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Structurally alternating copper(II) chains from oxalate and azide bridging ligands: syntheses and crystal structure of $[Cu_2(\mu\text{-ox})(deen)_2(H_2O)_2(ClO_4)_2]$ and $[\{Cu_2(\mu\text{-}N_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ (deen = $Et_2NCH_2CH_2NH_2$)

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The μ-oxalato dinuclear compound $[Cu_2(\mu\text{-ox})(deen)_2(H_2O)_2(ClO_4)_2]$ **1** and the derived alternating μ-oxalato-μ-azido chain $[\{Cu_2(\mu\text{-}N_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ **2**, where deen = *N*,*N*-diethylethane-1,2-diamine, have been synthesized and characterised. The crystal structures of **1** and **2** have been determined by single-crystal X-ray analysis. Their magnetic behaviour has been recorded between 300 and 4 K, showing strong antiferromagnetic coupling in each case. The data were fitted by the expression for a dinuclear copper(II) compound giving the parameters $J = -300(3)$ cm^{-1}, $g = 2.15(1)$ for **1** and $J = -287(1)$ cm^{-1}, $g = 2.28(1)$ for **2**.

Oxalate and azide are good examples of bridging groups able to transmit electronic effects between paramagnetic centres separated by more than 5 Å in the case of the former[1] and by more than 6 Å in the case of the latter.[2,3] Recently, with the aim of combining the oxalate and the azide superexchange pathways in the same compound, we have designed a strategy for nickel(II)[4] or copper(II)[5] as central atoms which uses dinuclear $[(H_2O)(triamine)Ni(ox)Ni(triamine)(H_2O)]^{2+}$ and $[(H_2O)(diamine)Cu(ox)Cu(diamine)(H_2O)]^{2+}$ compounds as starting products. In these compounds two H_2O ligands of different dinuclear units can be replaced by one bridging azide ligand, which can lead to the formation of μ-oxalato-μ-azido-dinickel(II) or -dicopper(II) alternating chains. The difference in the starting reagents is due to the fact that the copper(II) ion tends to adopt a five-co-ordinate arrangement. Surprisingly, with the same synthesis procedure the desired one-dimensional alternating nickel(II) compounds were synthesized,[4] but the starting dinuclear copper(II) derivative $[Cu_2(\mu\text{-ox})(tmen)_2(H_2O)_2][ClO_4]_2\cdot 1.25H_2O$[6] (tmen = $Me_2NCH_2CH_2NMe_2$), a hexanuclear compound was obtained;[5] $[Cu_6(\mu\text{-}N_3)_2(\mu\text{-ox})_3(tmen)_6(H_2O)_2][ClO_4]_4$, where the H_2O ligands terminate the growth of the one-dimensional compound. Here we describe a new attempt for copper(II) by using as starting product the new dinuclear $[Cu_2(\mu\text{-ox})(deen)_2(H_2O)_2(ClO_4)_2]$ **1** (deen = *N*,*N*-diethylethane-1,2-diamine) which has also been structurally and magnetically characterised by us. In this case the expected alternating chain $[\{Cu_2(\mu\text{-}N_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ **2** was obtained.

Experimental

Synthesis

$[Cu_2(\mu\text{-ox})(deen)_2(H_2O)_2ClO_4]_2$ 1. Copper(II) perchlorate hexahydrate (0.0027 mol), deen (0.0027 mol) and sodium oxalate (0.0014 mol) were mixed in water (75 cm^3). After 30 min a blue microcrystalline precipitate of complex **1** was filtered off. From the mother-liquor, blue monocrystals suitable for X-ray determination of **1** were collected 10 d later (Found: C, 24.9; H, 4.9; N, 8.2. Calc. for $C_{14}H_{36}Cl_2Cu_2N_4O_{14}$: C, 24.6; H, 5.3; N, 8.2%).

$[\{Cu_2(\mu\text{-}N_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ 2. Copper(II) perchlorate hexahydrate (0.0054 mol), deen (0.0054 mol) and sodium oxalate (0.0027 mol) were mixed in water (100 cm^3). After stirring at room temperature for 30 min a blue microcrystalline precipitate of complex **1** was formed. Sodium azide (0.0027 mol) in water (20 cm^3) was added to this suspension. The solution changed to green and the blue precipitate was almost completely dissolved. After 1 h of stirring the solution was filtered and left to evaporate in the air. Several times, crystals of complex **2** which were not suitable for X-ray diffraction were collected over 20 d, monitored by the appearance of the IR band corresponding to the bridging azide ligand at 2058s cm^{-1}. All the fractions were combined and recrystallised from water. Green monocrystals of **2** suitable for X-ray determination were obtained (Found: C, 28.8; H, 5.8; N, 16.3. Calc. for $C_{28}H_{64}Cl_2Cu_4N_{14}O_{16}$: C, 28.6; H, 5.5; N, 16.7%).

Spectral and magnetic measurements

The IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. Magnetic susceptibility measurements in the temperature range 300–4 K were carried out on polycrystalline samples with a pendulum-type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat and a Bruker B E15 electromagnet. The magnetic field was *ca.* 1.5 T. Diamagnetic corrections were estimated from Pascal's constants. The ESR spectra were recorded at room and liquid-nitrogen temperatures on a Bruker ES200 spectrometer at X-band frequency.

X-Ray crystallography

A crystal of complex **1** of dimensions 0.61 × 0.27 × 0.27 mm was mounted on a Stoe AED2 four-circle diffractometer equipped with graphite-monochromatised Mo-Kα radiation ($\lambda = 0.710\ 73$ Å). Data were collected using ω–θ scans out to 50° in 2θ. The lattice parameters were optimised from a least-squares refinement of the setting angles of 19 reflections and their equivalents in the range $14 < \theta < 17.5°$. Crystallographic data are summarised in Table 1. The structure was solved by direct methods using SHELXS 86.[7] The NRCVAX[8] system was used for all further calculations. Neutral complex atom scattering factors in NRCVAX are from ref. 9. The H atoms were located from difference maps and refined isotropically. The non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2. No corrections were made for absorption or extinction. Selected bond distances and angles are given in Table 2.

A prismatic blue crystal (0.1 × 0.1 × 0.2 mm) of complex **2** was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21°$) and refined by full-matrix least squares on F^2. Intensities were recorded with graphite-monochromatised Mo-Kα radiation ($\lambda = 0.710\ 69$ Å). 6740 Reflections were measured in the range $1.40 < \theta < 29.97°$, 4526 assumed as observed, applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; no significant decay was observed. The crystallographic data are listed in Table 1. Lorentz-polarisation and absorption corrections were made. The structure was solved by Patterson synthesis, using SHELXS 86[7] and refined by full-matrix least squares with SHELXL 93[10] using 6690 reflections (very negative intensities were discarded). The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = |\sigma^2(I) + (0.3287P)^2 + 3.1997P|^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from ref. 9. Maximum shift/e.s.d. = 0.25, mean shift/e.s.d. = 0.01. Maximum and minimum peaks in final difference synthesis 1.530 and −1.413 e Å^{-3}, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/291.

Results and Discussion

Infrared spectra

The IR spectrum of complex **1** shows principal bands corresponding to the co-ordinated oxalate at 1636s and 1654s cm^{-1}. The perchlorate anion presents bands at 1080s, 1120s, 1145s and 630m cm^{-1}. The spectrum of **2** shows a band corresponding to the bridging azide ligand at 2058s cm^{-1}. The principal band corresponding to the co-ordinated oxalate appears at 1650s cm^{-1} and the perchlorate anion presents bands at 1097s and 628m cm^{-1}.

Crystal structures

[Cu$_2$(μ-ox)(deen)$_2$(H$_2$O)$_2$(ClO$_4$)$_2$] 1. In the unit cell there are two independent non-centrosymmetric dinuclear molecules of [Cu_2(μ-ox)(deen)$_2$(H_2O)$_2$(ClO_4)$_2$] denoted **1a** and **1b**. An ORTEP[11] drawing of **1a** and **1b** with the atom-labelling scheme is presented in Fig. 1. The copper atoms are in a pseudo-octahedral environment with two oxalato oxygen and two deen nitrogen atoms in the basal plane. The co-ordinated water molecules are placed in two axial co-ordination sites, perpendicular to the Cu(ox)Cu plane and *trans* to each other. The pseudo-octahedral co-ordination is completed by one oxygen atom of the perchlorate anion. The bond lengths and angles for the two different dinuclear units, **1a** and **1b**, are very similar in the plane [Cu_2(μ-ox)(deen)$_2$]$^{2+}$, but the Cu–O (water) and Cu–O (perchlorate) distances are very different: in **1a**, Cu(1)–O(w1), Cu(2)–O(w2), Cu(1)–O(12) and Cu(2)–O(22) are 2.585(4), 2.524(4), 2.609(4) and 2.711(4) Å respectively, and in **1b**, Cu(3)–O(w3), Cu(4)–O(w4), Cu(3)–O(34) and Cu(4)–O(41) are 2.312(4), 2.317(4), 2.899(4) and 2.991(4) Å respectively. There are also hydrogen bonds between O(w1)···O(23), O(w2)···O(13), O(w3)···O(43) and O(w4)···O(33) with distances of 2.785(4), 2.766(4), 2.805(4) and 2.828(4) Å respectively, as seen in Fig. 2 for unit **1b**. As usual, the Cu(ox)Cu fragment is practically planar: deviations from the mean plane comprising Cu and oxalate (eight atoms) are less than 0.037 Å, O(2), for the dinuclear unit **1a** and 0.022 Å, O(3B), for the dinuclear unit **1b**. Units **1a** and **1b** are practically parallel: the dihedral angle between the Cu(ox)Cu fragments is 3.88°. The basal bond distances around the copper atoms are similar, in the range 1.969(4)–2.042(4) Å for **1a** and 1.962(4)–2.054(4) Å for **1b**. The C–C distances of the bridging oxalate ligand are 1.538(5) and 1.544(5) Å for **1a** and **1b** respectively. The structural parameters found in **1a** and **1b** are in the range of those in related dinuclear compounds.[12–14]

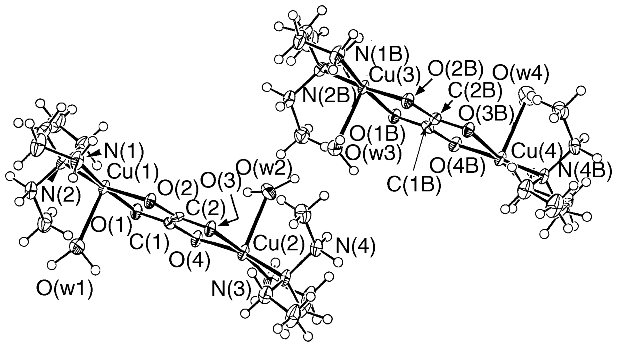

Fig. 1 An ORTEP drawing with the atom-labelling scheme for [Cu_2(μ-ox)(deen)$_2$(H_2O)$_2$(ClO_4)$_2$] **1**. The ClO_4^- are omitted for clarity

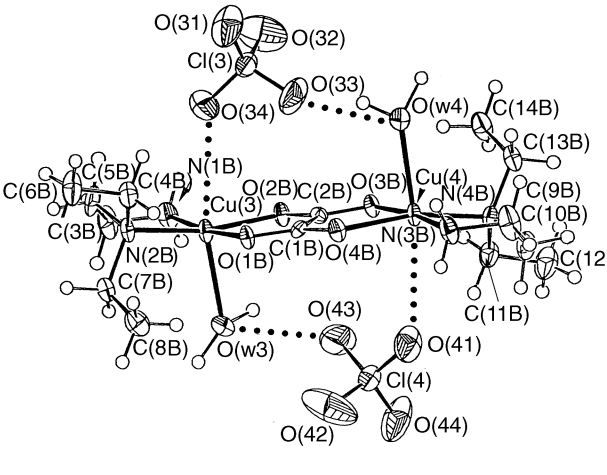

Fig. 2 An ORTEP drawing with the atom-labelling scheme for the dinuclear unit **1b**

[{Cu$_2$(μ-N$_3$)(μ-ox)(deen)$_2$}$_n$][ClO$_4$]$_n$ 2. In complex **2** the copper atoms are bridged alternately by oxalate and end-to-end azide ligands. An ORTEP[11] drawing of the chain with the atom-labelling scheme is shown in Fig. 3. The chain can be viewed as centrosymmetric dinuclear planar [$LCu(C_2O_4)CuL$]$^{2+}$ entities, L = deen, bridged through the copper atoms by end-to-end azide ligands in *trans* configuration. The copper atoms have a square-pyramidal environment, with two oxygen atoms of the oxalate bridge and two nitrogen atoms of deen occupying the base of the pyramid. The axial co-ordination site is occupied by one nitrogen atom of the bridging azide ligand. As usual the Cu(ox)Cu fragment is practically planar: deviations from the mean plane comprising Cu and oxalate (eight atoms) are less than 0.084 Å and the Cu(1) and Cu(2) atoms deviate by 0.013

Table 1 Crystal data and structure refinement for $[Cu_2(\mu\text{-ox})(deen)_2(H_2O)_2(ClO_4)_2]$ **1** and $[\{Cu_2(\mu\text{-N}_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ **2**

Formula	$C_{14}H_{36}Cl_2Cu_2N_4O_{14}$	$C_{28}H_{64}Cl_2Cu_4N_{14}O_{16}$
M	682.47	1177.99
T/K	213(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/a$
a/Å	12.308(4)	12.864(8)
b/Å	13.706(6)	12.4016(11)
c/Å	16.591(5)	15.417(2)
α/°	76.61(2)	
β/°	83.94(3)	109.29(3)
γ/°	74.29(2)	
U/Å^3	2618(2)	2322(2)
Z	4	2
D_c/g cm^{-3}	1.731	1.685
μ(Mo-Kα)/cm^{-1}	19.07	20.02
Data, restraints, parameters	9203, 0, 658	6690, 0, 291
$R1^a$	0.0426,	0.0550
$wR2^b$	0.0987	0.1782

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $|\Sigma|[(F_o)^2 - (F_c)^2]^2|/\Sigma(F_o)^4|^{\frac{1}{2}}$.

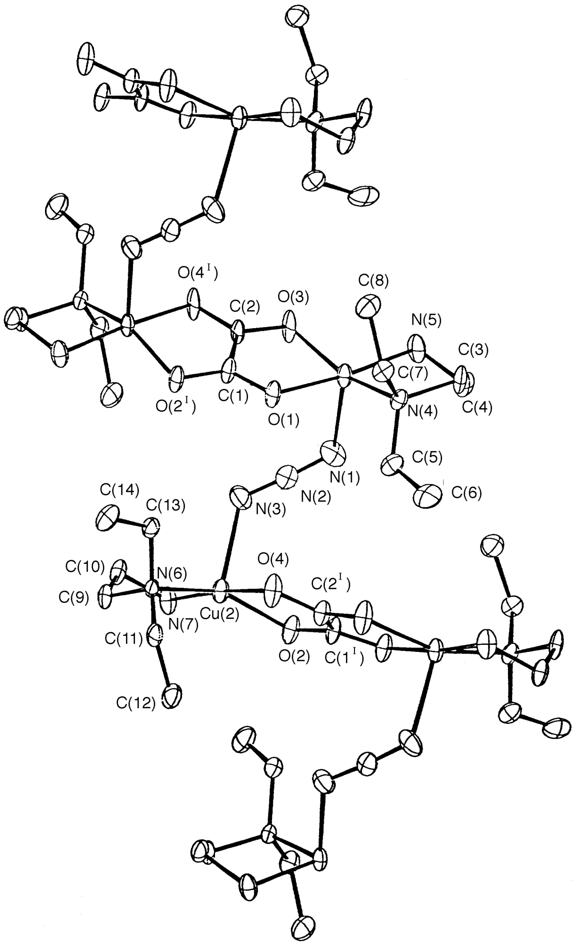

Fig. 3 An ORTEP drawing with the atom-labelling scheme for $[\{Cu_2(\mu\text{-N}_3)(\mu\text{-ox})(deen)_2\}_n][ClO_4]_n$ **2**

and 0.028 Å respectively. The basal bond distances around the copper atoms are very similar, in the range 1.979(4)–2.033(4) Å. The Cu–N (azide) distances are Cu(1)–N(1) 2.195(5) Å and Cu(2)–N(3) 2.221(5) Å. The C–C distance in the bridging oxalate ligand is 1.526(6) Å. The Cu–N–N angles are Cu(1)–N(1)–N(2) 119.7(4)° and Cu(2)–N(3)–N(2) 122.7(4)°. The Cu–N_3–Cu torsion angle is 61.9°. Consequently the Cu(ox)Cu mean planes are not parallel, the dihedral angle between two consecutive mean planes being 51.1°. The structural parameters of the dinuclear unit $[Cu_2(\mu\text{-N}_3)(\mu\text{-ox})(deen)_2]^{2+}$

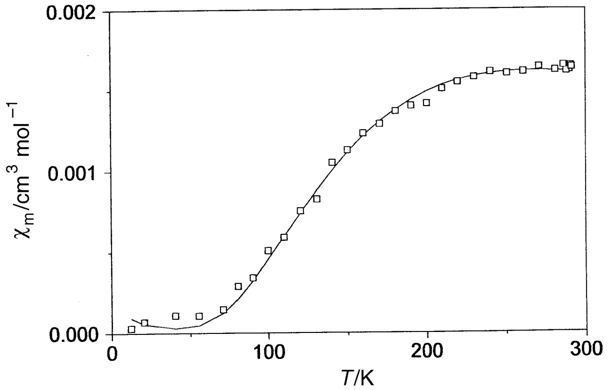

Fig. 4 Magnetic susceptibility plot of a polycrystalline sample of complex **1**. The solid line shows the best fit by the expression for the magnetic susceptibility of isotropically coupled $S = \frac{1}{2}$ ions in antiferromagnetic linear chains (see text)

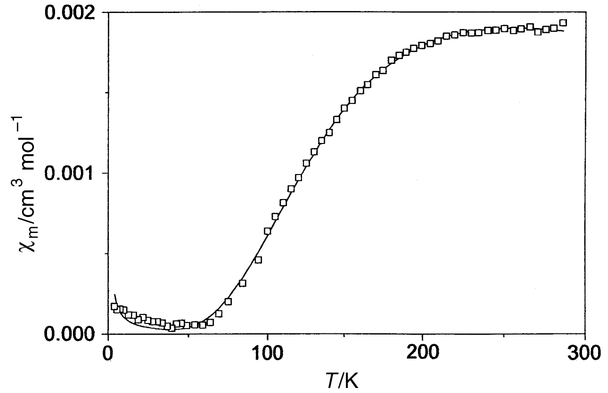

Fig. 5 Magnetic susceptibility plot of a polycrystalline sample of complex **2**. Details as in Fig. 4

of **2** are in the same range of those found in **1** and in related dinuclear compounds.[12–14]

Magnetic results

Complex 1. A plot of the molar magnetic susceptibility (for two copper atoms) *vs.* T for complex **1** is shown in Fig. 4. The χ_m value is 1.7×10^{-3} cm^3 mol^{-1} at room temperature and decreases with temperature reaching zero at approximately 40 K. The ESR spectra of polycrystalline samples of the new complex at X-band frequency were recorded at room and liquid-nitrogen temperatures. At room temperature **1** has $g_{\parallel} = 2.24$ and $g_{\perp} = 2.06$. At liquid-nitrogen temperature the signal practically vanishes.

The susceptibility data were fitted by the Bleaney–Bowers expression for the magnetic susceptibility of isotropically coupled dinuclear $S = \frac{1}{2}$ ions,[15] based on the spin Hamiltonian $H = -JS_AS_B$, adding an impurity term defined as the molar fraction of non-coupled species.[1] It is assumed that the impurity obeys the Curie law and has the same molecular weight and the same g factor as that of the actual compound. The criterion of best fit was the minimum value of $R = \Sigma_i(\chi_i\text{calc} - \chi_i\text{obs})^2/(i - n)$, where n is the number of free parameters ($n = 3$). The results of the fit, shown as the solid line in Fig. 4, were $J = -300(3)$ cm^{-1}, $g = 2.15(1)$, $\rho = 0.0013(4)$ with $R = 4.1 \times 10^{-8}$. The J value is similar to that evaluated for μ-oxalato-bridged dinuclear copper(II) complexes characterised by a non-centrosymmetric $Cu(C_2O_4)Cu$ core[13] and weaker than that evaluated for μ-oxalato-bridged dinuclear copper(II) complexes with a centrosymmetric $Cu(C_2O_4)Cu$ core ($-J = 330$–402 cm^{-1}).[12,14]

Complex 2. A plot of the molar magnetic susceptibility (for

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**

Cu(1)–N(1)	1.969(4)	Cu(1)–O(1)	1.975(3)	Cu(4)–O(3B)	1.984(3)	Cu(4)–O(4B)	2.012(3)
Cu(1)–O(2)	2.020(3)	Cu(1)–N(2)	2.042(4)	Cu(4)–N(4B)	2.046(4)	Cu(4)–O(w4)	2.317(4)
Cu(1)–O(w1)	2.585(4)	Cu(1)–O(12)	2.609(4)	N(1)–C(3)	1.475(6)	N(2)–C(4)	1.501(6)
Cu(2)–N(3)	1.973(4)	Cu(2)–O(3)	1.975(3)	O(1)–C(1)	1.249(6)	O(2)–C(2)	1.243(5)
Cu(2)–O(4)	2.007(3)	Cu(2)–N(4)	2.042(4)	O(3)–C(2)	1.251(6)	O(4)–C(1)	1.261(5)
Cu(2)–O(w2)	2.524(4)	Cu(2)–O(22)	2.711(4)	C(1)–C(2)	1.538(5)	C(3)–C(4)	1.499(7)
Cu(3)–N(1B)	1.967(4)	Cu(3)–O(1B)	1.973(3)	O(1B)–C(1B)	1.252(5)	O(2B)–C(2B)	1.242(5)
Cu(3)–O(2B)	2.019(3)	Cu(3)–N(2B)	2.054(4)	O(4B)–C(1B)	1.251(5)	C(1B)–C(2B)	1.544(5)
Cu(3)–O(w3)	2.312(4)	Cu(3)–O(34)	2.899(4)	O(3B)–C(2B)	1.254(5)		
Cu(4)–N(3B)	1.962(4)	Cu(4)–O(41)	2.991(4)				

O(1)–Cu(1)–O(2)	83.67(13)	N(1)–Cu(1)–N(2)	87.5(2)	N(3B)–Cu(4)–N(4B)	86.9(2)	O(3B)–Cu(4)–N(4B)	97.1(2)
O(1)–Cu(1)–N(2)	96.4(2)	O(2)–Cu(1)–N(2)	175.5(2)	O(4B)–Cu(4)–N(4B)	168.5(2)	N(3B)–Cu(4)–O(w4)	90.6(2)
N(1)–Cu(1)–O(w1)	87.5(2)	O(1)–Cu(1)–O(w1)	94.19(13)	O(3B)–Cu(4)–O(w4)	92.73(13)	C(1)–O(1)–Cu(1)	111.5(3)
N(1)–Cu(1)–O(12)	83.5(2)	O(1)–Cu(1)–O(12)	93.43(14)	C(2)–O(2)–Cu(1)	110.9(3)	C(2)–O(3)–Cu(2)	112.1(3)
N(3)–Cu(2)–O(3)	173.5(2)	N(3)–Cu(2)–O(4)	92.5(2)	C(1)–O(4)–Cu(2)	111.4(3)	O(1)–C(1)–C(2)	117.5(4)
O(3)–Cu(2)–O(4)	83.59(13)	N(3)–Cu(2)–N(4)	87.1(2)	C(3B)–N(1B)–Cu(3)	109.4(3)	C(4B)–N(2B)–Cu(3)	103.1(3)
N(3)–Cu(2)–O(w2)	89.2(2)	O(3)–Cu(2)–O(w2)	95.34(13)	C(1B)–O(1B)–Cu(3)	111.8(3)	C(2B)–O(2B)–Cu(3)	110.6(3)
N(3)–Cu(2)–O(22)	5.0(2)	O(3)–Cu(2)–O(22)	89.43(14)	C(2B)–O(3B)–Cu(4)	112.0(3)	C(1B)–O(4B)–Cu(4)	111.2(3)
N(1B)–Cu(3)–O(1B)	173.1(2)	N(1B)–Cu(3)–O(2B)	91.6(2)	O(4B)–C(1B)–C(2B)	116.5(4)	O(1B)–C(1B)–C(2B)	116.7(4)
O(1B)–Cu(3)–O(2B)	83.91(13)	N(1B)–Cu(3)–O(w3)	91.8(2)	O(2B)–C(2B)–O(3B)	126.5(4)	O(2B)–C(2B)–C(1B)	117.0(4)
O(1B)–Cu(3)–O(w3)	93.08(14)	O(3B)–Cu(4)–O(4B)	83.60(13)	O(3B)–C(2B)–C(1B)	116.6(4)		

Complex **2**

Cu(1)–O(1)	1.990(3)	Cu(1)–N(5)	1.998(4)	O(1)–C(1)	1.254(5)	O(2)–C(1)	1.263(5)
Cu(1)–O(3)	2.030(4)	Cu(1)–N(4)	2.031(3)	O(2)–Cu(2^{II})	2.033(3)	O(3)–C(2)	1.254(5)
Cu(1)–N(1)	2.195(5)	Cu(2)–N(7)	1.979(4)	O(4)–C(2)	1.261(5)	O(4)–Cu(2^{II})	1.989(3)
Cu(2)–O(4^{I})	1.989(3)	Cu(2)–N(6)	2.033(4)	N(1)–N(2)	1.186(6)	N(2)–N(3)	1.158(6)
Cu(2)–O(2^{I})	2.033(3)	Cu(2)–N(3)	2.221(5)	C(1)–C(2)	1.526(6)		

O(1)–Cu(1)–N(5)	174.2(2)	O(1)–Cu(1)–O(3)	83.73(13)	C(1)–O(2)–Cu(2^{II})	109.7(3)	C(2)–O(3)–Cu(1)	109.6(3)
N(5)–Cu(1)–N(4)	86.6(2)	O(3)–Cu(1)–N(4)	160.5(2)	C(2)–O(4)–Cu(2^{II})	111.4(3)	N(2)–N(1)–Cu(1)	119.7(4)
N(5)–Cu(1)–N(1)	92.2(2)	N(7)–Cu(2)–N(6)	86.8(2)	N(3)–N(2)–N(1)	177.3(6)	N(2)–N(3)–Cu(2)	122.7(4)
O(4^{I})–Cu(2)–O(2^{I})	83.80(13)	N(7)–Cu(2)–N(3)	90.9(2)	O(1)–C(1)–C(2)	116.8(4)	O(2)–C(1)–C(2)	117.2(4)
O(4^{I})–Cu(2)–N(3)	95.3(2)	C(1)–O(1)–Cu(1)	111.6(3)	O(3)–C(2)–C(1)	118.2(4)	O(4)–C(2)–C(1)	117.1(4)

Symmetry transformations used to generate equivalent atoms: I $x - \frac{1}{2}, -y + \frac{1}{2}, z$; II $x + \frac{1}{2}, -y + \frac{1}{2}, z$.

two copper atoms) *vs.* T for complex **2** is shown in Fig. 5. The χ_m value per two copper atoms is 1.9×10^{-3} cm^3 mol^{-1} at room temperature. It decreases with temperature reaching zero at approximately 40 K. The ESR spectra of polycrystalline samples of the new complex at X-band frequency were recorded at room and liquid-nitrogen temperatures. At room temperature only a wide signal appears, centred at $g = 2.12$. At liquid-nitrogen temperature the signal practically vanishes. The magnetic behaviour indicates a strongly antiferromagnetically coupled compound, and to calculate the J value we can consider an alternating chain or a dinuclear compound on the basis of the crystal structure: in the Cu(N$_3$)Cu fragment of the chain the Cu–N–N bond angles are close to 120°, the Cu-N (azide) bond lengths are in the 2.195–2.221 Å range, and the torsion angle Cu(1)–N$_3$–Cu(2) is 61.9°. In related dinuclear $[Cu(\mu\text{-}N_3)_2Cu]^{2+}$ compounds, $[Cu_2(N_3)_2(pmdien)_2][BPh_4]_2$ (pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) has a J value of -6.2 cm^{-1} with short and long Cu–N (azide) bond lengths in the bridges of 1.985(4) and 2.252(5) Å respectively and a Cu–N$_3$–Cu torsion angle of 5.6°;[16] $[Cu_2(\mu\text{-}N_3)_2(N_3)_2(tmen)_2]$ is not magnetically coupled, with short or long Cu–N (azide) bond lengths in the bridges of 1.979(5) and 2.456(6) Å respectively.[17] The Cu–N (azide) distances in **2** are similar to the long distance in the weakly coupled $[Cu_2(N_3)_2(pmdien)_2][BPh_4]_2$ and the coupling constant corresponding to the apical azide bridging ligand in **2** can reasonably be expected to be very low. Moreover, the Cu(1)–N$_3$–Cu(2) torsion angle in **2** is high, which also diminishes the J value.[3] From the analysis of the structural parameters we can consider magnetically isolated $[LCu(ox)CuL]^{2+}$ dimers for **2**. The χ_m *vs.* T data for the structurally alternating chain **2** were fitted as for **1** using the Bleaney–Bowers expression for the magnetic susceptibility of isotropically coupled dinuclear $S = \frac{1}{2}$ ions,[15] adding an impurity term defined as the molar fraction of non-coupled species.[1] The criterion of best fit was as before. The results of the fit, shown as the solid line in Fig. 5, were $J = -287(1)$ cm^{-1}, $g = 2.28(1)$, $\rho = 0.0010(1)$ with $R = 4.4 \times 10^{-8}$. The J value is very similar to that found for the hexanuclear $[Cu_6(\mu\text{-}N_3)_2(\mu\text{-}ox)_3(tmen)_6(H_2O)_2][ClO_4]_2$ $[-289(2)$ cm$^{-1}]$[5] and to that found for the starting compound **1**, but in **2** the Cu(C$_2$O$_4$)Cu core is centrosymmetric. To check the validity of considering magnetically isolated $[LCu(ox)CuL]^{2+}$ dimers for **2**, the χ_m *vs.* T values for **2** in the range 300–70 K were fitted by using the analytical expression derived by Hatfield[18] for an alternating ring chain of $n = 10$ local spins $\frac{1}{2}$, based on the spin Hamiltonian $H = J\Sigma|S_{2i}\cdot S_{2i-1} + \alpha S_{2i}\cdot S_{2i+1}|$ where α is the alternation parameter, 1 for a uniform chain and 0 for a dinuclear compound. The analytical expression is valid for $kT/|J| > 0.25$.[1,18] The results of the fit, $J = -282(1)$ cm^{-1}, $g = 2.25(1)$, $\alpha = 0.001(1)$, with $R = 2.3 \times 10^{-8}$, confirm the validity of considering magnetically isolated dinuclear units despite the structural disposition as an alternating μ-oxalato-μ-azido chain.

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