

Structurally alternating copper(II) chains from oxalate and azide bridging ligands: syntheses and crystal structure of $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ and $\{[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2]_n[\text{ClO}_4]_n\}$ ($\text{deen} = \text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)

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The μ -oxalato dinuclear compound $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **1** and the derived alternating μ -oxalato- μ -azido chain $\{[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2]_n[\text{ClO}_4]_n\}$ **2**, where $\text{deen} = N,N$ -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 $J = -300(3) \text{ cm}^{-1}$, $g = 2.15(1)$ for **1** and $J = -287(1) \text{ cm}^{-1}$, $g = 2.28(1)$ 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 former¹ 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 $[(\text{H}_2\text{O})(\text{triamine})\text{Ni}(\text{ox})\text{Ni}(\text{triamine})(\text{H}_2\text{O})]^{2+}$ and $[(\text{H}_2\text{O})(\text{diamine})\text{Cu}(\text{ox})\text{Cu}(\text{diamine})(\text{H}_2\text{O})]^{2+}$ 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 $[\text{Cu}_2(\mu\text{-ox})(\text{tmen})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2 \cdot 1.25\text{H}_2\text{O}$ ⁶ ($\text{tmen} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), a hexanuclear compound was obtained,⁵ $[\text{Cu}_6(\mu\text{-N}_3)_2(\mu\text{-ox})_3(\text{tmen})_6(\text{H}_2\text{O})_2][\text{ClO}_4]_4$, 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 $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **1** ($\text{deen} = N,N$ -diethylethane-1,2-diamine) which has also been structurally and magnetically characterised by us. In this case the expected alternating chain $\{[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2]_n[\text{ClO}_4]_n\}$ **2** was obtained.

Experimental

Synthesis

$[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **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 $\text{C}_{14}\text{H}_{36}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{14}$: C, 24.6; H, 5.3; N, 8.2%).

$\{[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2]_n[\text{ClO}_4]_n\}$ **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 2058 s 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 $\text{C}_{28}\text{H}_{64}\text{Cl}_2\text{Cu}_4\text{N}_{14}\text{O}_{16}$: 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 $0.61 \times 0.27 \times 0.27 \text{ mm}$ was mounted on a Stoe AED2 four-circle diffractometer

equipped with graphite-monochromatised Mo-K α radiation ($\lambda = 0.710\ 73\ \text{\AA}$). 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 $14 < \theta < 17.5^\circ$. Crystallographic data are summarised in Table 1. The structure was solved by direct methods using SHELXS 86.⁷ The NRCVAX⁸ 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 ($0.1 \times 0.1 \times 0.2\ \text{mm}$) 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 ($12 < \theta < 21^\circ$) and refined by full-matrix least squares on F^2 . Intensities were recorded with graphite-monochromatised Mo-K α radiation ($\lambda = 0.710\ 69\ \text{\AA}$). 6740 Reflections were measured in the range $1.40 < \theta < 29.97^\circ$, 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 86⁷ and refined by full-matrix least squares with SHELXL 93¹⁰ using 6690 reflections (very negative intensities were discarded). The function minimised was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = |\sigma^2(I) + (0.3287P)^2 + 3.1997P^{-1}|^{-1}$ 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 $-1.413\ \text{e}\ \text{\AA}^{-3}$, 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

$[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **1**. In the unit cell there are two independent non-centrosymmetric dinuclear molecules of $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ denoted **1a** and **1b**. An ORTEP¹¹ 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 $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2]^{2+}$, but the Cu–O (water) and Cu–O (perchlorate) distances are very different: in **1a**, Cu(1)–O(w1),

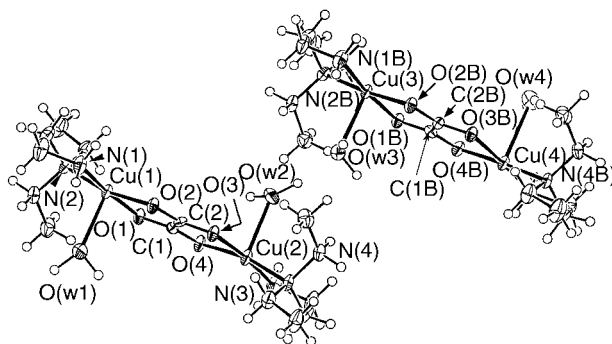


Fig. 1 An ORTEP drawing with the atom-labelling scheme for $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **1**. The ClO_4^- are omitted for clarity

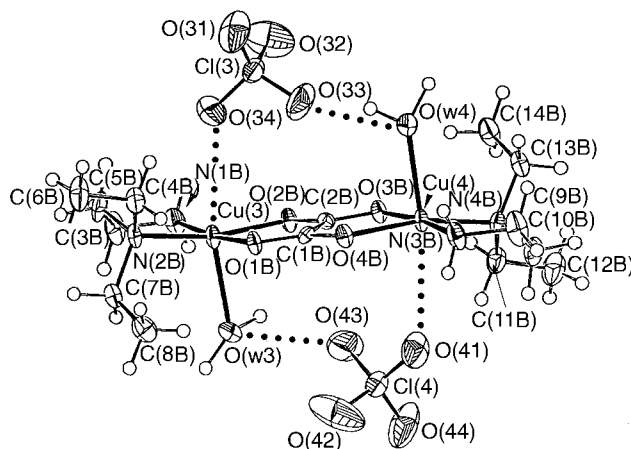


Fig. 2 An ORTEP drawing with the atom-labelling scheme for the dinuclear unit **1b**

Cu(2)–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) \AA 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) \AA respectively. There are also hydrogen bonds between O(w1) \cdots O(23), O(w2) \cdots O(13), O(w3) \cdots O(43) and O(w4) \cdots O(33) with distances of 2.785(4), 2.766(4), 2.805(4) and 2.828(4) \AA 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 \AA , O(2), for the dinuclear unit **1a** and 0.022 \AA , 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) \AA for **1a** and 1.962(4)–2.054(4) \AA for **1b**. The C–C distances of the bridging oxalate ligand are 1.538(5) and 1.544(5) \AA 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}

$[\{\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2\}_n][\text{ClO}_4]_n$ **2**. In complex **2** the copper atoms are bridged alternately by oxalate and end-to-end azide ligands. An ORTEP¹¹ drawing of the chain with the atom-labelling scheme is shown in Fig. 3. The chain can be viewed as centrosymmetric dinuclear planar $[\text{LCu}(\text{C}_2\text{O}_4)\text{CuL}]^{2+}$ 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 \AA and the Cu(1) and Cu(2) atoms deviate by 0.013

Table 1 Crystal data and structure refinement for $[\text{Cu}_2(\mu\text{-ox})(\text{deen})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ **1** and $[\{\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2\}_n][\text{ClO}_4]_n$ **2**

Formula	$\text{C}_{14}\text{H}_{36}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{14}$	$\text{C}_{28}\text{H}_{64}\text{Cl}_2\text{Cu}_4\text{N}_{14}\text{O}_{16}$
<i>M</i>	682.47	1177.99
<i>T</i> /K	213(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/a$
<i>a</i> /Å	12.308(4)	12.864(8)
<i>b</i> /Å	13.706(6)	12.4016(11)
<i>c</i> /Å	16.591(5)	15.417(2)
α /°	76.61(2)	
β /°	83.94(3)	109.29(3)
γ /°	74.29(2)	
<i>U</i> /Å ³	2618(2)	2322(2)
<i>Z</i>	4	2
<i>D_c</i> /g cm ⁻³	1.731	1.685
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	19.07	20.02
Data, restraints, parameters	9203, 0, 658	6690, 0, 291
<i>R</i> 1 ^a	0.0426,	0.0550
<i>wR</i> 2 ^b	0.0987	0.1782

^a $\sum||F_o| - |F_c||/\sum|F_o|$. ^b $\sum[(F_o)^2 - (F_c)^2]^2/\sum(F_o)^4$.

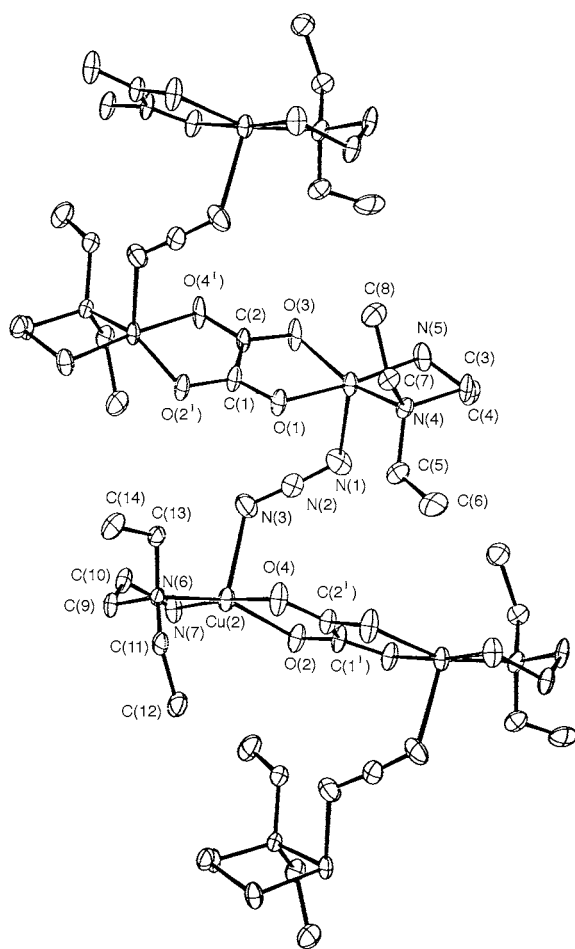


Fig. 3 An ORTEP drawing with the atom-labelling scheme for $[\{\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2\}_n][\text{ClO}_4]_n$ **2**

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–N₃–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 $[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-ox})(\text{deen})_2]^{2+}$

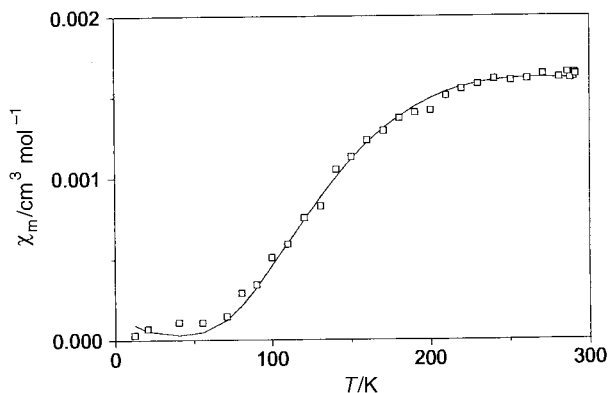


Fig. 4 Magnetic susceptibility plot of a polycrystalline sample of complex **1**. The solid line shows the best fit by the expression for the magnetic susceptibility of isotropically coupled $S = \frac{1}{2}$ ions in antiferromagnetic linear chains (see text)

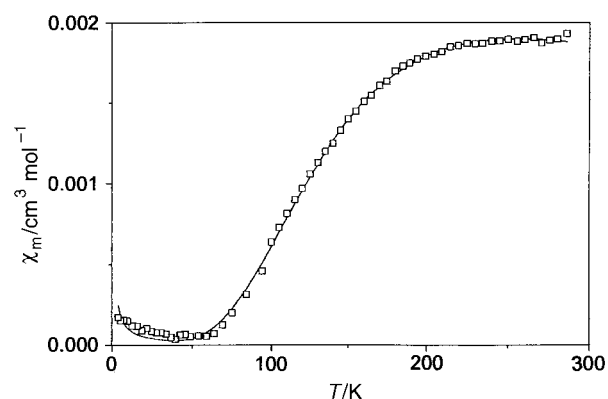


Fig. 5 Magnetic susceptibility plot of a polycrystalline sample of complex **2**. Details as in Fig. 4

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 $1.7 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ 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 $H = -JS_{\text{A}}S_{\text{B}}$, 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 $R = \sum_i (\chi_{i,\text{calc}} - \chi_{i,\text{obs}})^2 / (i - n)$, where *n* is the number of free parameters ($n = 3$). The results of the fit, shown as the solid line in Fig. 4, were $J = -300(3) \text{ cm}^{-1}$, $g = 2.15(1)$, $\rho = 0.0013(4)$ 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 $\text{Cu}(\text{C}_2\text{O}_4)\text{Cu}$ core¹³ and weaker than that evaluated for μ -oxalato-bridged dinuclear copper(II) complexes with a centrosymmetric $\text{Cu}(\text{C}_2\text{O}_4)\text{Cu}$ core ($-J = 330\text{--}402 \text{ cm}^{-1}$).^{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 ^H)	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 ^H)	1.989(3)
Cu(2)–O(4 ^f)	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 ^f)	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 ^H)	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 ^H)	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 ^f)–Cu(2)–O(2 ^f)	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 ^f)–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 $1.9 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ 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 $\text{Cu}(\text{N}_3)\text{Cu}$ 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 $\text{Cu}(1)\text{--N}_3\text{--Cu}(2)$ is 61.9° . In related dinuclear $[\text{Cu}(\mu\text{-N}_3)_2\text{Cu}]^{2+}$ compounds, $[\text{Cu}_2(\text{N}_3)_2(\text{pmdien})_2][\text{BPh}_4]_2$ (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–N₃–Cu torsion angle of 5.6° .¹⁶ $[\text{Cu}_2(\mu\text{-N}_3)_2(\text{N}_3)_2(\text{tmen})_2]$ 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 $[\text{Cu}_2(\text{N}_3)_2(\text{pmdien})_2][\text{BPh}_4]_2$ and the coupling constant corresponding to the apical azide bridging ligand in **2** can reasonably be expected to be very low. Moreover, the $\text{Cu}(1)\text{--N}_3\text{--Cu}(2)$ 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 $[\text{LCu}(\text{ox})\text{CuL}]^{2+}$ 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 suscepti-

bility 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 $J = -287(1) \text{ cm}^{-1}$, $g = 2.28(1)$, $\rho = 0.0010(1)$ with $R = 4.4 \times 10^{-8}$. The J value is very similar to that found for the hexanuclear $[\text{Cu}_6(\mu\text{-N}_3)_2(\mu\text{-ox})_3(\text{tmen})_6(\text{H}_2\text{O})_2][\text{ClO}_4]_2$ [$-289(2) \text{ cm}^{-1}$]⁵ and to that found for the starting compound **1**, but in **2** the $\text{Cu}(\text{C}_2\text{O}_4)\text{Cu}$ core is centrosymmetric. To check the validity of considering magnetically isolated $[\text{LCu}(\text{ox})\text{CuL}]^{2+}$ 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 Hatfield¹⁸ for an alternating ring chain of $n = 10$ local spins $\frac{1}{2}$, based on the spin Hamiltonian $H = \mathcal{J} \sum_i |S_{2i} \cdot S_{2i-1} + \alpha S_{2i} \cdot S_{2i+1}|$ 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, $J = -282(1) \text{ cm}^{-1}$, $g = 2.25(1)$, $\alpha = 0.001(1)$, 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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