ ones, while in other centers the opposite behavior is observed. However, in all cases the Cu–*N*_h ($\Delta = 1.951$ – 2.025 Å) and the Cu–*N*¹ ($\Delta = 1.993$ – 2.036 Å) bond lengths are in the range of those previously reported in similar copper complexes with sulfonamides [19,21,5]. The Cu–Cu distances in the unit 1 and 2 are similar to those of most of the structurally related complexes [19,28,40,41]. On the opposite, unit 3 presented a short Cu–Cu distance (2.535 Å) comparable with those of several complexes like $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2] \cdot 2\text{dmf}$ (2.541 Å) [42], $[\text{Cu}_2(N\text{-}p\text{-tolylsulfonyl pyridine})_4]$ (2.516 Å), and $[\text{Cu}_2(1,3\text{-di-phenyltriazinato})_4]$

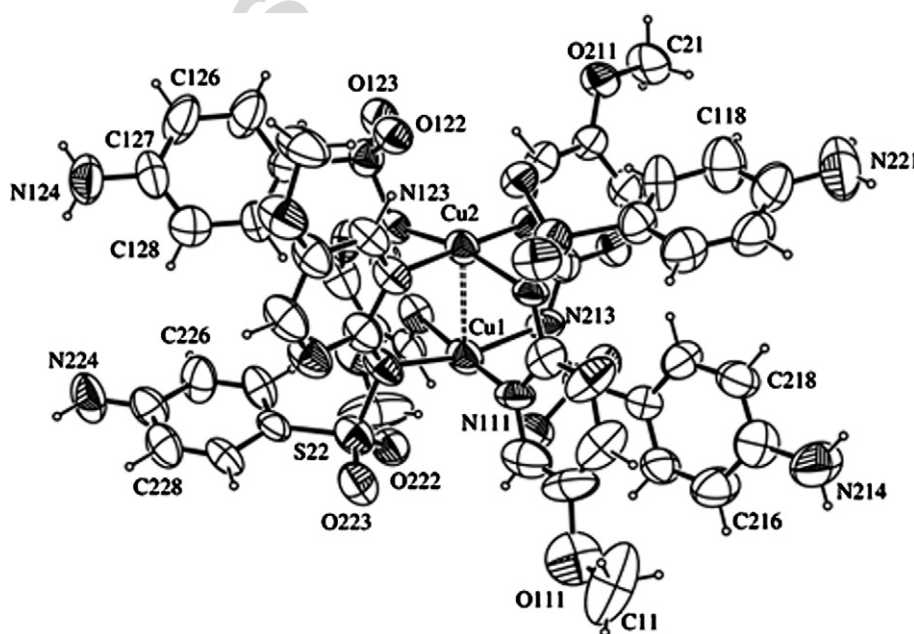


Fig. 2. ORTEP view of a dimeric unit of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$, showing the atoms labeling and the 30% probability ellipsoids.

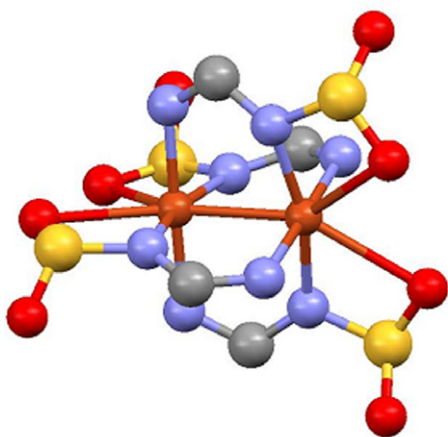


Fig. 3. Scheme of copper coordination environment.

(2.441 Å) [43]. This different Cu–Cu bond length in unit 3 seems to be related to an increment in two of the four Cu–O distances (see Table 2). It is interesting to observe that, in the three units, the sulfonamidic O atoms participate in a short interaction with the pyrimidinic N atoms, not bonded to the metal (ranging between 2.85(1) and 3.04(1) Å), forming a five member ring.

The square planar geometry of all copper ions presents distortions as it is shown in the Cu–N₄ plane distances in Table 2.

The bond angles of the Cu–N₄ square plane are close to 90°. The Cu–N₄ planes of each dimeric unit are almost coplanar and perpendicular to the Cu–Cu axes. Besides, the angles between the Cu–Cu axes for units 1 and 3 are almost parallel ($\alpha = 17.79(4)^\circ$) while for unit 1 and 2 are

almost perpendicular ($\alpha = 89.90(3)^\circ$). The N1–C–Nh angles of the unit 3 bridge are slightly greater than those of the dimeric units 1 and 2.

Taking into account these results, it can be said that units 1 and 2 present little difference between each other, differing by the orientation of the cyclic groups and their substituents while unit 3 differs in several bond distances and angles, principally in the Cu–Cu distance.

The study of the crystal packing shows that the three-dimensional structure is stabilized by several networks of inter- and intra-molecular interactions (see Table 3). The structure shows four H-bond intra-unit between the Nh and the sulfonic O of the same sulfonamide. Besides, three H-bond inter-unit are formed: one of them between the sulfonic O of one unit and the ⁴N of the second unit, the second one between the O from the –OCH₃ of one unit and the N_H of the other unit, and the third between two sulfonic oxygen of different units. The water molecules bond the dimeric units 2 and 3 through moderated hydrogen bonds [44] involving the O atoms from the –SO₂ groups, whereas unit 1 does not have any interaction with the water molecules. An interesting feature of this complex's crystal packing is that ligand arrangement gives rise to a hydrophilic region formed by the NH₂–Ar, the –SO₂N–, and the –OCH₃ groups placed to the external surface of a cylindrical area with a hydrophobic region in the inside. However, no stacking between the aromatic rings is observed.

3.2. Vibrational spectra

The IR and Raman spectra of the complex were compared with those of previously reported complexes

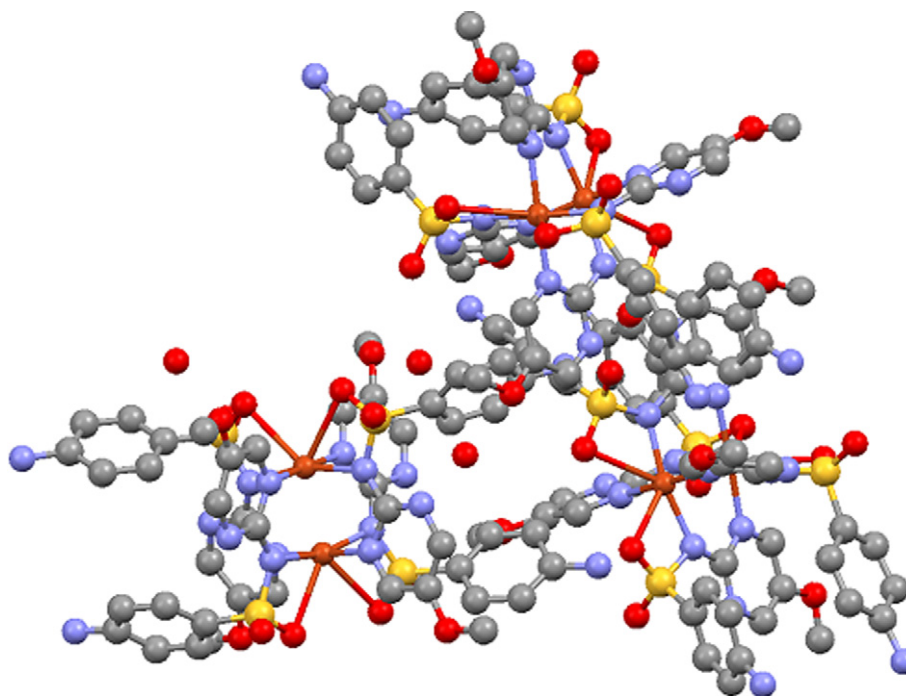


Fig. 4. ORTEP view of the asymmetric unit of [Cu₂(sulfameter)₄]₃ · 2.5H₂O.

Table 2
Selected bond distances (Å) and angles (°) for the three dimeric units of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$

Unit 1	Cu1–Nh	2.027(6)/1.956(7)	Cu2–Nh	2.017(6)/1.990(6)
	Cu1–N1	2.009(6)/2.008(6)	Cu2–N1	2.016(5)/2.012(6)
	Cu1–O _{sulfonic}	2.679(6)/2.566(6)	Cu2–O _{sulfonic}	2.725(6)/2.485(6)
	Cu1–N ₄ plane	0.1919(9)	Cu2–N ₄ plane	0.1731(9)
	<i>Cu1–Cu2 2.557(1)</i>			
	Nh–Cu1–N1	90.8(2)/88.3(2)/89.2(2)/90.8(2)	Nh–Cu2–N1	90.5(2)/89.5(2)/89.0(2)/90.5(2)
	N1–Cu1–N1	164.0(2)	N1–Cu2–N1	164.8(2)
	Nh–Cu1–Nh	176.9(3)	Nh–Cu2–Nh	177.5(3)
	Nh–Cu1–Cu2	91.3(2)/85.7(2)	Nh–Cu2–Cu1	92.0(2)/86.0(2)
	N1–Cu1–Cu2	79.90(18)/84.19(17)	N1–Cu2–Cu1	79.66(16)/85.16(17)
	¹ N–C–N _h	113.9(9)/115.0(9)/115.8(9)/118.0(9)		
Unit 2	Cu3–Nh	1.990(6)/1.990(6)	Cu4–Nh	2.012(6)/2.005(6)
	Cu3–N1	2.034(5)/2.008(5)	Cu4–N1	2.022(6)/2.005(5)
	Cu3–O _{sulfonic}	2.626(6)/2.545(6)	Cu4–O _{sulfonic}	2.600(6)/2.552(6)
	Cu3–N ₄ plane	0.1773(8)	Cu4–N ₄ plane	0.1437(8)
	<i>Cu3–Cu4 2.556(1)</i>			
	Nh–Cu3–N1	90.7(2)/89.9(2)/89.8(2)/89.1(2)	Nh–Cu4–N1	90.0(2)/88.4(2)/90.0(2)/91.5(2)
	N1–Cu3–N1	164.1(3)	N1–Cu4–N1	165.0(2)
	Nh–Cu3–Nh	177.8(3)	Nh–Cu4–Nh	178.3(2)
	Nh–Cu3–Cu4	89.2(2)/88.7(2)	Nh–Cu4–Cu3	90.46(19)/88.9(2)
	N1–Cu3–Cu4	82.47(16)/81.67(16)	N1–Cu4–Cu3	81.88(17)/83.24(17)
	¹ N–C–N _h	114.6(9)/116.6(9)/115.1(9)/115.3(9)		
Unit 3	Cu5–Nh	1.992(7)/1.990(6)	Cu6–Nh	2.018(6)/2.016(7)
	Cu5–N1	2.034(6)/1.978(6)	Cu6–N1	1.997(7)/1.992(6)
	Cu5–O _{sulfonic}	2.798(6)/2.509(6)	Cu6–O _{sulfonic}	2.749(6)/2.549(6)
	Cu5–N ₄ plane	0.1647(9)	Cu6–N ₄ plane	0.1519(9)
	<i>Cu5–Cu6 2.535(1)</i>			
	Nh–Cu5–N1	90.2(3)/88.0(2)/90.3(2)/90.3(2)	Nh–Cu6–N1	91.5(2)/90.1(3)/87.1(2)/90.5(2)
	N1–Cu5–N1	167.7(3)	N1–Cu6–N1	167.6(3)
	Nh–Cu5–Nh	174.6(4)	Nh–Cu6–Nh	175.5(3)
	Nh–Cu5–Cu6	86.6(2)/88.2(3)	Nh–Cu6–Cu5	89.5(2)/86.1(2)
	N1–Cu5–Cu6	85.74(18)/82.04(19)	N1–Cu6–Cu5	84.47(18)/83.3(2)
	¹ N–C–N _h	116.7(9)/117.5(9)/119.0(9)/117.1(9)		

[14,18,20,45–53]. Table 4 summarizes the main bands and their proposed assignments.

In Table 4, the bands of the complex assigned to $\nu_{\text{a}}(\text{NH})$ and $\nu_{\text{s}}(\text{NH})$ appeared at similar frequencies to those obtained for the free sulfameter, which agree with the fact that the amino group did not participate in the coordination. The Raman spectrum of the complex did not show these bands in accordance with the bibliographic data [53]. Furthermore, δNH_2 bands are almost unchanged in the IR spectra and have exhibited no Raman signals.

The free ligand spectrum presented a strong broad band at 3230 cm^{-1} possibly involving the NH stretching of the sulfonamide group and other vibrational modes characteristic of ligand. In the complex spectrum this band changed to a medium-intensity signal at 3238 cm^{-1} . The change in this band is probably due to the disappearance of the $\nu(\text{NH})$ of the sulfonamide group after deprotonation, remaining the other vibrational modes of the molecule. This behavior was previously reported in other copper complexes with sulfonamides [54].

The heteroaromatic ring motions cannot be interpreted as simple vibrational modes as most of them are of com-

plex origin and involve different vibrational types. Some ring absorption bands can shift upon complexation to metal ions through the nitrogen atom, but most of them are not metal-dependent. As shown Table 5, only one band presented a significant shift ($\Delta = 21\text{ cm}^{-1}$) to lower frequencies, while in most bands no change was observed.

The asymmetric and symmetric $-\text{SO}_2$ group stretching vibrations shifted to lower frequencies in the copper complex ($\Delta = 40\text{ cm}^{-1}$ and $\Delta = 27\text{ cm}^{-1}$, respectively). This behavior is in accordance with the fact that each copper interacts with two sulfonamide O atoms from two different sulfameter molecules as shown in Fig. 2.

Furthermore, complex spectrum showed a broad band at 3580 cm^{-1} assigned to the presence of a water molecule in the complex. Other bands corresponding to water molecule modes could not be assigned due to the fact that they were overlapped with other signals.

3.3. Electronic spectrum

The copper complex presented three wide bands at 358, 557, and 841 cm^{-1} . According to some authors, the band at

Table 3
Intra- and inter-molecular hydrogen bonds in the three dimeric units of $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$

D–H...A	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
<i>Intra-molecular interactions</i>				
N324–H32B...O113	0.880	3.155(7)	2.642(4)	118.2(4)
N424–H42A...O123	0.880	3.002(8)	2.182(5)	154.8(4)
N424–H42B...O512	0.880	2.885(8)	2.016(5)	168.8(4)
O1W–H11W...O423	0.850	2.865(9)	2.200(4)	135.0(5)
O1W–H12W...O613	0.850	2.785(9)	1.936(5)	176.8(5)
O2W–H21W...O423	0.850	3.236(7)	2.648(5)	127.5(4)
O2W–H21W...N422	0.850	2.829(8)	2.544(6)	100.8(4)
O2W–H21W...O1W	0.850	3.015(9)	2.785(8)	97.4(4)
O2W–H22W...O511	0.850	2.955(8)	2.108(6)	174.2(4)
O2W–H22W...O1W	0.850	3.015(9)	2.682(8)	104.9(4)
O3W–H31W...O413	0.850	2.896(8)	2.106(5)	154.5(4)
<i>Inter-molecular interactions</i>				
N224–H22C...O123 ⁱ	0.880	3.011(8)	2.146(5)	167.7(4)
N224–H22D...O512 ⁱ	0.880	2.993(8)	2.131(5)	166.5(4)
N124–H12A...O523 ⁱ	0.880	2.979(8)	2.259(5)	139.0(4)
N214–H21A...O422 ⁱⁱ	0.880	3.089(8)	2.315(4)	146.7(4)
N214–H21B...O321 ⁱⁱ	0.880	3.294(9)	2.536(6)	144.7(5)
N221–H22B...O311 ⁱⁱ	0.880	2.875(9)	2.066(5)	152.5(5)
N624–H62A...O322 ⁱⁱⁱ	0.880	3.092(7)	2.290(4)	151.5(4)
N324–H32A...O2W ⁱⁱⁱ	0.880	2.932(7)	2.084(5)	161.3(4)
N221–H22A...O311 ⁱⁱⁱ	0.880	3.14(1)	2.678(6)	113.6(5)
N221–H22A...O423 ⁱⁱⁱ	0.880	3.195(8)	2.733(4)	114.1(5)
N514–H51B...O313 ⁱⁱⁱ	0.880	2.970(7)	2.105(4)	167.5(4)
N314–H31B...O112 ^{iv}	0.880	3.208(7)	2.372(4)	158.7(4)
N314–H31B...N112 ^{iv}	0.880	3.20(1)	2.593(8)	127.2(4)
N314–H31A...O521 ^v	0.880	3.327(9)	2.935(7)	109.0(4)
N414–H41B...O623 ^v	0.880	2.955(7)	2.120(4)	158.0(4)
N314–H31A...O3W ^{vi}	0.880	2.985(9)	2.146(6)	159.2(4)
N414–H41A...N412 ^{vi}	0.880	3.105(9)	2.235(7)	169.7(4)
O3W–H32W...O622 ^{vii}	0.850	2.989(7)	2.299(5)	138.5(4)
O3W–H32W...O623 ^{vii}	0.850	3.234(7)	2.443(4)	155.0(4)
N614–H61B...O213 ^{viii}	0.880	3.282(8)	2.549(5)	141.3(4)
N614–H61B...N212 ^{viii}	0.880	3.126(9)	2.347(7)	147.6(4)
N524–H52A...O213 ^{viii}	0.880	3.04(1)	2.206(5)	157.4(6)
N514–H51A...O221 ^{ix}	0.880	2.907(8)	2.114(5)	149.5(4)
N624–H62B...O323 ^{ix}	0.880	2.918(8)	2.170(5)	142.4(4)
N614–H61A...O222 ^x	0.880	2.995(7)	2.202(4)	149.7(4)

Symmetry codes: i: $x, -y - 1/2, +z + 1/2$; ii: $x + 1, +y, +z$; iii: $-x - 1, -y, -z - 1$; iv: $-x - 1, -y, -z$; v: $-x - 2, -y, -z - 1$; vi: $-x - 2, -y, -z$; vii: $x, +y, +z + 1$; viii: $x - 1, +y, +z$; ix: $x, +y, +z - 1$; x: $x - 1, -y - 1/2, +z - 1/2$.

Table 4
Characteristic IR and Raman (R) bands (cm^{-1}) of the spectra of sulfameter and $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$ complex

IR (Sulfameter)	IR $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$	R $[\text{Cu}_2(\text{sulfameter})_4]_3 \cdot 2.5\text{H}_2\text{O}$	Assignment
–	3580 (m)	–	$\nu(\text{OH})$
3465 (s)	3467 (br, s)	–	$\nu_{\text{as}}(\text{NH}_2)$
3370 (s)	3369 (s)	–	$\nu_{\text{s}}(\text{NH}_2)$
3230 (s)	3238 (m)	–	$\nu(\text{NH})\text{sulf.}$
3072 (w)	3068 (w)	3065 (w)	$\nu(\text{=CH})\text{pyrimidine ring}$
1632 (s)	1630 (m)	–	$\delta(\text{NH}_2)$
1594 (s), 1502 (s)	1596 (s), 1503 (m)	1596 (s)	$\nu(\text{C=C})$ aromatic
1569 (s), 1464 (s), 1422 (s)	1548 (m), 1464 (s), 1422 sh	1500 (vw), 1455 (w), 1428 (w)	ν pyrimidinic ring
1320 (s, br)	1280 (s)	1285 (w)	$\nu_{\text{as}}(\text{SO}_2)$
1152 (s, br)	1125 (s)	1126 (s)	$\nu_{\text{s}}(\text{SO}_2)$
1090 (s)	1082 (s)	1086 (w)	$\delta(\text{CH})$ aromatic

ν (stretching), ν_{a} (asymmetric stretching), ν_{s} (symmetric stretching), br (broad), s (strong), m (medium), w (weak), (–) no band.

358 cm^{-1} is related to a binuclear nature of copper complexes [32], while other authors assigned it as either metal–ligand [14,45] or ligand–metal [50] charge transfers.

In this case, the first assignment is in accordance with the structure found for the complex. In spite of this, there are different copper-sulfonamide complexes which present

Table 5

EPR parameters obtained by spectral simulation using EASYSIM Program for $S = 1$ paramagnetic system

Dimer species	g -Factor (± 0.001)	D (cm^{-1})	E (cm^{-1})	A_{\parallel} (MHz)
1	$g_z = 2.240$	0.12	0.002	230
	$g_y = 2.039$			
	$g_x = 2.041$			
2	$g_z = 2.250$	0.18	0.005	275
	$g_y = 2.043$			
	$g_x = 2.043$			

The experimental spectra used in simulation were measured at X- and Q-band spectrometer at room temperature.

this band and do not bear dimeric structure [21]. The other two bands correspond to d–d transitions [51].

3.4. EPR measurements

The X-band EPR spectrum (Fig. 5A) of the title complex shows major lines centered at ~ 150 , ~ 270 , ~ 315 , and ~ 380 mT. This set of resonances can be rationalized in terms of a coupled dimer ($S = 1$) of Cu(II) ions. The copper coupling is antiferromagnetic as determined from the absence of EPR signal at 4 K, which indicates a $S = 0$ ground state for the spin system. The $g = 2$ (~ 315 mT) resonance in this case is most likely due to mononuclear impurities in the sample.

In the $S = 1$ case, the zero-field contribution gives rise to two allowed transitions per principal direction (x, y, z) [55], thus yielding a six-line pattern in the EPR spectrum [56]. The resonance fields for each of those transitions are denoted H_{x1} , H_{x2} , H_{y1} , H_{y2} , H_{z1} , H_{z2} , and expressions for them can be found elsewhere [57]. The two major lines observed in Fig. 5A result from the overlap at X-band of resonance corresponding to H_{x1} and H_{y1} (~ 270 mT) and H_{x2} and H_{y2} (~ 380 mT). The H_{z2} EPR signal is barely seen as a slight shoulder around ~ 420 mT. Another resonance is observed at ca. 150 mT (Fig. 5A) and is due to a collapse of the half-field transition ($\Delta M_s = \pm 2$), present in coupled systems, with the H_{z1} resonance. At Q-band (Fig. 5B), the otherwise overlapped signals corresponding to the half-field (~ 580 mT) and H_{z1} (~ 990 mT) transitions are clearly resolved. The other resonance in the $g \sim 2$ region can also be unambiguously assigned to the additional peaks observed in the spectrum ($H_{x1}, H_{y1} \sim 1150$ mT and $H_{x2}, H_{y2} \sim 1250$ mT). Moreover, the Q-band spectrum reveals extra peaks that indicate the existence of a second magnetically non-equivalent copper dimer (see calculated spectra for each component in Fig. 5B). This second less intense component presents the same pattern of resonance fields discussed above.

To further investigate the origin of the spectra at both frequencies, we firstly performed spectral simulation of the Q-band spectrum (Fig. 5B) using the EasySpin package [58]. This software has been recently made available to the EPR community and is designed to address several types of EPR simulations including solid-state spectra of both sin-

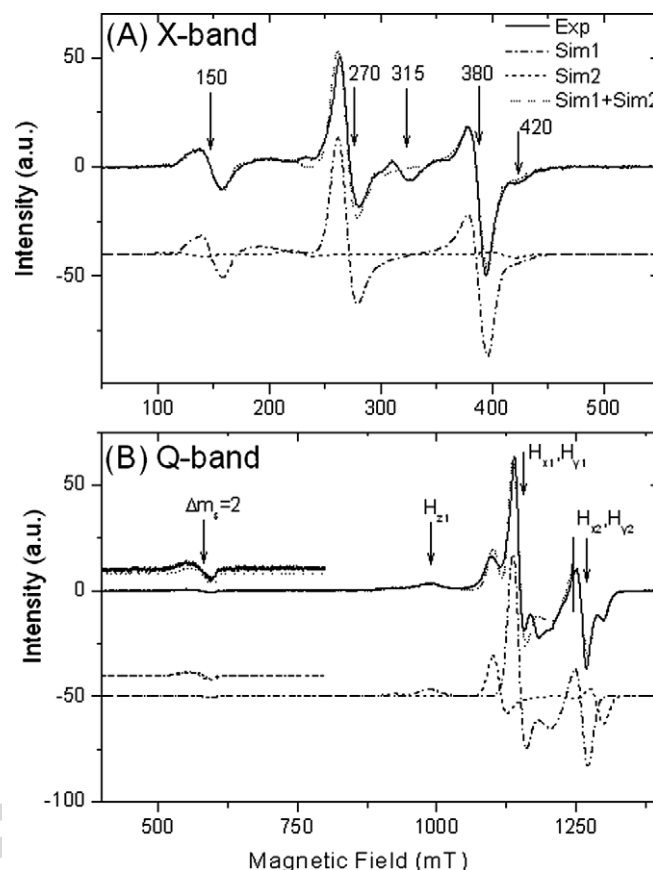


Fig. 5. (A) X- and (B) Q-band EPR spectra (solid lines) of polycrystalline sample of $[\text{Cu}_2(\text{sulfamer})_4]_3 \cdot 2.5\text{H}_2\text{O}$ and their respective simulations (short dotted lines) obtained using the EasySpin software. The calculated spectra for each component (sim1 and sim2) are also shown in the figure. Arrows indicate the resonance fields discussed in the text.

gle crystals and disordered systems with any electronic spin S . In our case, the spin Hamiltonian includes the following interactions:

$$\mathcal{H} = \beta B \cdot g \cdot S + S \cdot D \cdot S + S \cdot A \cdot I$$

where B is the applied magnetic field, g is the gyromagnetic tensor, D is the zero-field interaction or spin–spin tensor and A is the hyperfine interaction. The experimental spectrum was simulated with two sets of g -values (Table 5), which yielded a very reasonable calculated spectrum (Fig. 5B), thus confirming our initial assumption of two non-equivalent types of dimers. The g , A , and D parameters determined from the Q-band simulation were then used to simulate the X-band spectrum and resulted in a very good agreement (Fig. 5A – short dotted line). Minor adjustments in the linewidth parameters were made to achieve the best simulated spectra. The g - and D -values obtained from our simulation are in agreement with values previously determined for other copper dimers [42,19,59].

In our EPR spectrum we can then distinguish two sets of dimers (species 1 and 2), whose differences in coupling mechanism could be related to difference in the Cu–Cu distance as observed from the X-ray data. As described by

Casanova et al. [40], in this kind of copper arrangement this distance plays an important role in the exchange coupling.

4. Conclusions

This work showed a new copper(II) complex with sulfamer as ligand. Its structure presented three dimeric units in the asymmetric unit. Two of them are similar whilst the other presented structural differences. The EPR spectra indicated the copper coupling is antiferromagnetic and showed the existence of two magnetically non-equivalent dimers. The IR spectra is in accordance with the coordination of copper(II) through the sulfonamidic N and the heterocyclic N and the electronic spectra agreed with the structure found.

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Appendix A. Supplementary material

CCDC 289562 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2007.03.005](https://doi.org/10.1016/j.poly.2007.03.005).

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