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Syntheses and properties of binuclear copper(II) mixed-ligand complexes involving thiodiglycolic acid. The crystal structures of $[(phen)_2Cu(\mu\text{-tdga})Cu(phen)](NO_3)_2 \cdot 5H_2O$ and $[(H_2O)(pmdien)Cu(\mu\text{-tdga})Cu(pmdien)(H_2O)](ClO_4)_2$

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Abstract

Mixed-ligand binuclear Cu(II) complexes involving thiodiglycolate(2−) anion and nitrogen-donor ligands in the coordination sphere of composition $[(phen)_2Cu(\mu\text{-tdga})Cu(phen)](NO_3)_2 \cdot 5H_2O$ (**1**) and $[(H_2O)(pmdien)Cu(\mu\text{-tdga})Cu(pmdien)(H_2O)](ClO_4)_2$ (**2**), where phen = 1,10-phenanthroline, H_2tdga = thiodiglycolic acid, pmdien = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, have been prepared. Temperature dependence of magnetic susceptibility, EPR spectroscopy and single crystal X-ray analysis has been used to characterize these compounds. Magnetic susceptibility measurements over the 1.9–300 K temperature range revealed a weak antiferromagnetic interaction between two copper atoms with the exchange integral value $2J = -4.80$ cm^{-1} for **1** and -0.71 cm^{-1} for **2**. The bridging dianion of thiodiglycolic acid is coordinated in each of the two complexes in a different manner.

Keywords: Copper(II); Thiodiglycolic acid complexes; Crystal structures; EPR; Magnetic properties

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1. Introduction

Much attention has been focused in recent years towards characterization of binuclear and polynuclear transition metal complexes bridged by polyatomic ligands. The complexes are interesting not only from magnetochemical point of view, as many of them show magnetic exchange interactions, but also they can serve as potential models of biological systems [1,2]. The carboxylato ion often participates as an important ligand in many metalloenzymes. Complexes with dicarboxylic acids, for example oxalic [3–5], α,ω-dicarboxylic [6–8], thiophene-2,5-dicarboxylic [9,10] and dicarboxylic acids with varying chain lengths, conjugated or unconjugated [11], belong to the very often studied ones. Thiodiglycolic acid is a dicarboxylic acid and moreover it possesses a sulfur atom, which can also be coordinated. Structurally were characterized, for example, Cd(II), Zn(II) and Ni(II) thiodiglycolato complexes [12–16]. As follows from the Cambridge Structural Database, only two copper complexes involving the acid have been studied by single crystal X-ray analysis. The geometry around the copper atom in $[Cu(bpy)(tdga)(H_2O)] \cdot 4H_2O$ can be described as distorted octahedral with the metal center coordinated by two nitrogen atoms of bpy, two oxygen and a sulfur atom of tdga^{2-} and an oxygen atom of the water molecule [17]. [Cu(terpy)(tdga)], where terpy = 2,2′:6′,2″-terpyridyl forms polymeric chains of Cu(terpy) units bridged by the tdga^{2-} by oxygens of the carboxylate groups. The coordination geometry can be described as a distorted trigonal bipyramid [17].

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Regarding the biological relevance of copper and carboxylic acid moreover containing a sulfur atom, our efforts have focused on the preparation and characterization of Cu(II) complexes containing bridging thiodiglycolate(2−). We have also tried to prepare similar binuclear nickel complexes and were successful in the preparation of mixed ligand mononuclear ones. It was also of interest to know how the number of donor atoms and bulkiness of nitrogen ligands can play a role in the different kinds of coordination of the dianion to Cu(II). Two of the possible coordination modes of thiodiglycolate(2−) have been confirmed by single crystal X-ray analysis.

2. Experimental

2.1. Materials and methods

2.1.1. Safety note

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of these materials should be handled with great caution.

The chemicals and solvents were supplied from Aldrich and Lachema (Czech Republic). The C, H, N and S analyses were carried out on an EA 1108 instrument (FISONS). IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena).

Magnetic susceptibility measurements in the temperature range of 1.9–300 K were carried out on powdered samples of the complexes, at the magnetic field 5 kG using a Quantum Design SQUID Magnetometer (type MPMS-5). Corrections for diamagnetism of the constituent atoms were calculated using Pascal's constants. The value 60×10^{-6} cm^3 mol^{-1} was used as the temperature-independent paramagnetism of the Cu(II) ion. The effective magnetic moment was calculated per Cu(II) atom from the equation $\mu_{\mathrm{eff}} = 2.83\sqrt{\chi_{\mathrm{M}}T}$ B.M., where χ_{M} is the molar magnetic susceptibility corrected for diamagnetism of the constituent atoms [18].

EPR spectra were recorded at room temperature (r.t.), 77 and 4.3 K, on the spectrometer Bruker ESP 300, operating at X-band equipped with an ER 035M Bruker NMR gaussmeter and a HP 5350B Hewlett Packard microwave frequency counter. The EPR measurements at 4.3 K were performed on a conventional X-band reflection spectrometer equipped with an Oxford Instruments ESR-900 helium flow cryostat.

2.2. Syntheses

2.2.1. [(phen)$_2$Cu(μ-tdga)Cu(phen)](NO$_3$)$_2$·5H$_2$O (1)

A solution of tdgaH$_2$ (0.15 g, 1 mmol) in water (10 cm^3) neutralized with NaOH (0.08 g, 2 mmol) was added to an EtOH–water (1:1) solution (100 cm^3) of Cu(phen)$_2$(NO$_3$)$_2$·H$_2$O (1.13 g, 2 mmol). Blue–green crystals were obtained after a week standing at r.t. They were separated by filtration, washed with small amounts of water and dried in air. The obtained blue–green crystals were suitable for X-ray analyses. Yield: 62%. *Anal*. Calc.: C, 46.7; H, 3.7; N, 10.9; S, 3.1. Found: C, 46.9; H, 3.6; N, 10.5; S, 2.7%. IR (cm^{-1}): 1582 (ν_{as}COO), 1372 (ν_{sym}COO), 722 (νC–S).

2.2.2. [(H$_2$O)(pmdien)Cu(μ-tdga)Cu(pmdien)(H$_2$O)](ClO$_4$)$_2$ (2)

Pmdien (0.42 cm^3, 2 mmol) was added to a solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.74 g, 2 mmol) in water (50 cm^3). Consecutively, a solution of tdgaH$_2$ (0.15 g, 1 mmol) in water (10 cm^3) neutralized with KOH (0.11 g, 2 mmol) was slowly added. A blue–violet crystalline material was obtained immediately. The crystals were collected on a frit, washed with water and dried in air. Crystals of sufficient quality for X-ray analysis were obtained by recrystallization from hot water. Yield: 54%. *Anal*. Calc.: C, 30.8; H, 6.4; N, 9.8; S, 3.7. Found: C, 30.7; H, 6.4; N, 9.4; S, 3.4%. IR (cm^{-1}): 1580 (ν_{as}COO), 1376 (ν_{sym}COO), 720 (νC–S).

2.3. Crystal structure determinations

X-ray data of [(phen)$_2$Cu(μ-tdga)Cu(phen)](NO$_3$)$_2$·5H$_2$O (**1**) and [(H$_2$O)(pmdien)Cu(μ-tdga)Cu(pmdien)(H$_2$O)](ClO$_4$)$_2$ (**2**) were collected at 150 and 120 K, respectively, on a four-circle κ-axis KUMA KM-4 diffractometer equipped with an Oxford Cryostream cooler using graphite-monochromated Mo Kα radiation. Data collections for both compounds were performed using a CCD detector (KUMA Diffraction, Wroclaw). KM4CCD data reduction software was used for data reduction. The structures were solved using direct methods (SHELXS-97) [19]. The structure of **1** was refined anisotropically on F^2 using a full-matrix least-squares procedure (SHELXL-97) [20] with weight: $w = 1/[\sigma^2(F_o^2)+(0.0432P)^2+5.8158P]$, where $P=(F_o^2+2F_c^2)/3$, for **1**. All hydrogen atoms in this structure were located in difference Fourier maps and all their parameters were refined. The O(12) atom of the water molecule is disordered over two positions with fixed occupancy factors at 0.5. The largest peak and hole on the final difference map of **1** were 0.49 [0.96 Å from O(7)] and −0.92 [0.68 Å from Cu(2)] e Å^{-3}.

Owing to the bad quality of measured data, the structure of **2** was refined only isotropically with the weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2]$. An application of anisotropic refinement did not lead to a reduction of R-factors as well as an application of semi-empirical absorption correction (DIFABS) to the obtained data [21]. Hydrogen atoms were not placed in their theoretical positions and were not included into the calculation. We tried to measure several crystals at different temperatures (293 or 120 K) and we always obtained comparable results. This fact may probably relate to the size of the unit-cell and/or a modulated structure of the compound, but experimental limitations of the used device do not allow us to study it in detail. The largest peak and hole on the final difference map of **2** were 5.544 [0.18 Å from Cu(2)] and −1.615 [0.67 Å from O(2)] e Å^{-3}. Nevertheless, in spite of bad statistical results we assume that the manner of ligand coordination in **2** was unambiguously proved by X-ray analysis. Summaries of crystal data and structure refinements for **1** and **2** are given in Table 1.

Table 1
Data collection and refinement parameters for [(phen)$_2$Cu(μ-tdga)Cu(phen)](NO$_3$)$_2$·5H$_2$O (**1**) and [(H$_2$O)(pmdien)Cu(μ-tdga)Cu(pmdien)(H$_2$O)](ClO$_4$)$_2$ (**2**)

Complex	**1**	**2**
Empirical formula	$C_{40}H_{38}Cu_2N_8O_{15}S$	$C_{44}H_{100}Cl_4Cu_4N_{12}O_{24}S_2$
Formula weight	1029.92	1641.44
Temperature (K)	150(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.477(3)	8.2090(16)
b (Å)	15.969(3)	21.362(4)
c (Å)	21.154(4)	21.497(4)
α (°)		94.95(3)
β (°)	94.06(3)	98.70(3)
γ (°)		98.93(3)
Volume (Å^3)	4204.3(15)	3657.9(13)
Z	4	2
D_{calc} (Mg m^{-3})	1.627	1.490
Absorption coefficient (mm^{-1})	1.144	1.426
$F(000)$	2112	1712
Crystal size (mm)	0.60 × 0.50 × 0.20	0.40 × 0.40 × 0.20
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-25 \leq l \leq 18$	$-10 \leq h \leq 8$, $-27 \leq k \leq 27$, $-26 \leq l \leq 28$
Reflections collected	28 897	24 918
Independent reflections	7371 [R_{int} = 0.0797]	13 007 [R_{int} = 0.0726]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	7371/0/757	13 007/0/378
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0423$, $wR_2 = 0.1005$	$R_1 = 0.2108$, $wR_2 = 0.6423$
R indices (all data)	$R_1 = 0.0467$, $wR_2 = 0.1066$	$R_1 = 0.2154$, $wR_2 = 0.6545$
Goodness-of-fit on F^2	1.145	3.721
Largest difference peak and hole (e Å^{-3})	0.486 and −0.923	5.544 and −1.615

3. Results and discussion

3.1. X-ray crystal structures

The molecular structures of **1** and **2** are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Tables 2 and 3. The structure of **1** consists of two penta-coordinated Cu(II) atoms bridged by thiodiglycolate, five uncoordinated water molecules and also two uncoordinated nitrate anions. Both the stereochemistry around the copper atoms and the chromophore are different. We have used the angular structural parameter $\tau = (\beta - \alpha)/60$, as a general descriptor of five-coordinated copper centers, for determination of the coordination geometry ($\tau = 1$ for an ideal trigonal bypiramid and $\tau = 0$ for an ideal square pyramid) [22]. Thus, as showed by X-ray analysis, the coordination geometry around the Cu(1) atom in **1** can be described as a nearly ideal tetragonal pyramid ($\tau = 0.07$), whereas the donor-atom arrangement around the Cu(2) atom is considerably deformed with $\tau = 0.54$ and it represents an intermediate between trigonal bipyramid and tetragonal pyramid. The vicinity of the Cu(1) ion is constituted by two N-atoms of 1,10-phenanthroline, the S(1) and O(1) atoms of tdga(2−). These donor atoms are coordinated in a basal plane of the tetragonal pyramid. The O(4) atom of the second carboxylato group of the bridging tdga(2−) is bonded in an apical position of the polyhedron. The coordination geometry may be completed to octahedral by a non-bonded interaction of Cu(1) with the O(6) atom of the nitrato group [the Cu(1)–O(6) distance is 2.555(2) Å]. The Cu(2) surroundings is formed by four N-donor atoms of two 1,10-phenanthrolines and the O(3) atom of the latter carboxylato group. The intradimer Cu(1)–Cu(2) distance is equal to 4.6508(8) Å, while the interdimer Cu–Cu distances range from 8.7393(16) to 9.7673(18) Å.

The structure of **2** is composed from two crystallographically independent molecules. Each of the molecules consists of a binuclear Cu(II) unit and two uncoordinated perchlorate anions. All copper atoms are penta-coordinated in the same coordination geometry, which can be described as a distorted tetragonal pyramid (τ parameters for Cu(1), Cu(2), Cu(3) and Cu(4) are equal to 0.27, 0.18, 0.22 and 0.16, respectively). Three nitrogen atoms of the pmdien ligand and one oxygen atom of a carboxylato group of tdga(2−) lie

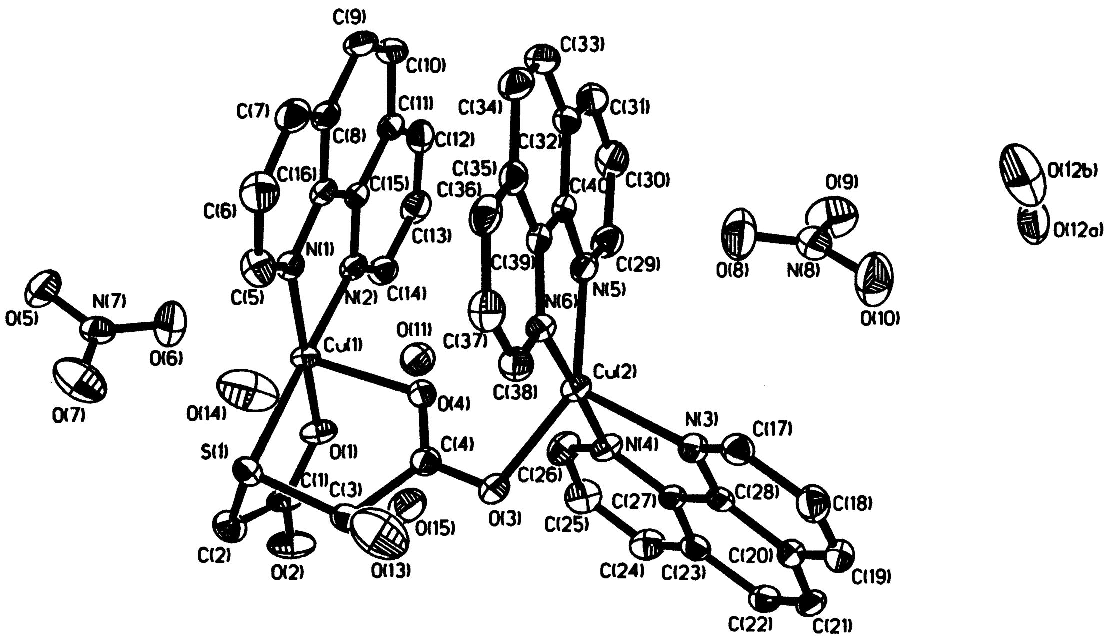

Fig. 1. A view of the molecular structure of **1**. The H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

in a basal plane of the tetragonal pyramid, meanwhile the oxygen atom of the coordinated water is bonded in an apical position. The copper atoms lie above the basal plane. The thiodiglycolate dianion forms a bridge between two copper atoms in the $[(H_2O)(pmdien)Cu(\mu\text{-}tdga)Cu(pmdien)(H_2O)]^{2+}$ unit and each of two carboxylato groups is bonded to the metal center through one oxygen atom only. The distances between

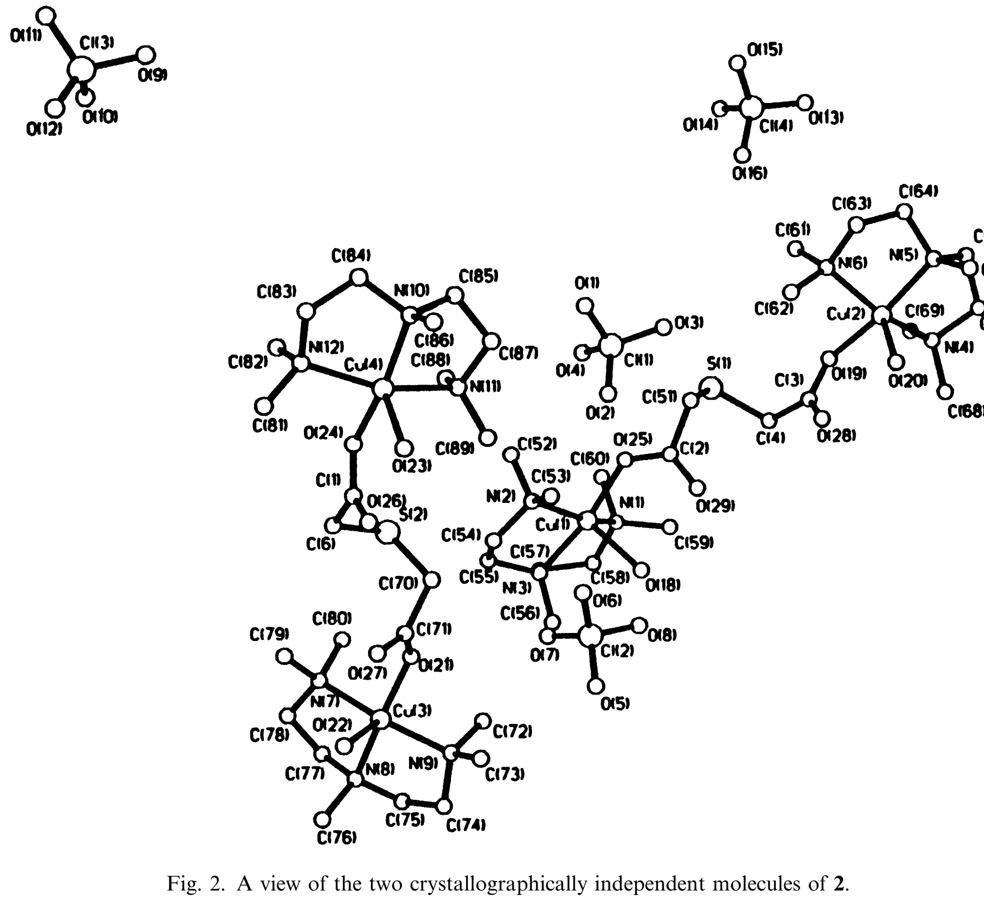

Fig. 2. A view of the two crystallographically independent molecules of **2**.

Table 2
Selected bond lengths (Å) and angles (°) for $[(phen)_2Cu(\mu\text{-}tdga)Cu(phen)](NO_3)_2\cdot 5H_2O$ (**1**)

Bond lengths			
Cu(1)–O(1)	1.9360(19)	Cu(2)–N(6)	1.987(2)
Cu(1)–N(1)	2.010(2)	Cu(2)–N(4)	1.999(2)
Cu(1)–N(2)	2.017(2)	Cu(2)–N(5)	2.053(2)
Cu(1)–O(4)	2.1808(19)	Cu(2)–O(3)	2.0716(19)
Cu(1)–S(1)	2.3698(8)	Cu(2)–N(3)	2.140(2)
Bond angles			
O(1)–Cu(1)–N(1)	174.48(8)	N(6)–Cu(2)–N(4)	178.24(9)
O(1)–Cu(1)–N(2)	92.87(9)	N(6)–Cu(2)–N(5)	81.92(9)
N(1)–Cu(1)–N(2)	82.20(9)	N(4)–Cu(2)–N(5)	99.61(9)
O(1)–Cu(1)–O(4)	93.70(8)	N(6)–Cu(2)–O(3)	89.67(8)
N(1)–Cu(1)–O(4)	89.32(8)	N(4)–Cu(2)–O(3)	88.57(9)
N(2)–Cu(1)–O(4)	96.17(8)	N(5)–Cu(2)–O(3)	146.08(8)
O(1)–Cu(1)–S(1)	86.06(6)	N(6)–Cu(2)–N(3)	99.27(9)
N(1)–Cu(1)–S(1)	98.90(7)	N(4)–Cu(2)–N(3)	80.84(9)
N(2)–Cu(1)–S(1)	178.63(6)	N(5)–Cu(2)–N(3)	117.05(9)
O(4)–Cu(1)–S(1)	83.05(5)	O(3)–Cu(2)–N(3)	96.69(8)

Table 3
Selected bond lengths (Å) and angles (°) for $[(H_2O)(pmdien)Cu(\mu\text{-}tdga)Cu(pmdien)(H_2O)](ClO_4)_2$ (**2**)

Bond lengths			
Cu(1)–O(25)	1.967(10)	Cu(3)–O(21)	1.953(10)
Cu(1)–N(3)	2.044(12)	Cu(3)–N(9)	2.004(12)
Cu(1)–N(1)	2.038(12)	Cu(3)–N(7)	2.045(13)
Cu(1)–N(2)	2.064(13)	Cu(3)–N(8)	2.048(11)
Cu(1)–O(18)	2.232(11)	Cu(3)–O(22)	2.226(11)
Cu(2)–O(19)	1.952(10)	Cu(4)–O(24)	1.951(10)
Cu(2)–N(4)	2.049(11)	Cu(4)–N(11)	2.065(13)
Cu(2)–N(5)	2.044(11)	Cu(4)–N(10)	2.055(12)
Cu(2)–N(6)	2.084(10)	Cu(4)–N(12)	2.082(12)
Cu(2)–O(20)	2.221(10)	Cu(4)–O(23)	2.241(10)
Bond angles			
O(25)–Cu(1)–N(3)	168.8(4)	O(19)–Cu(2)–N(4)	91.1(4)
O(25)–Cu(1)–N(1)	91.7(4)	O(19)–Cu(2)–N(5)	167.5(4)
N(3)–Cu(1)–N(1)	86.3(5)	N(4)–Cu(2)–N(5)	87.0(5)
O(25)–Cu(1)–N(2)	90.2(5)	O(19)–Cu(2)–N(6)	91.1(4)
N(3)–Cu(1)–N(2)	86.8(5)	N(4)–Cu(2)–N(6)	157.0(4)
N(1)–Cu(1)–N(2)	153.0(5)	N(5)–Cu(2)–N(6)	86.0(4)
O(25)–Cu(1)–O(18)	93.6(4)	O(19)–Cu(2)–O(20)	95.3(4)
N(3)–Cu(1)–O(18)	97.6(4)	N(4)–Cu(2)–O(20)	105.2(4)
N(1)–Cu(1)–O(18)	101.0(4)	N(5)–Cu(2)–O(20)	97.1(4)
N(2)–Cu(1)–O(18)	105.8(4)	N(6)–Cu(2)–O(20)	97.3(4)
O(21)–Cu(3)–N(9)	92.1(4)	O(24)–Cu(4)–N(11)	92.9(5)
O(21)–Cu(3)–N(7)	91.5(5)	O(24)–Cu(4)–N(10)	166.4(4)
N(9)–Cu(3)–N(7)	154.7(5)	N(11)–Cu(4)–N(10)	85.0(5)
O(21)–Cu(3)–N(8)	167.9(4)	O(24)–Cu(4)–N(12)	89.4(4)
N(9)–Cu(3)–N(8)	85.8(5)	N(11)–Cu(4)–N(12)	156.5(5)
N(7)–Cu(3)–N(8)	85.5(5)	N(10)–Cu(4)–N(12)	87.2(5)
O(21)–Cu(3)–O(22)	94.0(4)	O(24)–Cu(4)–O(23)	95.1(4)
N(9)–Cu(3)–O(22)	106.4(4)	N(11)–Cu(4)–O(23)	99.9(4)
N(7)–Cu(3)–O(22)	98.4(4)	N(10)–Cu(4)–O(23)	98.5(4)
N(8)–Cu(3)–O(22)	98.1(4)	N(12)–Cu(4)–O(23)	103.2(4)

Cu(II) centers in both dimeric units are nearly identical and are equal to 9.576(3) {Cu(1)–Cu(2)} and 9.575(3) Å {Cu(3)–Cu(4)}. The Cu–Cu intermolecular contacts in the structure of **2** lie in the range of 8.035(3)–9.784(3) Å.

3.2. Magnetic susceptibility measurements and EPR spectra

The structure of complex **1** consists of one dimeric $[(phen)_2Cu(\mu\text{-}tdga)Cu(phen)]^{2+}$ unit, in which the two copper ions have different coordination environments, two nitrate anions and five non-coordinated water molecules. Magnetic susceptibility of **1** was measured over the temperature range of 1.9–300 K and shows a maximum at 5 K (see Fig. 3), characteristic in the case of an antiferromagnetic interaction. The interaction in the binuclear complex leads to spin-singlet and -triplet states separated by $2J$, of which the value can be deduced from the temperature dependence of the molar magnetic susceptibility, using the Bleaney–Bowers expression [23] derived through the Hamiltonian $H = -2JS_1\cdot S_2$,

$$\chi_M = (N\beta^2 g^2/3kT)[1 + 1/3\ \exp(-2J/KT)]^{-1}$$

where $2J$ (singlet–triplet energy gap) expresses the intramolecular exchange interaction, $S_1 = S_2 = 1/2$ and N, β, g and T have their usual meaning.

When the complex is dissymmetrical, a very small additional term arising from the coupling of the Ms = 0 components of the singlet and the triplet occurs in the expression of χ_M [24,25] but this term is negligible when $|2J|$ is larger than a few wave numbers. A molecular field term was added to describe interdimer interactions [2]:

$$\chi_M^{mf} = \frac{\chi_M}{1 - (2zJ'\chi_M/Ng^2\beta^2)}$$

where χ_M is the molar susceptibility given by the Bleaney–Bowers expression, zJ' characterizes interactions between z Cu(II) neighbors (between dimeric units). A least-square fit of the data leads to the values of $2J = -4.80\ \text{cm}^{-1}$, $zJ' = -3.74\ \text{cm}^{-1}$, $g = 2.18$ and $R = 1.41 \times 10^{-4}$. R is the agreement factor defined as

$$R = \sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2 \Big/ \sum_i [(\chi_M T)_{obs}(i)]^2$$

The zJ' value, which characterizes interdimer interaction is surprisingly high and comparable to the intradimer antiferromagnetic interaction $2J$. It is possible because of the network of hydrogen bonds that exists in the crystal lattice in **1** and, as follows from crystallographic data, it is very difficult to discuss the number of interacting nearest neighbors (z).

The X-band EPR spectra of **1** at room temperature and at 77 K are identical and they are indicative of a d_{z^2} ground state (inverted type with $g_\parallel = 2.02 < g_\perp = 2.15$), see Fig. 4. It shows that a trigonal bipyramidal type of stereochemistry around the copper ion is observed in EPR spectra, like in the $[Cu(phen)_2(O_2CCH_3)][ClO_4]\cdot 2H_2O$ complex, also with two-coordinated phenanthrolines [26]. Splitting of the signal, observed at liquid

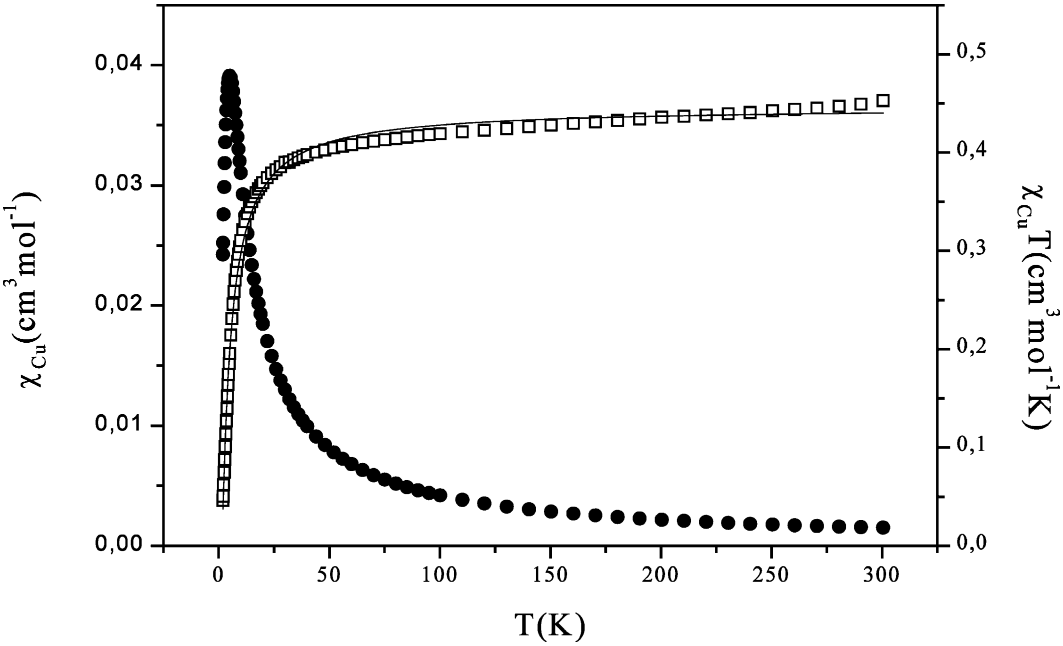

Fig. 3. Temperature dependence of χ_M and $\chi_M T$ for **1**. The solid line results from least-squares fitting of the data to the theoretical equation; see text.

helium temperature can confirm a weak antiferromagnetic exchange interaction and phase transition at 4.3 K, see Fig. 5.

The EPR spectrum of the polycrystalline sample of complex **2** is temperature independent and shows a pseudorhombic pattern (see Fig. 6), consisting of three g values: $g_1 = 2.21_2$, $g_2 = 2.08_1$, $g_3 = 2.04_8$. It is in fairly good agreement with the copper geometries obtained from the crystal structures. In **2** the copper ions are in a distorted square pyramidal arrangement with the copper ion above the basal plane. The complex exists as a dimer but EPR data did not show any signs of magnetic exchange interaction.

The results of susceptibility measurements of **2** are illustrated in Fig. 7 in the form of χ_M and $\chi_M T$ versus T (χ_M is magnetic susceptibility per Cu(II) ion). The room temperature $\chi_M T$ value 0.43 cm^3 K mol^{-1}, agrees with that expected for a magnetically isolated spin ($S = 1/2$) and is constant down to the low temperature region, where it decreases and reaches a value of 0.34 cm^3 K mol^{-1} at 1.9 K. It suggests very weak antiferromagnetic interactions in this compound.

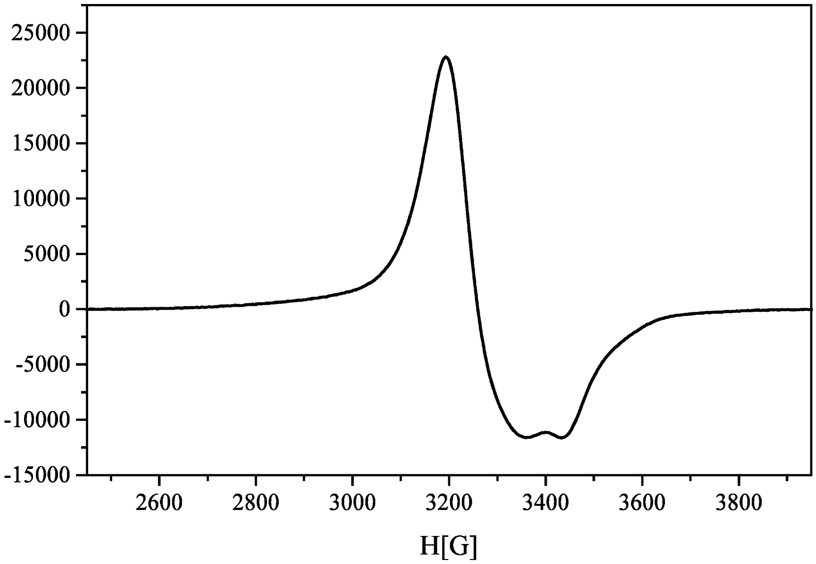

Fig. 4. X-band EPR spectrum of a powdered sample of **1** at 77 K.

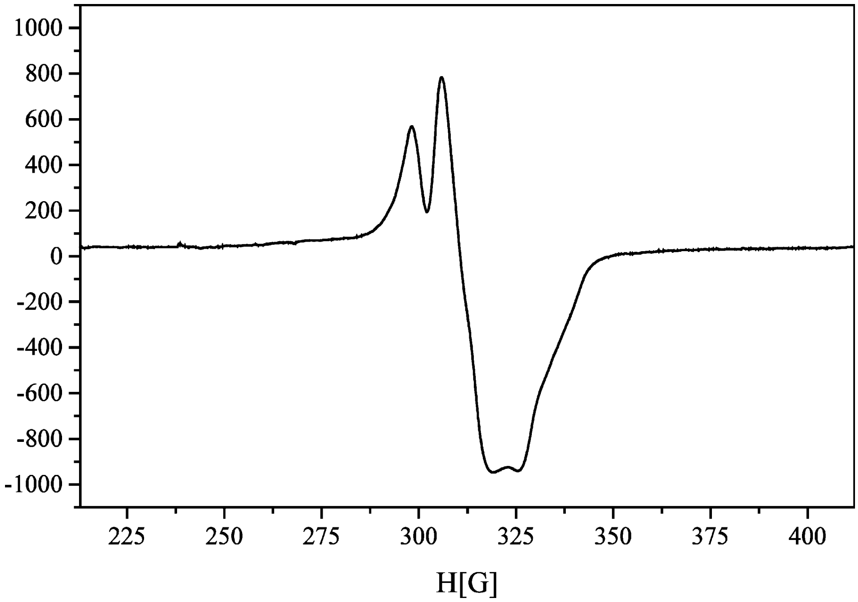

Fig. 5. X-band EPR spectrum of a powdered sample of **1** at 4.3 K.

The distances between Cu(II) centers in the dimeric units are comparable to intermolecular contacts in the structure and they are above 9.5 Å. Taking into account the dinuclear nature of this complex, magnetic data were fitted by a simple Bleaney–Bowers expression with a molecular field corrections term [2]. A least-square fit of the data leads to the values of $2J = -0.71$ cm^{-1}, $zJ' \approx 0$, $g = 2.05$ and $R = 1.41 \times 10^{-4}$. The fitting procedure confirms only very weak antiferromagnetic interaction in the complex **2**.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 187585 and 187678 for compounds **1** and **2**. 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).

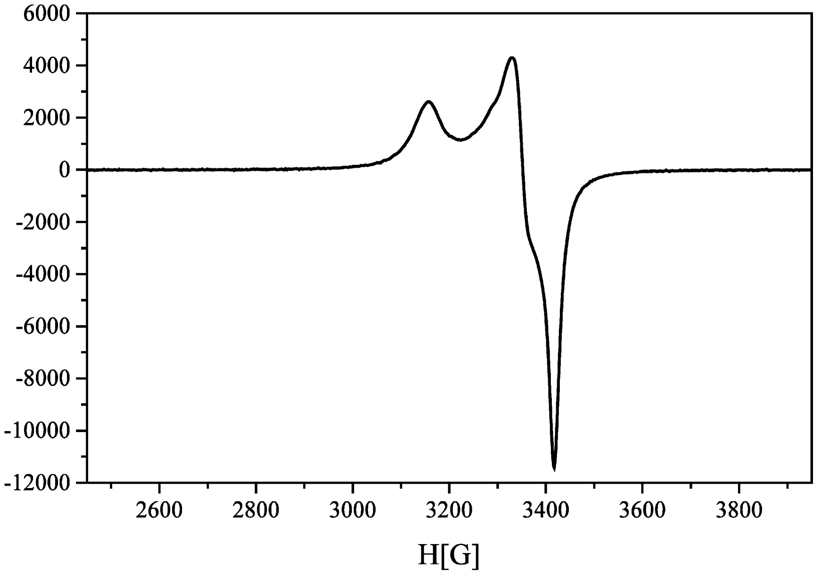

Fig. 6. X-band EPR spectrum of a powdered sample of **2** at 77 K.

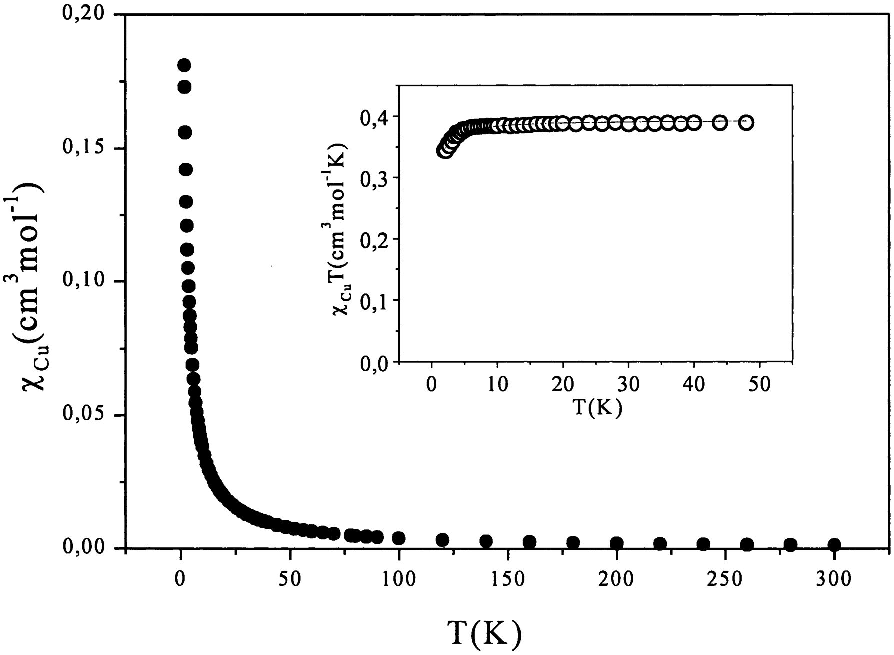

Fig. 7. Temperature dependence of χ_M and $\chi_M T$ for **2**. The solid line results from least-squares fitting of the data to the theoretical equation; see text.

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