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Oxalato complexes of copper(II) with chelating diamines. Crystal structure of [Cu(dmen)ox(H₂O)]₂[Cu(dmen)₂](ClO₄)₂

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Abstract

Four new oxalato complexes of copper(II) of composition $[Cu(dmen)ox(H_2O)]_2 [Cu(dmen)_2](CIO_4)_2$ (1) $(dmen = N, N-dimethylethylenediamine, H_2ox = oxalic acid), [(Cu(dmen)H_2O)_2ox](CIO_4)_2 · H_2O$ (2), $[Cu(tmen)(H_2O)(ox)Cu(aep)(H_2O)](CIO_4)_2$ (3) $(tmen = N, N, N', N'-tetramethylethylenediamine, aep = 2-(2-aminoethyl)pyridine) and <math>[(Cu(dben)NO_3)_2ox]$ (4) (dben = N, N'-dibenzylethylenediamine) have been prepared and characterised by IR and UV–Vis spectroscopies and magnetic measurements. The crystal structure of $[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](CIO_4)_2$ (1) has been determined by single-crystal X-ray analysis. The structure of 1 contains a neutral $[Cu(dmen)ox(H_2O)]$ complex, a cationic $[Cu(dmen)_2]^{2+}$ complex and perchlorate anions. The copper(II) atom of the neutral $[Cu(dmen)ox(H_2O)]$ unit possesses a distorted square-pyramidal environment with two oxygen atoms of oxalate and two nitrogen atoms of dmen in the basal plane and an oxygen atom of a water molecule in the apical position. The copper(II) atom of the cationic $[Cu(dmen)_2]$ unit shows a square-planar environment with four donor nitrogen atoms of two molecules of dmen. The temperature dependence of magnetic susceptibility for compounds 2–4 was measured. Magnetochemical measurements show that copper(II) ions in compounds 2–4 are antiferromagnetically coupled through the oxalate bridge, J = -157, -175 and -167 cm⁻¹ ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) for 2, 3 and 4, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(II) complexes; Oxalato complexes; Oxalato-bridged complexes; Magnetic properties; Crystal structures

1. Introduction

Binuclear copper(II) complexes with the oxalate dianion (ox) acting as a bis-bidentate bridging ligand are suitable model compounds for magneto-structural correlations. General trends of magnetic behaviour of these compounds are well established, the oxalate bridge being very efficient in transmission of the antiferromagnetic interactions between the two copper(II) atoms. Julve at al. [1,2] described a theory predicting the magnetic interactions in oxalato bridged Cu(II) complexes. Many binuclear copper(II) mixed-ligand complexes with oxalate as bridging ligand have been structurally characterised and it was found copper(II) can be five- or six-coordinated [2-30]. It was demonstrated that μ -oxalato-dicopper(II) complexes possesses J-values approximately from 0 to -200 cm^{-1} (H = $-2JS_1S_2$, $S_1 = S_2 = 1/2$). Further, it is known that complexes with tetragonal pyramidal geometry at both copper centres with oxalate coordinated in the basal plane give rise to J-values near -200 cm⁻¹ [2,6,8,11,13,24,25,28-30]. A weak interaction (the observed J-values are in the range from +1.1 to -37.4 cm^{-1}) was found in the case of octahedral, trigonal bipyramidal or tetragonal pyramidal (with one oxygen atom of oxalate coordinated in the basal plane and the other in the apical position) arrangements of copper(II) atoms [9,17,23,25]. Recently, we prepared and characterised binuclear u-oxalato copper(II) complexes $[(Cu(1,3-pn))_2 ox](ClO_4)_2$ (1,3-pn = 1,3-diaminopropane)

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 $(J = -127 \text{ cm}^{-1}), [(Cu(ept))_2 \text{ ox}](ClO_4)_2 \text{ (ept} = N-(2-1)^{-1})$ aminoethyl)-1,3-diaminopropane) [31], [(Cu(aep)- $H_2O_2ox[(NO_3)_2 (aep = 2-(2-aminoethyl)pyridine) (J =$ cm^{-1}), $[(Cu(ept))_2 ox](NO_3)_2 \cdot H_2O$ -160[28], (medpt = 3,3'-diamino-N- $[(Cu(medpt))_2 ox](ClO_4)_2$ methyl-dipropylamine) (J = +1.9) cm^{-1}), [(Cu- $(medpt)_{2}ox](NO_{3})_{2}\cdot 2 \ 2/3H_{2}O \ [29] \ (J = -2.6 \ cm^{-1}),$ [(Cu(trimeen)H₂O)₂ox](ClO₄)₂·2H₂O (trimeen = N, N, N'-trimethylethylenediamine) $(J = -172 \text{ cm}^{-1}),$ $[(Cu(trimeen)H_2O)_2ox](NO_3)_2 \cdot 2H_2O \ (J = -168 \ cm^{-1})$ and $[(Cu(dieten)H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (dieten = N, N'diethylenediamine) $(J = -172 \text{ cm}^{-1})$ [30].

We have extended the series of amine ligands by dmen (N,N-dimethylenediamine) and dben (N,N'-dibenzylethylenediamine) with the aim to prepare new binuclear µ-oxalato copper(II) complexes. Therefore, we carried out the reaction of copper(II) perchlorate (or copper(II) nitrate), the appropriate amine and sodium oxalate and prepared binuclear µ-oxalato copper(II) complexes $[(Cu(dmen)H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (2) and $[(Cu(dben)NO_3)_2 ox]$ (4). Our attempts to prepare the analogous complexes $[(Cu(dmen)H_2O)_2ox](NO_3)_2$ and [(Cu(dben)H₂O)₂ox](ClO₄)₂ led only to non-reproducible products. Surprisingly, the reaction of copper(II) perchlorate, N,N-dimethylethylenediamine, sodium oxalate and potassium cyanate in aqueous solution did not result in a complex with oxalato or cyanato bridging ligands but the mononuclear oxalato complex [Cu(dme $n)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1).

Julve et al. [2] prepared an interesting binuclear oxalato-bridged complex with non-equal copper(II) centres (each copper atom is coordinated by a different blocking ligand) of composition [Cu(tmen)(H₂O)(ox)-Cu(dien)](ClO₄)₂ (tmen = N, N, N', N'-tetramethylethylenediamine, dien = diethylenetriamine). With the aim to extend the series of these compounds we tried the reaction [Cu(tmen)ox]·4H₂O, copper(II) perchlorate and 2-(2-aminoethyl)pyridine (aep) that results in the formation of the complex [Cu(tmen)(H₂O)(ox)Cu(aep)-(H₂O)](ClO₄)₂ (**3**).

The prepared compounds were characterised by elemental analysis, IR and UV–Vis spectroscopies and magnetic susceptibility measurements. The crystal structure of the complex $[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2]$ - $(ClO_4)_2$ (1) has been determined by a single-crystal X-ray analysis.

2. Experimental

2.1. Chemicals and methods

The starting material $Cu(ClO_4)_2 \cdot 6H_2O$ was obtained by the reaction of basic copper(II) carbonate and $HClO_4$ (Carlo Erba) in aqueous solution (the reaction mixture was concentrated to crystallisation, the solid was filtered off and dried at 35 °C under an infralamp). N,Ndimethylethylenediamine, N,N'-dibenzylethylenediamine and 2-(2-aminoethyl)pyridine (Aldrich), sodium oxalate and Cu(NO₃)₂·3H₂O (Lachema Brno) and KOCN (Fluka) were used without further purification. Compound [Cu(tmen)ox]·4H₂O was prepared according to the literature [2].

Elemental analyses (C, H, N) were performed on a Fisons EA1108 CHN instrument. Absorption UV–Vis spectra (33000-11000 cm⁻¹) were recorded on a SPECORD M40 instrument in Nujol, IR spectra (4000-400 cm⁻¹) on a SPECORD IR 80 instrument using the Nujol technique. The magnetic susceptibilities were measured in the temperature range liquid nitrogen to room temperature (r.t.) by the Faraday method on the balance constructed in Nicholas Copernicus University (complexes **3** and **4**) and in Palacký University (complexe **2**) with Hg[Co(NCS)₄] as a calibrant [32]. The molar susceptibilities of all complexes were corrected for diamagnetism using Pascal's constants [33].

Crystals of $[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1) of X-ray quality were obtained from water by slow evaporation of solvent at r.t. The reflections were collected at 150 K on a four-circle κ -axis KUMA KM-4 diffractometer. The structure was solved by the heavy method using atom the program SHELXS-97 [34]. All non-hydrogen atoms were refined anisotropically [35] by a full-matrix least-squares with the weight procedure $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [F_o^2 + 2F_c^2]/3$, $w_1 = 0.0740$, $w_2 = 3.4700$. Parameters of all hydrogen atoms were refined isotropically. The crystal data and structure refinement details for [Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2 (1) are given in Table 1, whereas selected bond lengths and angles are listed in Table 2.

2.2. Syntheses

Caution! Perchlorates and perchlorate salts of metal complexes with organic ligands are potentially explosive. A small amount of material only should be prepared and it should be handled with care.

2.2.1. $[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1)

A solution of 0.22 g (2.71 mmol) of KOCN and 0.36 g (2.69 mmol) of sodium oxalate in 25 cm³ of water was added to a solution of 2.00 g (5.40 mmol) of Cu(ClO₄)₂· $6H_2O$ and 0.59 cm³ (5.37 mmol) of N,N-dimethylethylenediamine in 10 cm³ of water. After 1 h of stirring the reaction mixture was concentrated to crystallisation in a water bath. The obtained dark blue crystals were filtered off and dried in air. The yield was 0.6 g (45%).

2.2.2. $[(Cu(dmen)H_2O)_2ox](ClO_4)_2 \cdot H_2O(2)$

A solution of 0.18 g (1.34 mmol) of sodium oxalate in 15 cm^3 of water was added to a solution of 1.00 g (2.70

Table 1 Crystal data and structure refinement parameters for $[Cu(dmen)-ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1)

Formula	$C_{10}H_{26}ClCu_{1.5}N_4O_9$
Formula weight $(g \text{ mol}^{-1})$	477.11
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.4920(10)
b (Å)	8.501(2)
<i>c</i> (Å)	17.079(3)
α (°)	94.38(3)
β (°)	100.68(1)
γ (°)	103.80(3)
V (Å ³)	892.3(3)
Ζ	2
Calculated density (Mg m^{-3})	1.776
Absorption coefficient (mm^{-1})	2.006
F(000)	493
Crystal size (mm)	$0.35 \times 0.30 \times 0.25$
θ Range for data collection (°)	3.67-29.21
Index ranges	$-5 \le h \le 8, -11 \le k \le 11,$
	$-23 \le l \le 23$
Reflection collected/unique	7649/4279 [$R_{\rm int} = 0.0297$]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4279/0/258
Goodness-of-fit on F^2	1.080
Final <i>R</i> factor $[I > 2\sigma(I)]$	$R_1 = 0.0431, wR_2 = 0.1440$
R factor (all data)	$R_1 = 0.0461, wR_2 = 0.1454$
Largest difference peak and hole (e ${\rm \AA}^{-3})$	0.972 and -0.780

Table 2

Selected b	ond lengt	hs (A) and	l angles (°)) for[Cu(dmen)ox(H ₂ O)] ₂ [Cu-
$(dmen)_2](0)$	$ClO_{4})_{2}(1)$				

Bond lengths	
Cu(1)–O(4)	1.940(3)
Cu(1)-O(3)	1.957(3)
Cu(1)-N(2)	2.015(3)
Cu(1)-N(1)	2.022(3)
Cu(1)-O(9)	2.345(3)
Cu(2) - N(4)	1.994(3)
Cu(2)-N(3)	2.095(3)
Bond angles	
O(4)-Cu(1)-O(3)	84.50(11)
O(4) - Cu(1) - N(2)	95.18(12)
O(3)-Cu(1)-N(2)	164.41(13)
O(4)-Cu(1)-N(1)	175.16(11)
O(3)-Cu(1)-N(1)	92.57(11)
N(2)-Cu(1)-N(1)	86.61(12)
O(4) - Cu(1) - O(9)	87.68(11)
O(3)-Cu(1)-O(9)	105.97(11)
N(2)-Cu(1)-O(9)	89.57(12)
N(1)-Cu(1)-O(9)	96.84(11)
N(4)-Cu(2)-N(3)	85.30(12)
$N(4a)^{a} - Cu(2) - N(3)$	94 70(12)

^a Symmetry transformations used to generate equivalent atoms: -x, -y+1, -z+1.

mmol) of Cu(ClO₄)₂·6H₂O and 0.30 cm³ (2.73 mmol) of N,N-dimethylethylenediamine in 25 cm³ of water. The resulting dark blue solution was concentrated to 15 cm³ to crystallisation by heating. A small amount of solid formed was discarded. The filtrate was allowed to stand overnight. The light blue microcrystals were filtered off, washed with a small amount of water and dried in air. The yield was 0.35 g (40%).

2.2.3. $[Cu(tmen)(H_2O)(ox)Cu(aep)(H_2O)](ClO_4)_2$ (3)

A solution of 0.50 g (1.35 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ and 0.16 cm³ (1.34 mmol) of 2-(2-aminoethyl)pyridine in 20 cm³ of water was added to a solution of 0.46 g (1.35 mmol) of [Cu(tmen)ox] $\cdot 4H_2O$ in 15 cm³ of water. The resulting dark blue solution was concentrated to 10 cm³ to crystallisation by heating. A small amount of light blue powder formed was discarded. The filtrate was allowed to stand overnight. The obtained blue polycrystalline product was filtered off and dried in air. The yield was 0.2 g (22%).

2.2.4. $[(Cu(dben)NO_3)_2ox](4)$

A solution of 0.14 g (1.04 mmol) of sodium oxalate in a minimum amount of water was added to a solution of 0.50 g (2.07 mmol) of Cu(NO₃)₂·3H₂O and 0.49 cm³ (2.08 mmol) of N,N'-dibenzylethylenediamine in ethanol (25 cm³) and water (10 cm³). The reaction mixture was filtered and the filtrate was allowed to stand overnight. The blue microcrystalline product was filtered off, washed with water and ethanol and dried in air. The yield was 0.7 g (85%).

3. Results and discussion

3.1. Structure of complex 1

The structure of $[Cu(dmen)ox(H_2O)]_2[Cu-(dmen)_2](ClO_4)_2$ (1) is made up of neutral $[Cu(dmen)-ox(H_2O)]$ units, cationic $[Cu(dmen)_2]^{2+}$ units and un-



Fig. 1. A view (thermal ellipsoids are drawn at 40% probability level) of $[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1).

Table 3			
Elemental	analysis	of the	complexes

Complex	Found (Calc.) (%)			
	С	Н	N	
$[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2$ (1)	24.6 (25.2)	4.7 (5.5)	11.9 (11.8)	
$[(Cu(dmen)H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (2)	19.1 (18.6)	4.3 (4.7)	7.8 (8.7)	
$[Cu(tmen)(H_2O)(ox)Cu(aep)(H_2O)](ClO_4)_2 (3)$	26.2 (26.4)	4.4 (4.6)	8.1 (8.2)	
$[(Cu(dben)NO_3)_2 ox] (4)$	49.8 (49.2)	4.9 (5.2)	10.2 (9.5)	

coordinated perchlorate anions (Fig. 1). The [Cu(dmen)ox(H₂O)] complex, $[Cu(dmen)_2]^{2+}$ cation and perchlorate anion, in a 2:1:2 molar ratio, coexist. The copper atom of the neutral [Cu(dmen)ox(H₂O)] unit shows a distorted square-pyramidal environment with the two oxygen atoms of oxalate and two nitrogen atoms of dmen building the basal plane and an oxygen atom of a water molecule in the apical position. The inplane Cu-N and Cu-O bond lengths ranges from 1.940(3) to 2.022(3) Å and the axial Cu-O bond distance 2.345(3) Å is significantly longer than the inplane Cu–N and Cu–O bond lengths. The value of the τ parameter (17.9) [36] discloses a square-pyramidal shape of the coordination polyhedron (ideal τ value for square-pyramidal situation is 0 and for trigonal bipyramidal situation is 100). The copper atom of the cationic $[Cu(dmen)_2]^{2+}$ unit is situated on a crystallographic centre of symmetry and shows a square-planar environment with four nitrogen atoms from two molecules of dmen. The one Cu-N bond length (1.994(3) Å) is shorter than the other Cu-N bond length (2.095(3) Å). This difference may be explained by steric hindrance from the methyl groups bonded to donor nitrogen atom.

The neutral complex [Cu(dmen)ox(H₂O)] has squarepyramidal arrangement around the copper(II) atom with the two oxygen atoms of oxalate and two nitrogen atoms of N,N-dimethylethylenediamine forming the basal plane and an oxygen atom of a water molecule in the apical position as in the analogous complex [Cu(L)ox(H₂O)] (L = N,N'-dimethylethylenediamine) [37] (its structure has been known since 1973).

3.2. IR and UV-Vis

The characteristic IR spectra group vibrations of the complexes prepared are as follows: $v_3(ClO_4)$ 1056–1100

Table 4Magnetic properties of the complexes

cm⁻¹ (s), v_4 (ClO₄) 624–620 cm⁻¹ (s), v_{asym} (OCO) 1642–1668 cm⁻¹ (s) and δ (OCO) 752–788 cm⁻¹ (m). These values are consistent with coordinated oxalate [7,12,38,39] and uncoordinated perchlorate [28,29,40] anions.

The UV–Vis absorption spectra of Cu(II) complexes are characterised by a strong band in the range 11 000– 16 000 cm⁻¹ corresponding to a d–d transition [41]. In the present compounds, the maxima for 1 (16 250), 2 (16 450), 3 (14 900) and 4 (15 700 cm⁻¹) with ε_{max} (mol⁻¹ dm³ cm⁻¹; per Cu) equal to 62 (1), 115 (2), 140 (3) and 103 (4), respectively, correspond to this band.

3.3. Magnetic properties

The magnetic susceptibility of the mononuclear complex [Cu(dmen)ox(H₂O)]₂[Cu(dmen)₂](ClO₄)₂ (1) was measured at r.t. only. The observed value of the magnetic moment (1.82 μ_B per Cu) is in accordance with the literature data for magnetically diluted compounds of copper(II).

The variable-temperature magnetic moment and magnetic susceptibility in the range 84–295 K (compound 2) and 78–298 K (compounds 3 and 4) for solid samples is shown in Figs. 2–4. The magnetic moment are dependent on temperature and decreases from 1.31–1.40 $\mu_{\rm B}$ (per Cu) at 298 (or 295) K to 0.29–0.30 $\mu_{\rm B}$ (per Cu) at 78 (or 84) K (see Tables 3 and 4). This implies rather strong antiferromagnetic coupling mediated by the oxalate bridge.

Magnetic measurements show that complexes 2-4 behave like a common copper(II) dimers ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) (see Figs. 2–4). The molar magnetic susceptibility was expressed by the modified Bleaney–Bowers equation allowing for the presence of paramagnetic impurity [42]:

Complex	$\mu_{\rm eff}$ (per Cu)/ $T[\mu_{\rm B}]$ (K)	$J (\mathrm{cm}^{-1})$	g	P (%)
$[Cu(dmen)ox(H_2O)]_2[Cu(dmen)_2](ClO_4)_2 (1)$	1.82/294			
$[(Cu(dmen)H_2O)_2ox](ClO_4)_2 \cdot H_2O(2)$	1.40/295-0.30/84	-157	2.150	0
$[Cu(tmen)(H_2O)(ox)Cu(aep)(H_2O)](ClO_4)_2$ (3)	1.31/298-0.30/78	-175	2.108	1.63
$[(Cu(dben)NO_3)_2 ox] (4)$	1.35/298-0.29/78	-167	2.123	0.86



Fig. 2. Variation of corrected molar magnetic susceptibility (\bullet) and effective magnetic moment (\bigcirc) per mole of [(Cu(dmen)H₂O)₂ox](ClO₄)₂·H₂O (**2**) complex with temperature. The circles are the experimental points, the solid lines are theoretical lines.

$$\chi_{\rm M}^{\rm corr} = 2(Ng^2\beta^2/3kT)[1+1/3 \exp(-2J/kT)]^{-1}(1-P) + (Ngi_i^2\beta^2/4kT)P + N\alpha$$

where $\chi_{\rm M}^{\rm corr}$ is the corrected molar magnetic susceptibility per copper(II) dimer, *P* is the mole fraction of the monomeric copper(II) impurities, g_i is the average *g* factor of the impurity which was fixed at 2.15 throughout the present study, -2J is the singlet-triplet separation, $N\alpha$ is the temperature independent paramagnetism equal to 120×10^{-6} cm³ mol⁻¹ (per dimer), and the other symbols have their usual meanings. The best fit parameters *J*, *g* and *P*, were obtained by using a non-linear least-squares program. The exchange integral does not depend on the *g*_i value within range 2.1–2.2 and $N\alpha$ within the reasonable range, whereas changes on *g*-value and *P* are negligible. As a convenient statistical indicator of the quality of the least-squares fits, the discrepancy index $\sigma_{dis} = [\Sigma(\chi_{obs} - \chi_{calc})^2/$



Fig. 3. Variation of corrected molar magnetic susceptibility (\bullet) and effective magnetic moment (\bigcirc) per mole of [Cu(tmen)(H₂O)(ox)Cu-(aep)(H₂O)](ClO₄)₂ (**3**) complex with temperature. The circles are the experimental points, the solid lines are theoretical lines.



Fig. 4. Variation of corrected molar magnetic susceptibility (\bullet) and effective magnetic moment (\bigcirc) per mole of [(Cu(dben)NO₃)₂ox] (4) complex with temperature. The circles are the experimental points, the solid lines are theoretical lines.

 $\Sigma(\chi_{obs})^2$ ^{1/2}) was employed. The least-square fit (see Table 4) of the data yields $J = -157 \text{ cm}^{-1}$ ($\sigma_{dis} = 3.99 \times 10^{-3}$), $J = -175 \text{ cm}^{-1}$ ($\sigma_{dis} = 3.08 \times 10^{-3}$) and $J = -167 \text{ cm}^{-1}$ ($\sigma_{dis} = 4.74 \times 10^{-3}$) ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) for **2**, **3** and **4**, respectively.

Hence, the compounds 2-4 exhibit a strong antiferromagnetic exchange interaction that can be explained by the tetragonal pyramidal coordination of copper with oxalate oxygen atoms in basal positions, so that the x^2 v^2 magnetic orbital on Cu is directed ideally for overlap with the oxalate sigma orbitals [1,2]. The observed Jvalues for 2 (-157), 3 (-175) and 4 (-167 cm⁻¹) are similar to those of $[(Cu(L)H_2O)_2ox](ClO_4)_2$ (L = N,Ndiethyl-1,2-diaminoethane) $(J = -150 \text{ cm}^{-1})$ [24], $[(Cu(L)H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (L = N,N'-diethyl-1,2diaminoethane) $(J = -172 \text{ cm}^{-1})$ [30], [(Cu(aep)-(H₂O))₂ox](ClO₄)₂ $(J = -160 \text{ cm}^{-1})$ [28] or [(Cu(tmen)- $H_2O_2ox[(ClO_4)_2 \cdot 1.25H_2O (J = -193 \text{ cm}^{-1})]$ [2]. These four complexes [2,24,28,30] contain the square pyramidal arrangement of copper(II) with bridging oxalate and bidentate amine coordinated in the basal plane. The water oxygen atom is coordinated in the apical position. The square pyramidal coordination with oxalate oxygen atoms and blocking diamine nitrogen atoms in basal positions is supposed for complexes 2, 3 and 4, too.

4. Supplementary material

Supplementary data are available on request, quoting the deposition number 171583, from the 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).

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