SYNTHESIS AND CHARACTERIZATION OF (μ-OXALATO)NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES WITH CHELATING POLYAMINES

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New binuclear complexes of the type $[(Ni(aep)_2)_2ox](ClO_4)_2$ (**1**) (aep = 2-(2-aminoethyl)pyridine, H_2ox = oxalic acid), $[(Ni(ept)H_2O)_2ox](NO_3)_2$ (**2**), (ept = *N*-(2-aminoethyl)-1,3-diaminopropane), $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ (**3**), $[(Cu(ept))_2ox](NO_3)_2 \cdot H_2O$ (**4**) and $[(Zn(L))_2ox](ClO_4)_2 \cdot n\,H_2O$ (L = ept, n = 0 (**5**); L = *N*,*N*′-bis(3-aminopropyl)-1,2-diaminoethane (3,2,3-tet), n = 4 (**6**)) have been prepared and studied by IR and UV-VIS spectroscopies. Spectroscopic data are consistent with oxalate-bridged structures between six-coordinate (N_4O_2 or N_3O_3) Ni(II) (compounds **1** and **2**), (N_2O_3 or N_3O_2) Cu(II) (compounds **3** and **4**) or (N_3O_2 or N_4O_2) Zn(II) (compounds **5** and **6**). The crystal structure of $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ (**3**) has been determined by single-crystal X-ray analysis. The copper atom is coordinated by two oxygen atoms of the oxalato ligand, two nitrogen atoms belonging to aep and one oxygen atom of water in a square-pyramidal arrangement. The intermetallic distance of Cu(1)–Cu(1a) is 5.204(2) Å. The temperature dependence of magnetic susceptibilities (94–298 K) was measured for **1** and **3**. Magnetochemical measurements show that metal ions in these compounds are antiferromagnetically coupled, J = –17 and –160 cm^{-1} ($H = -2JS_1S_2$) for **1** and **3**, respectively.

Key words: Chelates; Nickel(II) complexes; Copper(II) complexes; Zinc(II) complexes; Oxalato-bridged complexes; Oxalates; Magnetic properties; Crystal structure.

The magnetic behaviour of copper(II) and nickel(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 the antiferromagnetic interactions between the two paramagnetic centres. 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-coordinate μ-oxalato dicopper(II) complexes posses J-values from approximately zero to approximately

–200 cm^{-1}. Further, it is known that complexes with square planar or tetragonal pyramidal geometry at both copper centers give rise to *J*-values near –200 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 (Cambridge Structural Database): $[Cu(dien)(ox)Cu(tmen)H_2O](ClO_4)_2$ (dien = diethylenetriamine, tmen = *N,N,N′,N′*-tetramethyl-1,2-diamino ethane)[3], $[(Cu(tmen)H_2O)_2ox](ClO_4)_2 \cdot 1.25\ H_2O$ (ref.[3]), $[(Cu(tmen)(2\text{-meim}))_2ox](PF_6)_2$ (2-meim = 2-methylimidazole)[3], $[(Cu(tmen)H_2O)_2ox](PF_6)_2 \cdot 2\ H_2O$ (ref.[15]), $[(Cu(L))_2ox](PF_6)_2$ (L = *N,N,N′,N′′,N′′*-pentaethyldiethylenetriamine)[15], $[(Cu(bpy)H_2O)_2ox][Cu(bpy)ox](NO_3)_2$ (refs[11,16]), $[(Cu(bpy)H_2O)_2ox][Cu(bpy)ox](SO_4)$ (ref.[17]), $[(Cu(bpy)H_2O)_2ox][Cu(bpy)ox](BF_4)_2$ and $[(Cu(bpy)H_2O)_2ox][Cu(bpy)ox](ClO_4)_2$ (ref.[18]) and $[(Cu(bpy)H_2O)_2ox]L_2$ (L^- = saccharide) (bpy = 2,2′-bipyridine)[19], $[(Cu(L))_2ox](BPh_4)_2$ (L = *N,N,N′,N′′,N′′*-pentaethyldiethylenetriamine)[20], $[(Cu(L)H_2O(NO_3))_2ox]$ and $[(Cu(L)H_2O)_2ox]_2(PF_6)_3(ClO_4) \cdot H_2O$ (L = 7-bromo-5-(2-pyridyl)-3*H*-benzo[*e*][1,4]diazepin-2(1*H*)-one)[21], $[(Cu(L)(L'))_2ox] \cdot$benzene (L = tmen, HL′ = $(CF_3)_3COH$)[22], $[(Cu(L)H_2O)_2ox](PF_6)_2 \cdot L \cdot 3\ H_2O$ and $[(Cu(L)NO_3)ox(Cu(L)(NO_3)H_2O)]_2[(Cu(L)(NO_3))ox(Cu(L)(NO_3))]$ (ref.[23]) and $[(Cu(L)NO_3)_2ox] \cdot 2\ H_2O$ (ref.[13]) (L = 4-methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methylpyrimidine), $[(Cu(dien))_2ox](ClO_4)_2$ (ref.[5]), $[(Cu(dien))_2ox](ClO_4)_2 \cdot H_2O$ (ref.[24]), $[(Cu(L)H_2O)_2ox][(Cu(L))_2ox](ClO_4)_4 \cdot 2\ H_2O$ (L = 2,2′:6′,2′′-terpyridine)[12], $[(Cu(L))_2ox](BF_4)Cl$ (L = 3,6,9,13,16,19-hexaaza-1(2,5),11(2,5)-dioxophenacycloicosaphane)[25], $[(Cu(L))_2ox]$ (HL = bis(2-pyridylcarbonyl)amide)[8], $[(Cu(L)H_2O)_2ox](ClO_4)_2$ (L = *N,N*-diethyl-1,2-diaminoethane)[26] and $[(Cu(L))_2ox](ClO_4)_2$ (L = *N,N′*-bis(2-pyridylmethyl)-1,2-diaminoethane or *N,N′*-bis(2-pyridylmethyl)-*N,N′*-dimethyl-1,2-diaminoethane)[14]. Nonoyama *et al.*[10] prepared complex $[Cu_2ox(aep)_2](NO_3)_2 \cdot 2\ H_2O$ and characterized it by measuring the magnetic moment at room temperature (μ_{eff} = 1.44 BM).

The octahedral nickel(II) oxalato dinuclear compounds containing tetraaza macrocycles, tetraaza amines or two diamines (NiN_4O_2 chromophore), or triamine and water (NiN_3O_3 chromophore) are also known[5,6,14,27–29]. Magnetostructural data of the oxalato-bridged nickel(II) complexes have revealed that the magnetic coupling *J* ($H = -2JS_1S_2$), which varies from –11 to –20 cm^{-1}, is strongly dependent on the nature of the donor atoms of terminal ligands[30]. Recently Escuer *et al.*[28] characterized compound $[(Ni(3,2,3\text{-tet}))_2ox](ClO_4)_2 \cdot 2\ H_2O$ by X-ray study and magnetic mesurement ($J = -14\ cm^{-1}$).

The binuclear μ-oxalato complexes of zinc(II) have been studied less than nickel(II) or copper(II), undoubtedly because they are not magnetochemically interesting. Curtis *et al.*[4,5] synthesized the compounds $[(Zn(en)_2)_2ox](ClO_4)_2$ (en = 1,2-diaminoethane) and $[(Zn(L))_2ox](ClO_4)_2$ (L = trien (triethylenetetramine) or L = dpt (dipropylenetriamine)) and determined the crystal structure of complex $[(Zn(dpt))_2ox](ClO_4)_2$. Shvelashvili[31] prepared analogous complexes $[(Zn(en)_2)_2ox]X_2$ ($X = NCS^-, NO_3^-$). Recently Glerup *et al.*[14] characterized compounds $[(Zn(L))_2ox](ClO_4)_2 \cdot n\ H_2O$ (L = (*N,N′*-bis(2-pyridylmethyl)-

1,2-diaminoethane), $n = 0$; L = (*N*,*N*′-bis(2-pyridylmethyl)-1,3-diaminopropane, $n = 0.5$; L = (*N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-dimethyl-1,2-diaminoethane), $n = 0$).

The aim of this work was the preparation and structural characterization of new binuclear μ-oxalato complexes of copper(II), nickel(II) or zinc(II) with 2-(2-aminoethyl)pyridine (aep), *N*-(2-aminoethyl)-1,3-diaminopropane (ept) or *N*,*N*′-bis(3-aminopropyl)-1,2-diaminoethane (3,2,3-tet) of compositions $[(Ni(aep)_2)_2ox](ClO_4)_2$ (**1**), $[(Ni(ept)(H_2O))_2ox](NO_3)_2$ (**2**), $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ (**3**), $[(Cu(ept))_2ox](NO_3)_2 \cdot H_2O$ (**4**), $[(Zn(ept))_2ox](ClO_4)_2$ (**5**) and $[(Zn(3,2,3\text{-tet}))_2ox](ClO_4)_2 \cdot 4\ H_2O$ (**6**) and comparison with analogous known μ-oxalato complexes. The compounds prepared were characterized by elemental analysis, IR and UV-VIS spectroscopies and variable temperature magnetic susceptibility measurements. The crystal structure of the complex $[(Cu(aep)(H_2O))_2ox](ClO_4)_2$ has been determined by a single-crystal X-ray analysis.

EXPERIMENTAL

Chemicals and Methods

The starting materials $Ni(ClO_4)_2 \cdot 6\ H_2O$, $Cu(ClO_4)_2 \cdot 6\ H_2O$ and $Zn(ClO_4)_2 \cdot 6\ H_2O$ were obtained by the reaction between basic copper(II) carbonate, basic nickel(II) carbonate or zinc(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 under infralamp). 2-(2-Aminoethyl)pyridine and *N*,*N*′-bis(3-aminopropyl)-1,2-diaminoethane, *N*-(2-aminoethyl)-1,3-diaminopropane (Aldrich) as well as sodium oxalate, $Ni(NO_3)_2 \cdot 6\ H_2O$ and $Cu(NO_3)_2 \cdot 3\ H_2O$ (Lachema Brno) were used as received.

Elemental analysis of carbon, hydrogen and nitrogen was performed on a Fisons Instruments EA1108 CHN instrument. Absorption UV-VIS spectra (33 000–11 000 cm^{-1}) were recorded on a SPECORD M40 instrument in Nujol, IR spectra (4 000–400 cm^{-1}) a SPECORD IR 80 instrument using the Nujol technique. Magnetic susceptibility was measured in the 94–298 K range using the Gouy method with $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were calculated from Pascal constants.

Crystals of $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ suitable for the single crystal X-ray study were obtained from water by slow evaporation at room temperature. The reflections were collected on a KUMA KM-4 four-circle diffractometer using an ω–2θ scan mode. The stability of the crystal was checked by monitoring three standards after every 200 reflections (correction for decay was not applied, final coefficient for decay correction was 0.983 (–1.69% loss of intensity), KUMA KM-4 software) Unit-cell parameters were determined by least-squares refinement of 42 reflections in the range of $9.9 < 2\theta < 25.5°$.

The structure was solved by the heavy-atom method (Program SHELXS86)[32] and the anisotropic refinement was performed[33]. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares procedure with the weight $w = 1/[\sigma^2(F_o)^2 + (0.0635P)^2 + 1.3082P]$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were located from difference Fourier maps and refined with isotropic thermal parameters 20% larger than the equivalent *U* values of the atoms to which they are attached, except for those bonded to O(2) atom. Each of the C(2), C(3), C(4), C(5), C(6) and C(7) atoms is disordered over two positions with occupancy factors 0.50(1) and 0.50(1), 0.50(1) and 0.50(1), 0.50(1) and 0.50(1), 0.50(1) and 0.50(1), 0.50(1) and 0.50(1), and 0.55(1) and 0.45(1), respectively. The highest residual peak (0.86 e $Å^{-3}$) was located 1.00 Å from the Cu(1) atom. The crystal data and structure refinement details for $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ are given in Table I and Table II gives selected bond lengths and angles.

Syntheses

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.

[(Ni(aep)$_2$)$_2$ox](ClO$_4$)$_2$ (**1**). A solution of 0.18 g (1.34 mmol) of sodium oxalate in 20 cm^3 water was added to a solution of 1.00 g (2.73 mmol) of Ni(ClO$_4$)$_2$·6 H$_2$O and 0.66 cm^3 (5.51 mmol) of 2-(2-aminoethyl)pyridine in 30 cm^3 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 on air. The yield was 0.65 g (27%).

Complexes **2**–**6**. These complexes were obtained analogously: [(Ni(ept)H$_2$O)$_2$ox](NO$_3$)$_2$ (**2**) from Ni(NO$_3$)$_2$·6 H$_2$O (1.00 g, 3.44 mmol), *N*-(2-aminoethyl)-1,3-diaminopropane (0.43 cm^3, 3.41 mmol), sodium oxalate (0.23 g, 1.72 mmol), yield 0.2 g (20%); [(Cu(aep)H$_2$O)$_2$ox](ClO$_4$)$_2$ (**3**) from sodium oxalate (0.18 g, 1.34 mmol), Cu(ClO$_4$)$_2$·6 H$_2$O (1.00 g, 4.14 mmol), 2-(2-aminoethyl)pyridine (0.32 cm^3, 2.67 mmol), yield 0.55 g (60%); [(Cu(ept))$_2$ox](NO$_3$)$_2$·H$_2$O (**4**) from sodium oxalate (0.28 g, 2.09 mmol), Cu(NO$_3$)$_2$·3 H$_2$O (1.00 g, 4.14 mmol), *N*-(2-aminoethyl)-1,3-diaminopropane (0.52 cm^3, 4.13 mmol), yield 0.3 g (25%); [(Zn(ept))$_2$ox](ClO$_4$)$_2$ (**5**) from sodium oxalate (0.18 g, 1.34 mmol), Zn(ClO$_4$)$_2$·6 H$_2$O (1.00 g, 2.69 mmol), *N*-(2-aminoethyl)-1,3-diaminopropane (0.47 cm^3, 2.70 mmol), yield 0.5 g (55%)

TABLE I
Crystal data and structure refinement parameters for [(Cu(aep)H$_2$O)$_2$ox](ClO$_4$)$_2$ (**3**)

Molecular formula	$C_{16}H_{24}Cl_2Cu_2N_4O_{14}$
Molecular weight, g mol^{-1}	694.37
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system, space group	triclinic, $P\bar{1}$ (No.2)
Unit cell dimensions, Å, °	a = 7.513(2), α = 87.45(3) b = 9.004(2), β = 87.36(3) c = 10.1216(2), γ = 65.76(3)
Volume, Å^3	623.7(2)
Z; calculated density, Mg m^{-3}	1; 1.849
Absorption coefficient, mm^{-1}	1.996
F(000)	352
Crystal size, mm	0.60 × 0.50 × 0.20
θ range for data collection, °	2.01–27.56
Index ranges	$-8 \le h \le 8$; $-11 \le k \le 10$; $12 \le l \le 12$
Refections collected, unique	4 767, 2 508 [R_{int} = 0.1055]
Refinement method	Full-matrix least-squares on F^2
Data; restraints; parameters	2 508; 0; 229
Goodness-of-fit on F^2	1.041
Final R factor [$I > 2\sigma(I)$]	$R1$ = 0.0501, $wR2$ = 0.1201
R factor (all data)	$R1$ = 0.0598, $wR2$ = 0.1280
Largest diff. peak and hole	0.861 and –0.736 e Å^{-3}

and [(Zn(3,2,3-tet))$_2$ox](ClO$_4$)$_2$·4 H$_2$O (**6**) from sodium oxalate (0.18 g, 1.34 mmol), Zn(ClO$_4$)$_2$·6 H$_2$O (1.00 g, 2.69 mmol), *N*,*N*′-bis(3-aminopropyl)-1,2-diaminoethane (0.47 cm^3, 5.51 mmol), yield 0.65 g (60%).

RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table III. Figures 1–3 summarize their spectral and magnetic properties.

The characteristic group vibrations in the IR spectra of complexes prepared are as follows: ν_3(ClO$_4$) (1 080–1 085 cm^{-1}), ν_4(ClO$_4$) (622–628 cm^{-1}), ν_{asym}(CO$_2$) (1 630–1 654 cm^{-1}), ν_{sym}(CO$_2$) (1 310–1 348 cm^{-1}) and δ(CO$_2$) (792–800 cm^{-1}). These values are consistent with tetradentate oxalate[29,34] and ionic perchlorate[35] anions.

TABLE II
Selected bond lengths (Å) and angles (°) for [(Cu(aep)H$_2$O)$_2$ox](ClO$_4$)$_2$ (**3**)

Atoms	Lengths	Atoms	Angles
Cu1–N1	1.995(4)	N2–Cu1–O1	168.6(2)
Cu1–N2	1.963(3)	N1–Cu1–O3	174.0(1)
Cu1–O1	1.985(3)	N2–Cu1–N1	95.4(2)
Cu1–O3	1.992(3)	O1–Cu1–O3	83.4(1)
Cu1–O2	2.378(3)	N2–Cu1–O2	97.6(2)
Cu1–Cu1a[a]	5.204(2)	O1–Cu1–O2	91.3(1)
O1–C1	1.248(5)	N1–Cu1–O2	92.7(2)
O2–C1a[a]	1.260(4)	O3–Cu1–O2	90.3(1)
C1–C1a[a]	1.511(7)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 2$.

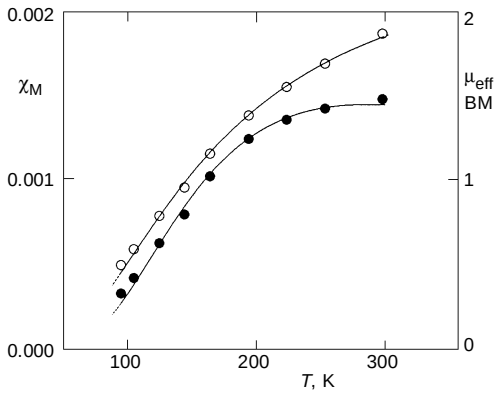

FIG. 1
The paramagnetic susceptibility χ_M (●) and effective moment μ_{eff} (○) *vs* temperature for [(Cu(aep)H$_2$O)$_2$ox](ClO$_4$)$_2$ (**3**). The circles are experimental points, the solid lines are theoretical ones. This curve (χ_M) was calculated using Eq. (*1*)

The UV-VIS absorption spectra of Cu(II) complexes are characterized by a strong band in the range 13 000–18 000 cm^{-1} corresponding to a *d–d* transitions[36]. In the present compounds, the maxima at 15 000 or 16 000 cm^{-1} for **3** and **4**, respectively, can correspond to these bands. In the Ni(II) complexes, the bands at 17 000 (**1**) or 17 500 cm^{-1} and 28 000 cm^{-1} (**2**) may be assigned to ν_2 and ν_3, respectively, in octahedral environment[36].

TABLE III
Elemental analysis of the complexes prepared

Complex	Calculated/Found		
	% C	% H	% N
$[(Ni(aep)_2)_2ox](ClO_4)_2$ (**1**)	40.4	4.5	12.6
	40.1	4.5	12.2
$[(Ni(ept)H_2O)_2ox](NO_3)_2$ (**2**)	24.0	5.7	18.7
	23.5	5.7	17.9
$[(Cu(aep)H_2O)_2ox](ClO_4)_2$ (**3**)	27.7	3.5	8.1
	28.7	3.1	8.2
$[(Cu(ept))_2ox](NO_3)_2 \cdot H_2O$ (**4**)	24.4	5.5	18.9
	24.2	5.3	18.5
$[(Zn(ept))_2ox](ClO_4)_2$ (**5**)	22.1	4.6	12.9
	21.9	5.2	12.3
$[(Zn(3,2,3\text{-tet}))_2ox](ClO_4)_2 \cdot 4\ H_2O$ (**6**)	26.8	6.5	13.9
	26.2	6.2	13.9

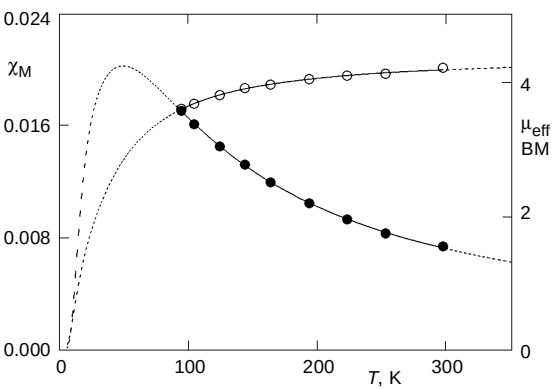

FIG. 2
The paramagnetic susceptibility χ_M (●) and effective moment μ_{eff} (○) *vs* temperature for $[(Ni(aep)_2)_2ox](ClO_4)_2$ (**1**). The circles are the experimental points, the solid lines are theoretical ones. This curve (χ_M) was calculated using Eq. (*2*)

The spectroscopic data are consistent with oxalate-bridged dimeric structures for all six complexes. Tetragonal pyramidal five-coordination is confirmed by X-ray structure determination of **3** and octahedral geometry is proposed for the nickel complexes **1** and **2**. Pentacoordination can be suggested for compounds **4** and **5** and hexacoordination for compound **6**.

Magnetic measurements show that complex **3** behaves like a classical copper(II) dimer (0.49 BM at 94.4 K to 1.87 BM at 297.5 K; $H = -2JS_1S_2$, $S_1 = S_2 = 1/2$). The data follow the Bleaney–Bowers equation[37] (*1*):

$$\chi_M = \left(\frac{\mu_0 N g^2 \beta^2}{3kT}\right)\left(\frac{6\exp(2J/kT)}{1+3\exp(2J/kT)}\right) + N_\alpha \quad . \qquad (1)$$

The least-square-fit[38] (Fig. 1) of the data yields $J = -160$ cm^{-1} and $g = 2.1$ for $[(Cu(aep)H_2O)_2ox](ClO_4)_2$. Hence, the compound **3** exhibits strong antiferromagnetic exchange interaction can be explained by the tetragonal pyramidal coordination of copper, so that the x^2–y^2 magnetic orbitals on Cu are directed ideally for overlap with the oxalate σ orbitals[2,3].

The effective magnetic moment of 2.98 BM at 297.5 K per Ni(II) ($[Ni(aep)_2)_2ox](ClO_4)_2$) is typical for octahedrally coordinated nickel(II). The variable-temperature magnetic moment and magnetic susceptibility in the range 94–298 K for a solid sample of the title compound is shown in Fig. 2. The magnetic moment is temperature dependent and decreases from 4.22 BM mol^{-1} (2.98 BM per Ni^{2+}) at 298 K to 3.69 BM at 94 K. This

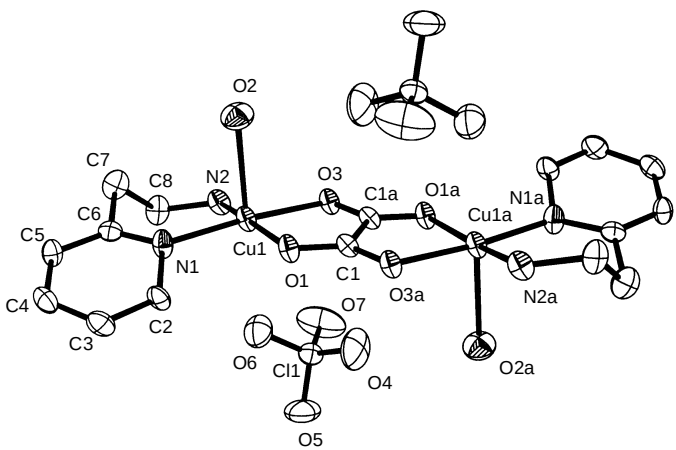

FIG. 3

A perspective view of the molecule $[(Cu(aep)H_2O)_2ox](ClO_4)_2$ (**3**). The C2, C3, C4, C5, C6 and C7 atoms are disordered over two positions (see the text) and the atoms in the second positions are omitted for the clarity

proves that there is also an antiferromagnetic coupling mediated by the oxalate bridge. The magnetic behaviour of this complex could be interpreted using isotropic spin Hamiltonian $H = -2JS_1S_2$, where $S_1 = S_2 = 2/2$ and J is the exchange integral. The experimental data have been fitted to the expression[6] (*2*)

$$\chi_M = \left(\frac{\mu_0 N g^2 \beta^2}{3kT}\right)\left(\frac{30 \exp(6J/kT) + 6 \exp)2J/kT)}{5 \exp(6J/kT) + 3 \exp(2J/kT) + 1}\right) + N_\alpha \qquad (2)$$

for an HDVV (Heisenberg–Dirac–van Vleck)-dimer model (Fig. 2). The best parameters are $J = -17$ cm^{-1}, $g = 2.2$. For Ni(II) complexes in octahedral geometry, the metal x^2–y^2 orbital is half occupied and is oriented such as to allow the overlap with the oxalate σ-orbitals. For 1, the observed J-value of –17 cm^{-1} is similar to that of $[Ni_2(1,3\text{-pn})_4ox](ClO_4)_2$ (ref.[39]) (1,3-pn = 1,3-diaminopropane) ($J = -18$ cm^{-1}) or $[Ni_2en_4ox](NO_3)_2$ ($J = -16$ cm^{-1})[27].

The structure of copper(II) complex **3** was determined by a single-crystal X-ray diffraction. The molecular structure consists of the binuclear centrosymmetric $[(Cu(aep)H_2O)_2ox]^{2+}$ cation and perchlorate anions. A view of the molecule is shown in Fig. 3. Principal bond distances are listed in Table II. The binuclear cation is composed of two $Cu^{II}(aep)(H_2O)$ units bridged by a bis-bidentate oxalate anion. The coordination polyhedron of Cu(1) is formed by two oxygen atoms O(1), O(3) of $C_2O_4^{2-}$, two nitrogen atoms N(1), N(2) of aep and O(2) of H_2O. The Cu(1) is five-coordinate and lies only 0.106(2) Å away from the least-squares plane fitted through the N(1), N(2), O(1) and O(3) atoms. The in-plane Cu–O bond distances are 1.985(3) and 1.992(3) Å, and Cu–N bond distances are 1.995(4) and 1.963(3) Å. The Cu(1)–O(2) bond distance is 2.378(3) Å. Thus, the coordination geometry around the Cu(1) ion can be described as a distorted tetragonal pyramid. As usual, the Cu–C_2O_4–Cu fragment is virtually planar and deviations from the least-squares plane fitted through the Cu(1)–C(1)–O(1)–O(3)–C(1a)–O(1a)–O(3a)–Cu(1a) atoms are lower than 0.031(2) Å. The Cu(1)···Cu(1a) distance of 5.204(2) Å falls within the range found for similarly coordinated μ-oxalato Cu(II) complexes.

Supplementary Material

A complete lists of bond distances and angles, coordinates of all non-hydrogen atoms, anisotropic displacement parameters and observed and calculated structure factors are available from the author (Z. T.) upon request.

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