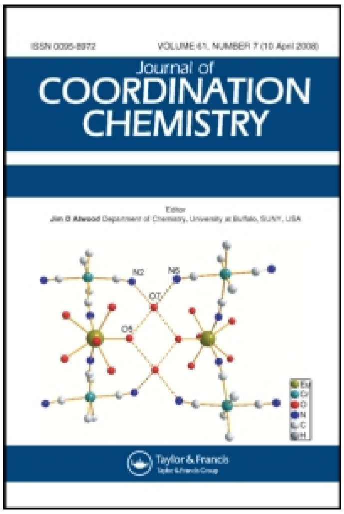

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Synthesis and Characterization of Binuclear (μ-Oxalato) Copper(II) Complexes with *N,N'*-Diethylethylenediamine or *N,N,N'*-Trimethylethylenediamine

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SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR (μ-OXALATO) COPPER(II) COMPLEXES WITH *N,N′*-DIETHYLETHYLENEDIAMINE OR *N,N,N′*-TRIMETHYLETHYLENEDIAMINE

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Three new binuclear μ-oxalato copper(II) complexes of composition $[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (**1**) (*N,N′*-dieten = *N,N′*-diethylethylenediamine, H_2ox = oxalic acid), $[(Cu(\text{trimeen})H_2O)_2ox](ClO_4)_2 \cdot 2H_2O$ (**2**) (trimeen = *N,N,N′*-trimethylethylenediamine) and $[(Cu(\text{trimeen})H_2O)_2ox](NO_3)_2 \cdot 2H_2O$ (**3**) have been isolated from the reactions of $Cu(ClO_4)_2 \cdot 6H_2O$ (or $Cu(NO_3)_2 \cdot 3H_2O$), the appropriate amine and Na_2ox in water and have been characterized by IR and electronic spectroscopy and magnetic measurements. The crystal structure of $[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2.H_2O$ (**1**) has been determined by single-crystal X-ray analysis. The structure of (**1**) consists of binuclear cations $[(N,N'\text{-dieten})H_2O)Cu(ox)Cu(N,N'\text{-dieten})H_2O)]^{2+}$, perchlorate anions and water molecules of crystallization. The copper atom is coordinated by two oxygen atoms of the oxalato ligand, two nitrogen atoms belonging to *N,N′*-dieten and one oxygen atom of water in a distorted square-pyramidal arrangement. The temperature dependence of magnetic susceptibilities (78–293 K) was measured for **1**–**3**. Magnetochemical measurements show that copper(II) ions in these compounds are antiferromagnetically coupled with $J = -172\,\text{cm}^{-1}$, $-172\,\text{cm}^{-1}$ and $-168\,\text{cm}^{-1}$ ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) for **1**, **2** and **3**, respectively.

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

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INTRODUCTION

The magnetic behaviour of copper(II) dimers in which the oxalate anion acts as a *bis*-bidentate bridging ligand is well-known. General trends of magnetic properties of the compounds are well-established, the oxalate bridge being very efficient in transmission of antiferromagnetic interactions between the two paramagnetic centers. The magnetic properties of dinuclear oxalato-bridged complexes have been thoroughly discussed by Hoffmann [1] on the basis of the molecular orbital theory. Kahn and coworkers [2,3] have described a theory predicting the magnetic interactions in oxalato bridged Cu(II) complexes. It was demonstrated that five-coordinated μ-oxalato-dicopper(II) complexes possess J values from approximately zero to $-200\,\text{cm}^{-1}$ ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$). 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 $-200\,\text{cm}^{-1}$. The μ-oxalato-dicopper(II) complexes have rich stereochemistry (Cu(II) can be four-, five- or six-coordinated) [4–14]. Many binuclear copper(II) mixed-ligand complexes with oxalate as bridging ligand have been structurally characterized [3,8,11,14–35]. The aim of this work was the preparation and structural characterization of new binuclear μ-oxalato complexes of copper(II) with *N,N′*-diethylethylenediamine (*N,N′*-dieten) or *N,N,N′*-trimethylethylenediamine (trimeen) of formulae $[(\text{Cu}(N,N'\text{-dieten})\text{H}_2\text{O})_2\text{ox}](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**1**), $[(\text{Cu(trimeen)H}_2\text{O})_2\text{ox}](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**2**) and $[(\text{Cu(trimeen)H}_2\text{O})_2\text{ox}](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ (**3**) and comparison with analogous known μ-oxalato copper(II) complexes. The compounds prepared were characterized by elemental analysis, IR and electronic spectroscopy and variable temperature magnetic susceptibility measurements. The crystal structure of the complex $[(\text{Cu}(N,N'\text{-dieten})(\text{H}_2\text{O}))_2\text{ox}](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**1**) has been determined by a single-crystal X-ray analysis.

EXPERIMENTAL

Chemicals and Methods

The starting material $\text{Cu(ClO}_4)_2\cdot 6\text{H}_2\text{O}$ was obtained by the reaction between basic copper(II) carbonate and HClO_4 (Carlo Erba) in aqueous solution (the reaction mixture was concentrated to crystallization, the solid was filtered off and dried at 35°C). *N,N,N′*-trimethylethylenediamine, *N,N′*-diethylethylenediamine (Aldrich) as well as sodium oxalate and $\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O}$ (Lachema Brno) were used as received.

Elemental analyses of carbon, hydrogen and nitrogen were performed on a Fisons Instruments EA1108 CHN instrument. Absorption spectra (33000–11000 cm^{-1}) were recorded on a Specord M40 instrument in nujol and IR spectra (4000–400 cm^{-1}), a Specord IR 80 instrument using the nujol technique. Magnetic susceptibilities were measured between liquid nitrogen and room temperatures by the Faraday method on a balance constructed in the Nicholas Copernicus University with $Hg[Co(NCS)_4]$ as calibrant [36]. Molar susceptibilities of complexes were corrected for diamagnetism using Pascal's constants [37].

Crystal Structure Determination

Crystals of $[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (**1**) suitable for the single crystal X-ray study were obtained from water by slow evaporation at room temperature. Data were collected using a Siemens SMART CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). Almost a full sphere of the reciprocal lattice was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure time of 30 s per frame. Preliminary orientation matrices were obtained from the first frames using SMART [38]. The frames were integrated using the preliminary orientation matrix which was updated every 100 frames. Final cell parameters were obtained by refinement of the positions of 8186 reflections with $I > 10\sigma(I)$ after integration of all the frames using SAINT [38]. The data were empirically corrected for absorption and other effects using SADABS [39] based on the method of Blessing [40]. The structure was solved by direct methods and refined by full-matrix least-squares methods on all F^2 data using SHELXTL [41]. The non-H atoms were refined anisotropically. One of the perchlorates showed rotational disorder and was refined with three different orientations with a common chlorine atom and geometry restrained to ideal tetrahedral; the occupancies of these three orientations were refined to approx. 58, 27 and 18%, respectively. The hydrogen atoms of water molecules were not localized; other hydrogen atoms were constrained to the ideal geometry using an appropriate riding model. For methyl groups, C-H distances (0.96 Å) and C-C-H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on threefold averaged circular Fourier synthesis.

Crystal data and structure refinement details for $[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2.H_2O$ (**1**) are given in Table I. Atomic coordinates of non-hydrogen atoms and equivalent isotropic displacement parameters are

TABLE I Crystal data and structure refinement details for [(Cu(*N,N*′-dieten)$H_2O)_2$ox]$(ClO_4)_2 \cdot H_2O$ (**1**)

Empirical formula	$C_{14}H_{38}Cl_2Cu_2N_4O_{15}$
Formula weight	700.46
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Aba2*
Unit cell dimensions	$a = 16.45410(10)$ Å
	$b = 26.7591(3)$ Å
	$c = 13.0197(2)$ Å
Volume	5732.53(11) $Å^3$
Z, Calculated density	8, 1.623 Mg/m^3
Absorption coefficient	1.740 mm^{-1}
F(000)	2896
Crystal size	1,10 × 0.14 × 0.06 mm
Theta range for data collection	1.96 to 30.90°
Limiting indices	$-21 \le h \le 23$, $-38 \le k \le 38$, $-18 \le l \le 17$
Reflections collected/unique	31353/8391 [$R(int) = 0.0453$]
Completeness to $\theta = 30.90$	97.5%
Absorption correction	empirical [39,40]
Max. and min. transmission	0.9028 and 0.2506
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8391/153/414
Goodness-of-fit on F^2	1.064
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1310$
R indices (all data)	$R_1 = 0.0812$, $wR_2 = 0.1462$
Absolute structure parameter	0.005 (17)
Largest diff. peak and hole	0.868 and −0.375 e. $Å^{-3}$

summarized in Table II. Selected bond lengths and angles are listed in Table III.

Preparation

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

[(Cu(N,N′-dieten)$H_2O)_2$ox]$(ClO_4)_2$.H_2O (**1**)

A solution of 0.18 g (1.34 mmol) of sodium oxalate in 20 cm^3 of water was added to a solution of 1.00 g (2.70 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ and 0.39 cm^3 (2.70 mmol) of *N,N*′-diethylethylenediamine in 30 cm^3 of water. The reaction mixture was concentrated by heating to 15 cm^3. The blue solid formed was filtered off, washed with a small amount of water and dried at 40°C in air.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[(\text{Cu}(N,N'\text{-dieten})\text{H}_2\text{O})_2\text{ox}](\text{ClO}_4)_2.\text{H}_2\text{O}$ (**1**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu(1)	2248(1)	2852(1)	2649(1)	34(1)
Cu(2)	2771(1)	4396(1)	4998(1)	43(1)
Cl(1)	3888(1)	3471(1)	1004(1)	42(1)
Cl(2)	3370(1)	1172(1)	−686(1)	59(1)
O(1)	2904(2)	3020(1)	3887(3)	43(1)
O(2)	3147(2)	3689(1)	4883(3)	43(1)
O(3)	2168(2)	4233(1)	3718(3)	44(1)
O(4)	1940(2)	3571(1)	2708(3)	37(1)
O(5)	1164(2)	2604(2)	3721(3)	56(1)
O(6)	3753(3)	4797(2)	4059(4)	70(1)
O(7)	3500(3)	3931(1)	1284(4)	72(1)
O(8)	3345(2)	3060(2)	1175(4)	65(1)
O(9)	4614(3)	3406(2)	1581(4)	78(1)
O(10)	4079(3)	3487(2)	−76(3)	72(1)
O(11A)[a]	2680(6)	1529(3)	−584(7)	79(3)
O(12A)[a]	3561(9)	1001(4)	297(7)	94(4)
O(13A)[a]	3104(8)	775(3)	−1311(8)	85(3)
O(14A)[a]	3963(7)	1457(4)	−1170(10)	106(4)
O(11B)[a]	3380(20)	1689(6)	−690(30)	73(7)
O(12B)[a]	2618(11)	965(10)	−440(30)	106(8)
O(13B)[a]	4000(15)	973(13)	10(20)	101(9)
O(14B)[a]	3630(20)	906(12)	−1670(16)	116(10)
O(11C)[a]	3450(30)	1679(9)	−900(40)	79(10)
O(12C)[a]	2748(18)	1069(11)	40(30)	75(8)
O(13C)[a]	4061(19)	859(17)	−430(30)	103(11)
O(14C)[a]	3110(30)	1050(20)	−1687(17)	146(13)
O(15)	4819(4)	4288(3)	2912(6)	119(3)
N(1)	1604(2)	2707(2)	1377(3)	39(1)
N(2)	2710(3)	2167(2)	2552(4)	53(1)
N(3)	3360(3)	4488(2)	6317(4)	44(1)
N(4)	2151(3)	5023(2)	5364(4)	48(1)
C(1)	2819(3)	3474(2)	4136(4)	36(1)
C(2)	2255(3)	3785(2)	3456(4)	37(1)
C(3)	1693(4)	2148(2)	1234(7)	80(3)
C(4)	2542(6)	1978(2)	1537(6)	73(2)
C(5)	741(3)	2865(2)	1417(4)	46(1)
C(6)	293(4)	2797(3)	424(5)	63(2)
C(7)	3651(4)	2126(3)	2816(7)	71(2)
C(8)	3938(5)	1601(3)	2813(8)	93(3)
C(9)	3153(4)	4979(2)	6713(5)	61(2)
C(10)	2263(4)	5092(2)	6477(5)	60(2)
C(11)	4243(4)	4390(2)	6258(6)	64(2)
C(12)	4654(4)	4367(3)	7331(7)	76(2)
C(13)	1281(4)	5053(2)	5060(6)	66(2)
C(14)	907(5)	5572(3)	5218(7)	89(2)

[a] Atoms having non-unit occupancy factors.

TABLE III Selected bond lengths [Å] and angles [°] for $[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (**1**)

Cu(1)–N(2)	1.990(4)
Cu(1)–O(4)	1.991(3)
Cu(1)–O(1)	1.991(4)
Cu(1)–N(1)	2.005(4)
Cu(1)–O(5)	2.360(4)
Cu(2)–N(3)	1.987(5)
Cu(2)–O(3)	1.988(4)
Cu(2)–O(2)	1.996(3)
Cu(2)–N(4)	2.020(4)
Cu(2)–O(6)	2.291(4)
O(1)–C(1)	1.264(5)
O(2)–C(1)	1.253(6)
O(3)–C(2)	1.254(6)
O(4)–C(2)	1.242(6)
C(1)–C(2)	1.529(6)
N(2)–Cu(1)–O(4)	172.12(18)
N(2)–Cu(1)–O(1)	93.02(18)
O(4)–Cu(1)–O(1)	83.59(13)
N(2)–Cu(1)–N(1)	88.34(19)
O(4)–Cu(1)–N(1)	94.84(15)
O(1)–Cu(1)–N(1)	177.76(16)
N(2)–Cu(1)–O(5)	93.84(18)
O(4)–Cu(1)–O(5)	93.25(14)
O(1)–Cu(1)–O(5)	89.71(15)
N(1)–Cu(1)–O(5)	91.98(16)
N(3)–Cu(2)–O(3)	174.27(14)
N(3)–Cu(2)–O(2)	91.78(16)
O(3)–Cu(2)–O(2)	83.32(14)
N(3)–Cu(2)–N(4)	86.52(19)
O(3)–Cu(2)–N(4)	97.37(17)
O(2)–Cu(2)–N(4)	163.96(17)
N(3)–Cu(2)–O(6)	93.39(18)
O(3)–Cu(2)–O(6)	90.43(17)
O(2)–Cu(2)–O(6)	100.66(16)
N(4)–Cu(2)–O(6)	95.37(17)
C(1)–O(1)–Cu(1)	111.4(3)
C(1)–O(2)–Cu(2)	111.1(3)
C(2)–O(3)–Cu(2)	112.4(3)
C(2)–O(4)–Cu(1)	111.6(3)
O(2)–C(1)–O(1)	126.4(4)
O(2)–C(1)–C(2)	117.5(4)
O(1)–C(1)–C(2)	116.2(4)
O(4)–C(2)–O(3)	127.2(4)
O(4)–C(2)–C(1)	117.2(4)
O(3)–C(2)–C(1)	115.6(4)

The other complexes were obtained analogously; $[(Cu(trimeen)H_2O)_2ox](ClO_4)_2 \cdot 2H_2O$ (**2**) from $Cu(ClO_4)_2 \cdot 6H_2O$ (1.00 g, 2.70 mmol), *N,N,N′*-trimethylethylenediamine (0.35 cm^3, 2.70 mmol) and sodium oxalate (0.18 g, 1.34 mmol), $[(Cu(trimeen)H_2O)_2ox](NO_3)_2 \cdot 2H_2O$ (**3**) from sodium oxalate

(0.28 g, 2.08 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (1.00 g, 4.14 mmol) and *N,N,N′*-trimethylethylenediamine (0.54 cm^3, 4.15 mmol). Satisfactory analyses for all three complexes were obtained.

RESULTS AND DISCUSSION

IR and Electronic Spectra

The characterist ic group vibrations in the IR spectra of the complexes prepared are as follows: $\nu_3(ClO_4)$ (1076–1084 cm^{-1} (s)), ν_4 (ClO_4) (622–626 cm^{-1} (s)), ν_{asym}(OCO) (1652–1660 cm^{-1} (s)) and δ (OCO) (784–800 cm^{-1} (m)). These values are consistent with coordinated oxalate [4,6,12,17] and uncoordinated perchlorate [34,35,42] anions.

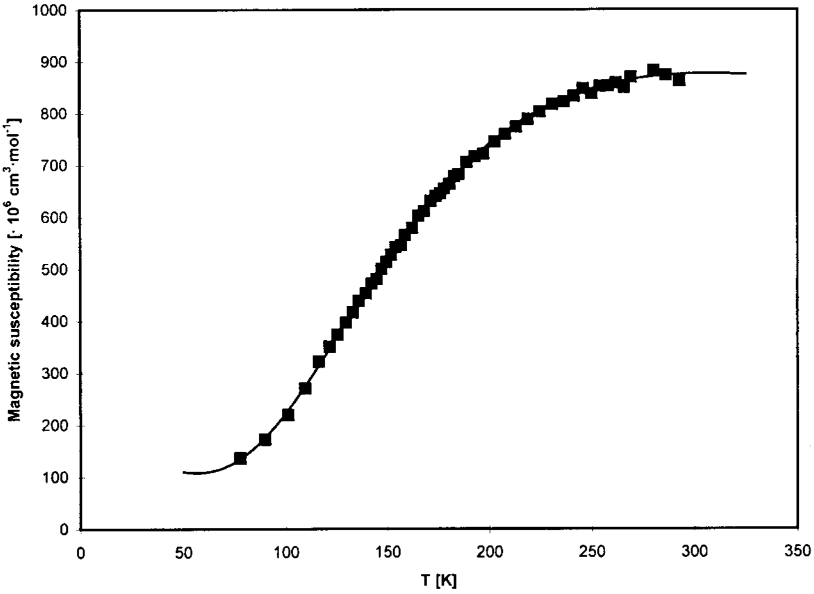
The electronic spectra of Cu(II) complexes are characterized by a strong band in the range 13000–18000 cm^{-1} corresponding to d-d transitions [43]. In the present compounds, the maxima at 16000 cm^{-1}, 16200 cm^{-1} and 15800 cm^{-1} for **1**, **2** and **3**, respectively, correspond to these bands. Spectroscopic data are consistent with oxalate-bridged dimeric structures for all three complexes. Tetragonal pyramidal five-coordination is confirmed by the X-ray structure determination of (**1**) and this arrangement is suggested for compounds **2** and **3** as well.

Magnetic Properties

Variable-temperature magnetic moments and magnetic susceptibilities in the range 78–293 K for solid samples of the compounds are shown in Figs. 1–3. The magnetic moments are temperature dependent and decrease from 1.36–1.42 BM (per Cu) at 293 K to 0.29–0.36 BM (per Cu) at 293 K (see Table IV). This proves that there is rather strong antiferromagnetic coupling mediated by the oxalate bridge. Magnetic measurement show that complexes **1–3** behave like a classical copper(II) dimers ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) (see Figs. 1–3). The molar magnetic susceptibility was

TABLE IV Spectroscopic and magnetic properties of the complexes

Complex	$\lambda_{max} \times 10^{-3}$ [cm^{-1}]	μ_{eff} (*per Cu*) [BM]/T[K]
$[(Cu(N,N'\text{-dieten})H_2O)_2ox](ClO_4)_2 \cdot H_2O$ (**1**)	16.0	1.42/293–0.29/78
$[(Cu(\text{trimeen})H_2O)_2ox](ClO_4)_2 \cdot 2H_2O$ (**2**)	16.2	1.37/293–0.34/78
$[(Cu(\text{trimeen})H_2O)_2ox](NO_3)_2 \cdot 2H_2O$ (**3**)	15.8	1.36/293–0.36/78



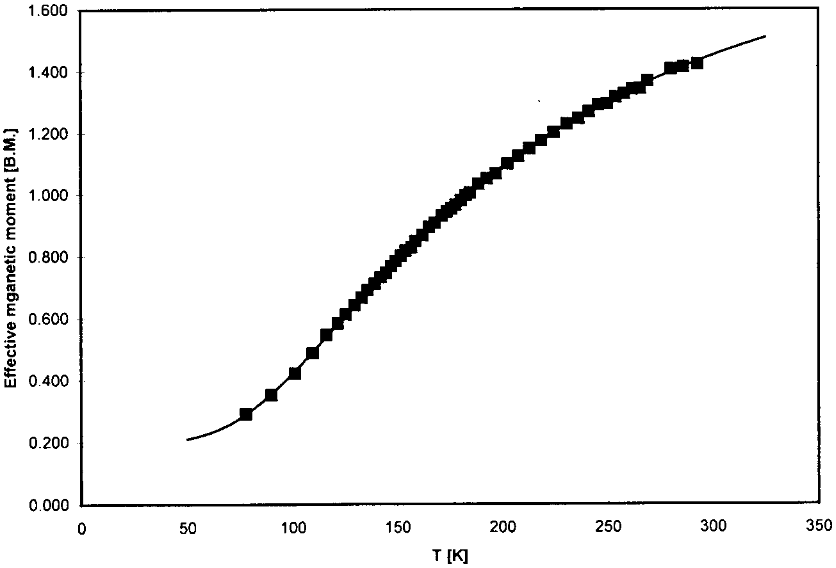
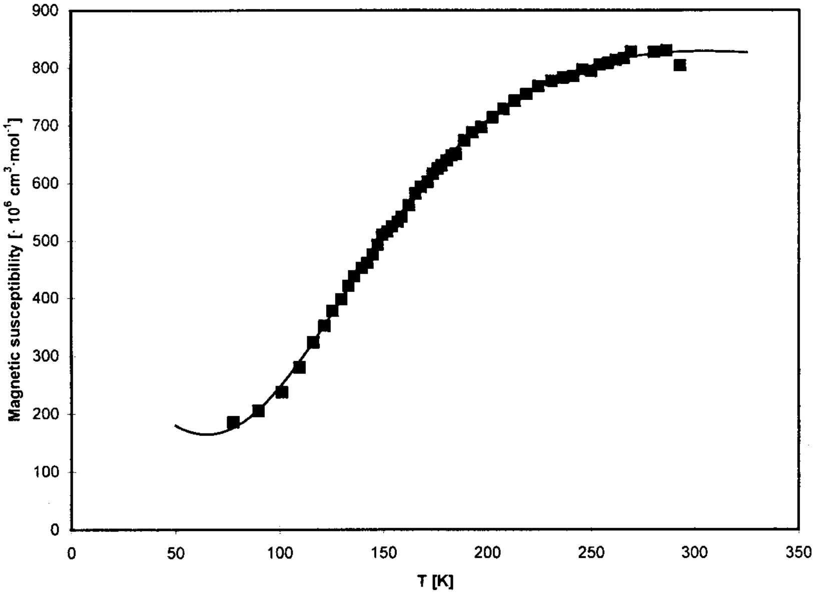


FIGURE 1 Temperature dependence of the molar magnetic susceptibility χ_M ($\times 10^6$ cm^3 mol^{-1}) and the effective magnetic moment μ_{eff} (per Cu) (BM) for [(Cu(*N*,*N*′-dieten)$H_2O)_2$ox]$(ClO_4)_2 \cdot H_2O$ (**1**). The squares are experimental points, the solid lines are theoretical lines. These curves were calculated using Eq. (1).



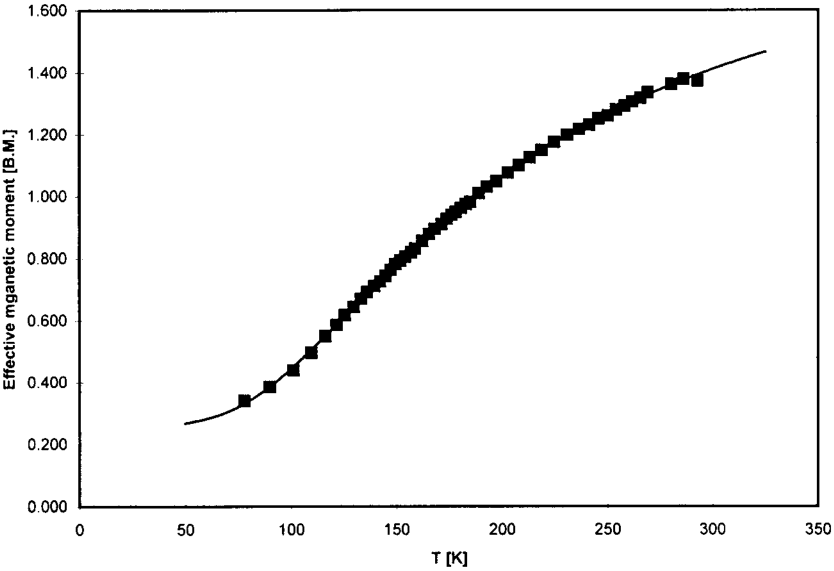
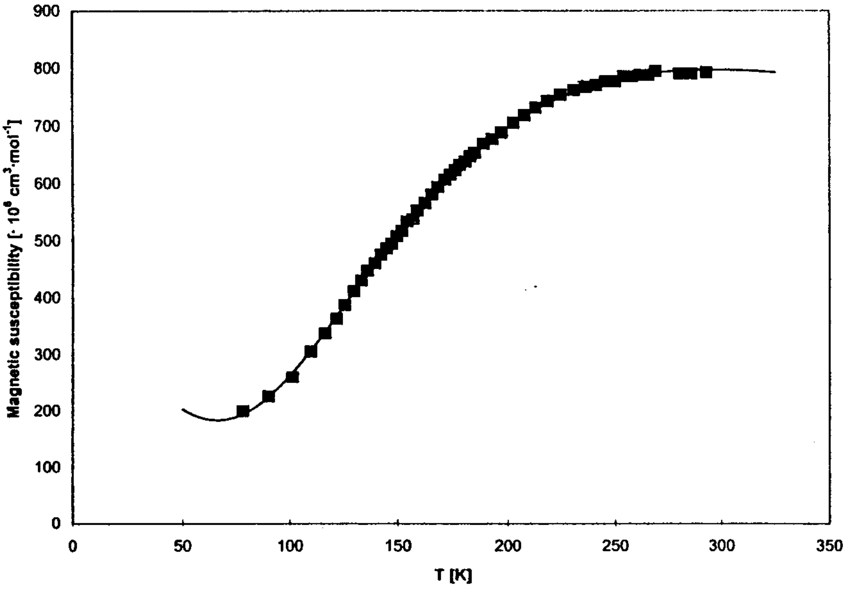


FIGURE 2 Temperature dependence of the molar magnetic susceptibility χ_M ($\times 10^6$ cm^3 mol^{-1}) and the effective magnetic moment μ_{eff} (per Cu) (BM) for [(Cu(trimeen) $H_2O)_2ox](ClO_4)_2 \cdot 2H_2O$ (**2**). The squares are experimental points, the solid lines are theoretical lines. These curves were calculated using Eq. (1).



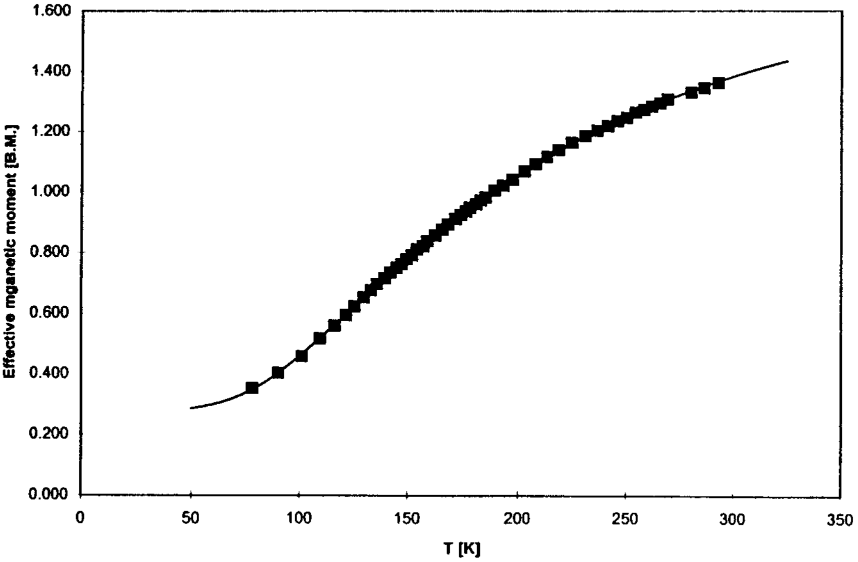


FIGURE 3 Temperature dependence of the molar magnetic susceptibility χ_M ($\times 10^6$ cm^3 mol^{-1}) and the effective magnetic moment μ_{eff} (per Cu) (BM) for $[(Cu(trimeen)H_2O)_2ox](NO_3)_2 \cdot 2H_2O$ (**3**). The squares are experimental points, the solid lines are theoretical lines. These curves were calculated using Eq. (1).

expressed by the modified Bleaney–Bowers equation allowing for the presence of paramagnetic impurity [44]

$$\chi_M^{\mathrm{corr}} = (Ng^2\beta^2/3kT)[1 + 1/3\exp(-2J/kT)]^{-1}(1 - P) \\ + (Ng_i^2\beta^2/4kT).P + N\alpha \qquad (1)$$

where χ_M^{corr} is corrected molar magnetic susceptibility per copper(II) atom, P is the mol 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, $N\alpha$ the temperature independent paramagnetism equal to $60 \times 10^{-6}\,\mathrm{cm}^{-3}.\mathrm{mol}^{-1}$, and the other symbols have their usual meanings. The best fit parameters J, g, and P, were obtained by using a nonlinear least-squares program. Exchange integrals do not depend on g_i, values within range 2.1–2.2 and N_α within a reasonable range, whereas changes of g values and P are negligible. As a convenient statistical indicator of the quality of the least-squares fits, the discrepancy index σ_{dis} ($\sigma_{\mathrm{dis}} = [\sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calc}})^2/\sum(\chi_{\mathrm{calc}})^2]^{1/2}$) was employed. The least-square-fit (see Table V) of the data yields $J = -172\,\mathrm{cm}^{-1}$, $-172\,\mathrm{cm}^{-1}$ and $-168\,\mathrm{cm}^{-1}$ ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$) for **1**, **2** and **3**, respectively.

Hence that the compounds **1–3** exhibit strong antiferromagnetic exchange interaction can be explained by the tetragonal pyramidal coordination of copper with oxalate oxygen atoms in basal positions, so that the x^2–y^2 magnetic orbital on Cu is directed ideally for overlap with the oxalate σ orbitals [2,3]. For **1**, **2** and **3**, the observed J values (-172, -172 and $-168\,\mathrm{cm}^{-1}$, respectively) are similar to those of $[(\mathrm{Cu(L)H_2O})_2\mathrm{ox}](\mathrm{ClO_4})_2$ (L = *N,N*-diethyl-1,2-diaminoethane) [29] ($J = -150\,\mathrm{cm}^{-1}$), $[(\mathrm{Cu(aep)(H_2O)})_2\mathrm{ox}](\mathrm{ClO_4})_2$ (aep = 2-(2-aminoethyl)pyridine) [34] ($J = -160\,\mathrm{cm}^{-1}$), $[(\mathrm{Cu(bpy)H_2O})_2\mathrm{ox}][\mathrm{Cu(bpy)ox}](\mathrm{NO_3})_2$ (bpy = 2,2′-bipyridine) ($J = -170\,\mathrm{cm}^{-1}$) [16] and $[(\mathrm{Cu(tmen)H_2O})_2\mathrm{ox}](\mathrm{ClO_4})_2.1.25\mathrm{H_2O}$ ($J = -193\,\mathrm{cm}^{-1}$) [3]. These four complexes contains 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. This square

TABLE V Magnetic data and parameters from the Bleaney–Bowers equation for copper(II) complexes

Complex	J [cm^{-1}]	g	P [%]	σ_{dis}
$[(\mathrm{Cu}(N,N'\text{-dieten})\mathrm{H_2O})_2\mathrm{ox}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**1**)	−172	2.30	0.56	8.07×10^{-3}
$[(\mathrm{Cu(trimeen)H_2O})_2\mathrm{ox}](\mathrm{ClO_4})_2\cdot 2\mathrm{H_2O}$ (**2**)	−172	2.23	1.36	9.48×10^{-3}
$[(\mathrm{Cu(trimeen)H_2O})_2\mathrm{ox}](\mathrm{NO_3})_2\cdot 2\mathrm{H_2O}$ (**3**)	−168	2.15	1.62	5.00×10^{-3}

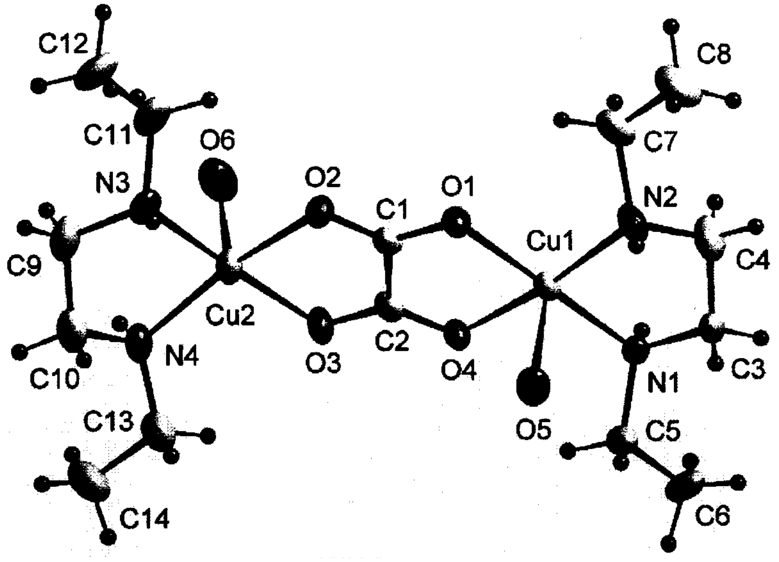


FIGURE 4 The $[(Cu(N,N'\text{-dieten})H_2O)_2ox]^{2+}$ ion including the atom labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

pyramidal coordination (confirmed from X-ray study for (**1**)) is supposed for complexes **2** and **3** as well.

Crystal Structure

The structure of **1** was determined by single-crystal X-ray diffraction. The molecular structure consists of binuclear $[(Cu(N,N'\text{-dieten})H_2O)_2ox]^{2+}$ cations, perchlorate anions and molecules of crystal water. A view of the $[Cu(N,N'\text{-dieten})H_2O)_2ox]^{2+}$ cation is shown in Fig. 4. Principal bond distances and angles are listed in Table III. The binuclear cation is composed of two $Cu^{II}(N,N'\text{-dieten})(H_2O)$ units bridged by a *bis*-bidentate oxalate dianion. The coordination polyhedron of Cu(II) is formed by two oxygen atoms of $C_2O_4^{2-}$, two nitrogen atoms of *N*,*N*′-dieten and one oxygen atom of water. The environment of both copper(II) ions is distorted square pyramidal with a water–oxygen atom in the apical position (the apical Cu–O distance being in the range 2.291(4)–2.360(4) Å) and the two oxalate–oxygen atoms and the two *N*,*N*′-dieten nitrogen atoms building the basal plane (basal Cu–O and Cu–N bonds vary within the ranges 1.988(4)–1.996(3) and 1.987(5)–2.020(4) Å, respectively).

Cu(1) (or Cu(2)) lies 0.0772(5) (or 0.1716(6)) Å away from the least-squares plane fitted through the N(1), N(2), O(1) and O(4) (or N(3), N(4), O(2) and O(3)) atoms, respectively. As usual, the Cu(1)-C_2O_4-Cu(2) fragment is virtually planar and deviation from the least-squares plane fitted through the Cu(1)-O(1)-O(4)-C(1)-C(2)-O(2)-O(3)-Cu(2) atoms at most is 0.0507(6) Å for Cu(2). The Cu(1)$\cdots$Cu(2) distance is 5.2113(7) Å, whereas the shortest intermolecular Cu$\cdots$Cu distance is 5.3839(8) Å.

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