DALTON

Synthesis, magnetic behaviour and structural characterization of the alternating hexanuclear copper(II) compound $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ (tmen = $Me_2NCH_2CH_2NMe_2$)

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The compound $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ **1** where tmen is *N,N,N′,N′*-tetramethylethane-1,2-diamine, was synthesized and characterized. Its crystal structure was determined by single-crystal X-ray analysis. The magnetic behaviour was recorded between 300 and 4 K, showing strong antiferromagnetic coupling. The magnetic susceptibility data were fitted by the expression for a dinuclear copper(II) compound giving the parameters $J = -289(2)$ cm^{-1}, $g = 2.03(1)$. Polycrystalline powder ESR spectra were recorded at variable temperature. The broad room-temperature signal having $g = 2.12$ vanished at approximately 55 K.

One-dimensional co-ordination compounds involving a repeated central atom and bridging ligand (generally homogeneous chains) are very numerous, but corresponding systems comprising a central atom and two different bridging ligands (alternating chains) are very scarce. Recently, we have designed a strategy for nickel(II) as central atom which uses as starting materials dinuclear $[(H_2O)(\text{triamine})Ni(C_2O_4)Ni(\text{triamine})(H_2O)]^{2+}$ compounds[1] in which the H_2O ligand can easily be replaced by a bridging azide ligand, thus constructing an alternating oxalate–azide nickel(II) chain.[2]

This scheme could perhaps be used for other central atoms such as copper(II). Habitually, copper(II) prefers a five-co-ordinate geometry and for this reason we have tried $[(H_2O)(tmen)Cu(C_2O_4)Cu(tmen)(H_2O)][ClO_4]_2\cdot 1.25H_2O$[3] (tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine) as starting material. Surprisingly, using the same synthesis procedure, not a one-dimensional but a hexanuclear compound was obtained, $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ **1**, where the H_2O ligands terminate the growth of the one-dimensional compound. Hexanuclear copper(II) compounds are not rare,[4–8] but the present one is an unusual example of a bridging alternating oligomer with a linear arrangement of copper atoms. From the structural parameters, the magnetic susceptibility of this compound can be analysed by considering isolated dinuclear $[LCu(C_2O_4)CuL]^{2+}$ entities: the coupling constant is $-289(2)$ cm^{-1}, with $g = 2.03(1)$. This value is lower than the $J = -385.4$ cm^{-1} found for the starting compound $[Cu_2(tmen)_2(C_2O_4)(H_2O)_2][ClO_4]_2\cdot 1.25H_2O$.[3]

Experimental

Synthesis

The complex $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ **1** was prepared by mixing copper(II) perchlorate hexahydrate (0.005 mol), *N,N,N′,N′*-tetramethylethane-1,2-diamine (0.005 mol), sodium oxalate (0.0025 mol) and sodium azide (0.0025 mol) in water (100 cm^3). From this solution blue monocrystals suitable for X-ray determination were collected after 2 weeks (yield *ca.* 55%) (Found: C, 27.1; H, 5.3; N, 13.1. Calc. for $C_{42}H_{104}Cl_4Cu_6N_{18}O_{32}$: C, 26.6; H, 5.5; N, 13.3%).

Spectral and magnetic measurements

Infrared spectra were recorded on a Nicolet 520 FT-IR spectrometer. Magnetic susceptibility measurements in the range 300–4 K were made on polycrystalline samples with an MPMS (5.5 T) Quantum Design instrument (with a SQUID detector). Diamagnetic corrections were estimated from Pascal's constants. The ESR spectra were recorded on a Bruker ES200 spectrometer at X-band frequency, with an Oxford liquid-helium cryostat for variable temperatures.

X-Ray crystallography

A prismatic blue crystal (0.1 × 0.1 × 0.2 mm) of complex **1** was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8 < \theta < 12°$) and refined by the least-squares method. Intensities were recorded with graphite-monochromatized Mo-Kα radiation (λ 0.710 69 Å) at 293(2) K. 22 819 Reflections were measured in the range $1.10 < \theta < 29.96°$, 7659 of which were assumed to be observed $[I > 2.5\sigma(I)]$. Three reflections were measured every 2 h as orientation and intensity control; no significant decay was observed. The crystallographic data, conditions used for the intensity-data collection, and some features of the structure refinement are listed in Table 1. Lorentz-polarization but not absorption corrections were made. The structure was solved by Patterson synthesis, using the SHELXS 86 computer program[9] and refined by full-matrix least squares on F^2, with the SHELXL 93 computer program,[10] using 15 343 reflections (very negative intensities were not employed). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$ where $w = [\sigma^2(I) + (0.1001P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Values of f, f' and f'' were taken from ref. 11. Maximum shift/e.s.d. = 0.18, mean shift/e.s.d. = 0.08. Maximum and minimum peaks in final difference synthesis 0.663 and -0.997 e Å^{-3}, respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Infrared spectrum

The IR spectrum of complex **1** shows bands corresponding to the azide ligand at 2052s cm^{-1}, a strong symmetric band at 1637 cm^{-1} due to the co-ordinated oxalate and bands at 1090s, 1130s and 624m cm^{-1} due to the perchlorate anions.

Crystal structure

The structure of $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ **1** consists of non-centrosymmetrical hexanuclear units $[(tmen)(H_2O)Cu(\mu\text{-}C_2O_4)Cu(tmen)(\mu\text{-}N_3)Cu(tmen)(\mu\text{-}C_2O_4)Cu(tmen)(\mu\text{-}N_3)Cu(tmen)(\mu\text{-}C_2O_4)Cu(tmen)(H_2O)]^{4+}$ isolated by ClO_4^- anions. The copper(II) atoms are bridged alternately by oxalate and azide ligands in an end-to-end fashion. An ORTEP[12] drawing with the atom-labelling scheme of the hexanuclear unit is shown in Fig. 1. The main bond lengths and angles are given in Table 2. The hexanuclear ensemble can be viewed as three dinuclear $[LCu(C_2O_4)CuL]^{2+}$, L = tmen, entities bridged by azide ligands. The central unit has the azide ligands *trans* but the two extreme ones have the azide ligand *cis* with respect to the water ligand, which points towards the central unit and ends the continuity as a one-dimensional compound. The six copper atoms are five-co-ordinated with a geometry approximating to a square pyramid. Since the hexanuclear unit is non-centrosymmetric, the Γ parameter ($\Gamma = 1$ for an ideal trigonal bipyramid, 0 for an ideal square pyramid),[13] is different for the six copper atoms: 0.21, 0.11, 0.003, 0.017, 0.13 and 0.24 for Cu(1) to Cu(6) respectively. The basal plane is formed by two O (oxalate) and two N (amine) atoms and the axial position is occupied by one N (azide) atom for Cu(2)–Cu(5) and one O (water) atom for Cu(1) and Cu(6). The Cu–N (azide) axial distances are 2.317(11), 2.197(11), 2.218(10) and 2.322(11) Å for Cu(2)–N(1), Cu(3)–N(3), Cu(4)–N(4) and Cu(5)–N(6) respectively. The Cu(1)–O(w1) and Cu(6)–O(w2) distances are 2.310(8) and 2.267(9) Å respectively. The structural parameters found for complex **1** are in the range of corresponding parameters for related dinuclear compounds $[Cu_2(tmen)_2(\mu\text{-}C_2O_4)(H_2O)_2][ClO_4]_2\cdot 1.25H_2O$[3] and $[Cu_2(tmen)_2(\mu\text{-}C_2O_4)(H_2O)_2][PF_6]_2$,[14] which have a 'chair' conformation.[15] The central dinuclear $(N_3)LCu(C_2O_4)CuL(N_3)$ unit in **1** also has the 'chair' conformation, but the two extreme dinuclear $(N_3)LCu(C_2O_4)CuL(H_2O)$ units have a 'boat' conformation due to the *cis* arrangement of the apical ligands.

Table 1 Crystal and structure refinement data for $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ **1**

Formula	$C_{42}H_{104}Cl_4Cu_6N_{18}O_{32}$
M	1896.4
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	7.993(7)
b/Å	18.558(2)
c/Å	26.656(2)
α/°	88.12(9)
β/°	83.03(2)
γ/°	89.14(4)
U/Å^3	3922(4)
Z	2
D_c/g cm^{-3}	1.602
μ(Mo-Kα)/cm^{-1}	18.22
Scan method	ω–2θ
No. parameters refined	1010
R[a]	0.059
*wR*2[b]	0.195

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

Magnetic results

The magnetic susceptibility χ_m of $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4\cdot 2H_2O$ is plotted *vs.* *T* in Fig. 2. The χ_m value per two copper atoms is 1.49×10^{-3} cm^3 mol^{-1} at room temperature, increasing slowly with decreasing temperature to a maximum of 1.51×10^{-3} cm^3 mol^{-1} at 270 K and then decreasing quickly reaching zero at approximately 50 K. This value slowly increases reaching a maximum of 7.1×10^{-4} cm^3 mol^{-1} at 4 K, indicating the presence of a small amount of paramagnetic impurity. The ESR spectra of polycrystalline

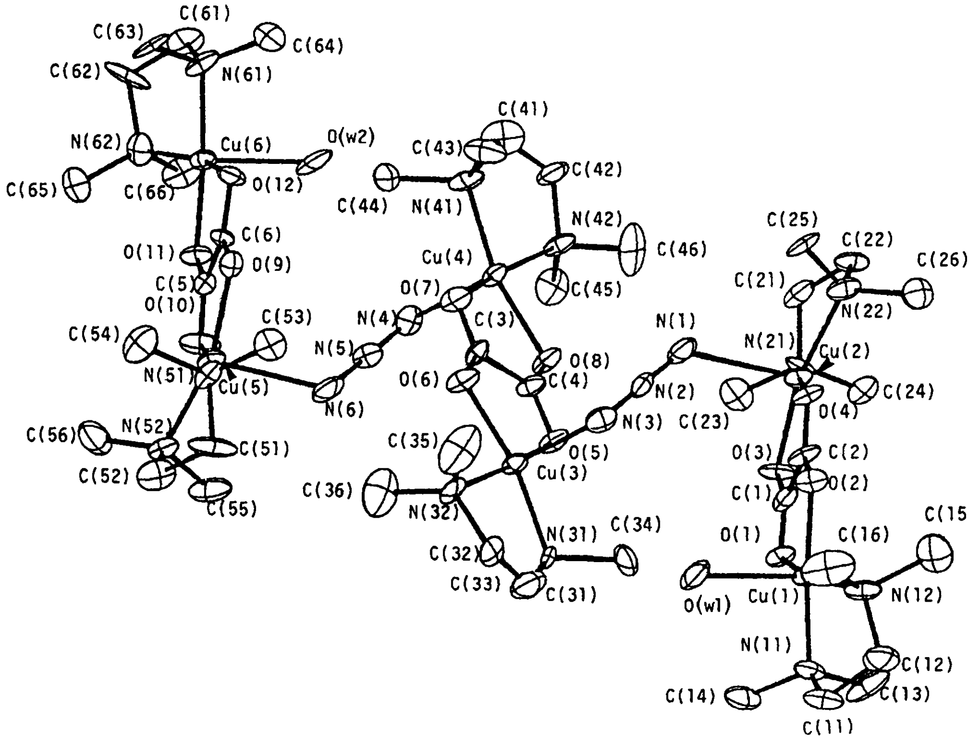

Fig. 1 An ORTEP drawing with the atom-labelling scheme of the hexanuclear unit $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2]^{4+}$

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

Cu(1)–O(2)	1.953(9)	Cu(3)–O(5)	2.023(7)	Cu(6)–O(11)	1.975(8)	O(7)–C(3)	1.253(13)
Cu(1)–O(1)	1.993(7)	Cu(3)–N(3)	2.197(11)	Cu(6)–O(12)	2.003(8)	O(8)–C(4)	1.242(13)
Cu(1)–N(11)	1.996(10)	Cu(4)–O(8)	2.020(8)	Cu(6)–N(61)	2.007(11)	C(3)–C(4)	1.547(10)
Cu(1)–N(12)	2.027(10)	Cu(4)–N(42)	2.020(9)	Cu(6)–N(62)	2.064(10)	O(9)–C(6)	1.261(12)
Cu(1)–O(w1)	2.310(8)	Cu(4)–N(41)	2.025(10)	Cu(6)–O(w2)	2.267(9)	O(10)–C(5)	1.246(13)
Cu(2)–O(3)	1.992(7)	Cu(4)–O(7)	2.050(8)	O(1)–C(1)	1.198(14)	O(11)–C(5)	1.270(13)
Cu(2)–N(22)	1.995(10)	Cu(4)–N(4)	2.218(10)	O(2)–C(2)	1.266(12)	O(12)–C(6)	1.285(13)
Cu(2)–O(4)	2.000(8)	Cu(5)–O(9)	1.982(9)	O(3)–C(1)	1.279(14)	C(5)–C(6)	1.55(2)
Cu(2)–N(21)	2.024(10)	Cu(5)–O(10)	1.987(7)	O(4)–C(2)	1.252(14)	N(1)–N(2)	1.154(14)
Cu(2)–N(1)	2.317(11)	Cu(5)–N(51)	1.999(8)	C(1)–C(2)	1.51(2)	N(2)–N(3)	1.168(13)
Cu(3)–N(32)	2.011(9)	Cu(5)–N(52)	2.051(11)	O(5)–C(4)	1.261(13)	N(4)–N(5)	1.186(13)
Cu(3)–O(6)	2.014(9)	Cu(5)–N(6)	2.322(11)	O(6)–C(3)	1.223(12)	N(5)–N(6)	1.144(14)
Cu(3)–N(31)	2.020(10)						

O(2)–Cu(1)–O(1)	83.5(3)	O(6)–Cu(3)–O(5)	82.3(3)	N(51)–Cu(5)–N(6)	94.2(4)	C(3)–O(7)–Cu(4)	111.7(7)
O(2)–Cu(1)–N(11)	175.1(4)	N(31)–Cu(3)–O(5)	92.5(4)	N(52)–Cu(5)–N(6)	102.2(4)	C(4)–O(8)–Cu(4)	111.8(7)
O(1)–Cu(1)–N(11)	94.7(4)	N(32)–Cu(3)–N(3)	100.8(4)	O(11)–Cu(6)–O(12)	86.0(3)	O(6)–C(3)–O(7)	126.6(10)
O(2)–Cu(1)–N(12)	92.7(4)	O(6)–Cu(3)–N(3)	95.1(4)	O(11)–Cu(6)–N(61)	173.8(4)	O(6)–C(3)–C(4)	117.6(8)
O(1)–Cu(1)–N(12)	161.9(4)	N(31)–Cu(3)–N(3)	100.8(4)	O(12)–Cu(6)–N(61)	92.7(4)	O(7)–C(3)–C(4)	115.8(7)
N(11)–Cu(1)–N(12)	87.6(4)	O(5)–Cu(3)–N(3)	94.3(4)	O(11)–Cu(6)–N(62)	90.2(4)	O(8)–C(4)–O(5)	126.4(10)
O(2)–Cu(1)–O(w1)	90.1(4)	O(8)–Cu(4)–N(42)	92.3(3)	O(12)–Cu(6)–N(62)	159.9(4)	O(8)–C(4)–C(3)	118.1(8)
O(1)–Cu(1)–O(w1)	96.6(3)	O(8)–Cu(4)–N(41)	162.1(4)	N(61)–Cu(6)–N(62)	89.0(5)	O(5)–C(4)–C(3)	115.4(8)
N(11)–Cu(1)–O(w1)	94.6(4)	N(42)–Cu(4)–N(41)	86.3(4)	O(11)–Cu(6)–O(w2)	91.3(4)	C(6)–O(9)–Cu(5)	110.6(7)
N(12)–Cu(1)–O(w1)	101.0(4)	O(8)–Cu(4)–O(7)	82.3(3)	O(12)–Cu(6)–O(w2)	94.8(4)	C(5)–O(10)–Cu(5)	110.7(7)
O(3)–Cu(2)–N(22)	166.6(4)	N(42)–Cu(4)–O(7)	162.0(4)	N(61)–Cu(6)–O(w2)	94.9(4)	C(5)–O(11)–Cu(6)	110.6(7)
O(3)–Cu(2)–O(4)	84.2(3)	N(41)–Cu(4)–O(7)	93.5(4)	N(62)–Cu(6)–O(w2)	105.0(4)	C(6)–O(12)–Cu(6)	108.6(7)
N(22)–Cu(2)–O(4)	91.9(4)	O(8)–Cu(4)–N(4)	94.4(4)	C(1)–O(1)–Cu(1)	111.8(8)	O(10)–C(5)–O(11)	126.1(11)
O(3)–Cu(2)–N(21)	93.7(3)	N(42)–Cu(4)–N(4)	100.8(4)	C(2)–O(2)–Cu(1)	110.3(7)	O(10)–C(5)–C(6)	117.1(10)
N(22)–Cu(2)–N(21)	88.7(4)	N(41)–Cu(4)–N(4)	103.4(5)	C(1)–O(3)–Cu(2)	110.1(7)	O(11)–C(5)–C(6)	116.8(10)
O(4)–Cu(2)–N(21)	173.2(4)	O(7)–Cu(4)–N(4)	96.7(4)	C(2)–O(4)–Cu(2)	110.1(7)	O(9)–C(6)–O(12)	126.2(10)
O(3)–Cu(2)–N(1)	93.1(4)	O(9)–Cu(5)–O(10)	84.9(3)	O(1)–C(1)–O(3)	126.3(12)	O(9)–C(6)–C(5)	116.4(10)
N(22)–Cu(2)–N(1)	100.0(5)	O(9)–Cu(5)–N(51)	95.1(4)	O(1)–C(1)–C(2)	116.8(11)	O(12)–C(6)–C(5)	117.3(9)
O(4)–Cu(2)–N(1)	92.3(4)	O(10)–Cu(5)–N(51)	172.1(4)	O(3)–C(1)–C(2)	116.9(11)	N(2)–N(1)–Cu(2)	120.9(10)
N(21)–Cu(2)–N(1)	94.2(4)	O(9)–Cu(5)–N(52)	164.0(4)	O(4)–C(2)–O(2)	124.9(11)	N(1)–N(2)–N(3)	178.2(14)
N(32)–Cu(3)–O(6)	92.7(4)	O(10)–Cu(5)–N(52)	91.5(4)	O(4)–C(2)–C(1)	117.9(10)	N(2)–N(3)–Cu(3)	123.6(9)
N(32)–Cu(3)–N(31)	88.2(4)	N(51)–Cu(5)–N(52)	86.4(4)	O(2)–C(2)–C(1)	116.9(11)	N(5)–N(4)–Cu(4)	119.9(8)
O(6)–Cu(3)–N(31)	163.6(4)	O(9)–Cu(5)–N(6)	93.6(4)	C(4)–O(5)–Cu(3)	112.1(6)	N(6)–N(5)–N(4)	178.2(13)
N(32)–Cu(3)–O(5)	164.5(4)	O(10)–Cu(5)–N(6)	93.7(4)	C(3)–O(6)–Cu(3)	112.6(7)	N(5)–N(6)–Cu(5)	122.6(10)

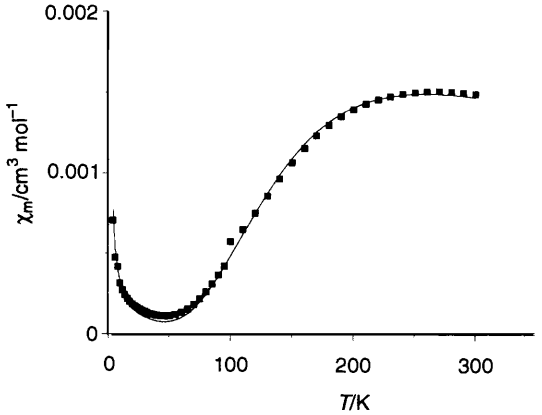

Fig. 2 Magnetic susceptibility of a polycrystalline sample of $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4{\cdot}2H_2O$. The solid line shows the best fit from the expression for the magnetic susceptibility of isotropically coupled $S = \frac{1}{2}$ ions in antiferromagnetic linear chains (see text)

samples of the new complex at X-band frequency were recorded at different temperatures from 280 to 4 K. At room temperature only a wide signal appears, centred at $g = 2.12$. Its intensity decreases with temperature and vanishes at approximately 55 K. At the same time the signal is split: at 77 K three signals are observed at $g_1 = 2.00$, $g_2 = 2.05$ and $g_3 = 2.15$.

The magnetic behaviour indicates a strongly antiferromagnetically coupled compound. To our knowledge there is no published expression for a linear alternating hexanuclear copper(II) compound, but we can suggest some approximations on the basis of the crystal structure: we can consider isolated $[LCu(C_2O_4)CuL]^{2+}$ dimers because in the two Cu–N$_3$–Cu bridges there are relatively long Cu–N (azide) distances: 2.317(11) and 2.322(11) Å for Cu(2)–N(1) and Cu(5)–N(6) respectively with short distances of 2.197(11) and 2.218(10) Å for Cu(3)–N(3) and Cu(4)–N(4) respectively. In related $[Cu(\mu\text{-}N_3)_2Cu]^{2+}$ compounds, $[Cu_2(pmdien)_2(N_3)_2][BPh_4]_2$ (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[16] and $[Cu_2(tmen)_2(\mu\text{-}N_3)_2(N_3)_2]$ is not magnetically coupled with a short and long Cu–N (azide) bond lengths in the bridges of 1.979(5) and 2.456(6) Å respectively.[17] The long Cu–N (azide) distances in **1** are intermediate between the same distances in $[Cu_2(pmdien)_2(N_3)_2][BPh_4]_2$ and $[Cu_2(tmen)_2(\mu\text{-}N_3)_2(N_3)_2]$: from the *J* values of these compounds the coupling constants corresponding to the azide bridging ligands in **1** can be reasonably expected to be negligible. With this consideration, the susceptibility data were fitted by the Bleaney–Bowers expression for the magnetic susceptibility of isotropically coupled dinuclear $S = \frac{1}{2}$ ions,[18] adding an impurity term τ, defined as the molar fraction of non-coupled species.[19] It is assumed that the impurity follows the Curie law and has the same molecular weight and the same *g* factor as those of compound **1**. The criterion of best fit was the minimum value of $R = \Sigma_i\,(\chi_i^{calc} - \chi_i^{obs})^2/(i - n)$, where *n* is the number of free parameters ($n = 3$). The results of the fit, shown as the solid line in Fig. 2, gave $J = -289(2)$ cm^{-1}, $g = 2.03(1)$ and $\tau = 0.0040(1)$ with $R = 4.73 \times 10^{-8}$. The assumption of uniform isolated dimers is an oversimplification in that the three dinuclear $[LCu(C_2O_4)CuL]^{2+}$ entities have different structural parameters, and, in the case of the central one, different axial ligands: the J and g values obtained are really mean values, but the calculation of the individual J and g parameters by fitting procedures is ambiguous and different sets of parameters may be given good fits. The found J value is lower than that of -385.4 cm^{-1} for the dinuclear starting compound $[(H_2O)(tmen)Cu(C_2O_4)Cu(tmen)(H_2O)][ClO_4]_2\cdot1.25H_2O$.[3] This lowering may be due to the transformation of the centrosymmetric $[(H_2O)(tmen)Cu(C_2O_4)Cu(tmen)(H_2O)][ClO_4]_2\cdot1.25H_2O$[3] units to the non-centrosymmeric $[LCu(C_2O_4)L]^{2+}$ units in **1**. The decrease in the antiferromagnetic contribution to the exchange interaction which results upon lowering of the symmetry has been studied by Kahn and co-workers[20–23] and proposed by Soto Tuero *et al.*[24] as responsible for the low J value of -284 cm^{-1} found in the non-centrosymmetric μ-oxalato binuclear copper(II) complex $[(mpym)(H_2O)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]\cdot H_2O$ [mpym = mepirizole, 4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine].

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