A Novel Type of Twisted Antiparallel Double-chain Structure with Stacking Between the Two Strands. Structure, Synthesis and Magnetic Properties of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ [L = 1*H*-1,2,4-triazole-3,5-dicarboxylate(3−), dien = 3-Azapentane-1,5-diamine]†

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The synthesis and structure of a completely new type of copper(II) polymer $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$, where L = 1*H*-1,2,4-triazole-3,5-dicarboxylate(3−) and dien = diethylenetriamine (1,4,7-triazaheptane), is reported. The compound crystallizes in the tetragonal space group $P\bar{4}2_1c$, with $a = b = 15.845(3)$, $c = 22.743(1)$ Å and $Z = 8$. Least-squares refinement of 818 reflections with $I > 2\sigma(I)$ and 174 parameters gave $R = 0.0694$, $R' = 0.0969$. The polymer is essentially a double chain, the building blocks of which are trinuclear copper(II) entities arranged zigzag clockwise and anticlockwise parallel to each other. The copper–copper distances within the trinuclear unit are Cu(1)···Cu(2) 5.937(4), Cu(1)···Cu(3) 4.014(6) and Cu(2)···Cu(3) 5.937(4) Å. The two strands of the chain are linked to each other by apical Cu–O bonds with Cu(2)···Cu(2′) 3.498(6) Å. The magnetic susceptibility data (5.8–284 K) are interpreted on the basis of an exchange Hamiltonian function giving J_1[Cu(1)–Cu(3)] = −30.0 cm⁻¹, J_2[Cu(2)–Cu(2′)] = −1.5 cm⁻¹ and g = 2.0. The nature and the strength of the antiferromagnetic exchange are discussed on the basis of the structural features, and compared with previously reported magneto-structural data for related copper(II) compounds with N^1,N^2- and N^1,N^4-linked 1,2,4-triazole ligands.

Chain-like structures are not unusual in chemistry. Well known examples are the double-helical structures of nucleic acids. The stability of nucleic acids originates from Watson and Crick-type hydrogen bonding between the two strands and stacking interactions between the aromatic bases along the strands, *i.e.* perpendicular to the chain direction. The amino acid sequence of proteins leads to the formation of α helices,[1,2] which can be further stabilized by transition-metal ions.[3-6] For example with iron(II) species as peptide side-chain 'cross-linking' agents even triple-stranded helices of proteins have been obtained.[7-9] The formation of helices is also known with conjugated polydentate ligands such as poly(bipyridine),[10] poly(biphenanthroline)[10,11] and hexapyridine ligands.[12,13] In combination with transition-metal ions the spontaneous assembly of double-helical complexes may occur. Recently, it has been found that even with the small oxygen-donating oxalate ligand interlocked helical chains can be formed with copper(II)[14]

The trianion 1*H*-1,2,4-triazole-3,5-dicarboxylate appears to be an ideal ligand with which to obtain polynuclear copper(II) compounds, since seven O and N donor atoms are available for co-ordination. Furthermore, the ligand is not always triply deprotonated. Moreover, 1,2,4-triazole ligands are known to link metal ions, either *via* N^1,N^2 [15-21] or N^1,N^4.[22] The N^1,N^2 bridging mode is most frequently observed and single,[15-17] double[18-20] and even triple[21] ligand bridges between copper(II) ions have been found and magneto-structural relations established. The compound $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ [L = 1*H*-1,2,4-triazole-3,5-dicarboxylate (3−) and dien = diethylenetriamine (3-azapentane-1,5-diamine)] contains the 1,2,4-triazoles in both didentate co-ordination modes. Its structure represents a completely new type of inorganic double-chain structure, with strong stacking interactions between the two strands and stacking parallel to the chain. This paper describes the synthesis and structure of this unusual compound together with its magnetic properties.

Experimental

Materials and Measurements.—Commercially available solvents, glycolic acid, hydrazine hydrate and copper(II) perchlorate hexahydrate were used without further purification. Elemental analyses (C, H, N and Cu) were performed by the Microanalytical Laboratory of University College, Dublin. The UV/VIS spectra were recorded on a Perkin Elmer 330 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference, and X-band EPR spectra on a JEOL RE2x electron spin resonance spectrometer. Magnetic susceptibilities were measured in the temperature range 5.8–284 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnetic, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. Magnetic data were fitted to theoretical expressions by means of a Simplex routine.[23]

Synthesis of the Potassium 1H-1,2,4-*Triazole*-3,5-*dicarboxylate*(1 −).—The potassium salt $KH_2L\cdot H_2O$ was synthesized by standard basic potassium permanganate oxidation of 3,5-bis(hydroxymethyl)-1*H*-1,2,4-triazole with work-up as described previously.[24] 3,5-Bis(hydroxymethyl)-1*H*-1,2,4-triazole was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non SI unit employed: emu (cm³) = 10⁶/4π SI (m³)

Table 1 Crystal data and details of the structure determination for $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$

Empirical formula	$C_{12}H_{23}Cu_3N_9O_{13}$
M	692.1
Crystal system	Tetragonal
Space group	$P\bar{4}2_1c$
a/Å	15.845(3)
b/Å	15.845(3)
c/Å	22.743(1)
$\alpha = \beta = \gamma$/°	90
U/Å^3	5709.9
Z	8 (trinuclear unit)
D_m/g cm^{-3}	1.69
D_c/g cm^{-3}	1.61
F(000)	2792
μ(Mo-Kα)/cm^{-1}	24.0
λ/Å	0.710 73 (Mo-Kα)
Transmission factors	0.732–0.822
Crystal size/mm	0.2 × 0.2 × 0.3
Temperature/K	298
Scan type	ω–2θ
Min., max. 2θ/°	2, 22
Scan width/°	1.00 + 1.00 tanθ
Number of measured reflections	4212
Number of unique reflections [$I > 2\sigma(I)$]	818
Number of refined parameters	174
$R\ [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$	0.0694
$R'\ \{[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.0969 (total reflection set)
Weighting scheme	$1/[\sigma^2(F) + 0.0025F^2]$
S (goodness of fit)	1.9130
Min., max. residual density/e Å^{-3}	1.402, −1.135

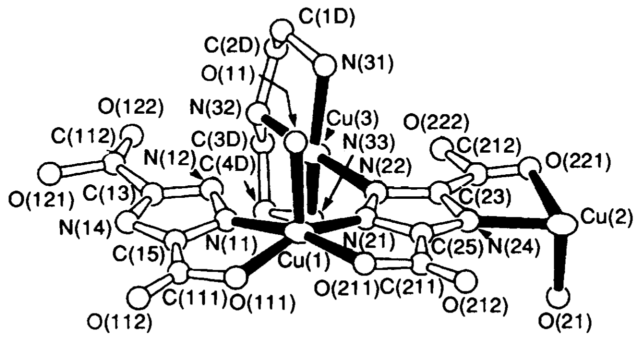

Fig. 1 An ORTEP[30] projection of the asymmetric unit of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ showing the atomic labelling

synthesized by standard deamination of 4-amino-3,5-bis(hydroxymethyl)-4*H*-1,2,4-triazole by sodium nitrite as described in the literature.[25] The amino compound was synthesized from glycolic acid and hydrazine.[26,27] The elemental analysis was consistent with the given formula (Found: C, 22.05; H, 2.25; N, 20.15. $C_4H_4KN_3O_5$ requires C, 22.55; H, 1.90; N, 19.70).

Synthesis of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$.—The copper(II) polymer was formed from a stirred slurry of KH_2LH_2O (1 mmol, 0.21 g) in water (40 cm^3) to which solid copper(II) perchloratehexahydrate (4 mmol, 1.4 g) was added. To the clear light blue reaction mixture was added dien (4 mmol, 0.41 g), dissolved in water (10 cm^3). The dark blue solution was filtered and blue crystals formed upon slow evaporation of the water at room temperature. UV/VIS: 15.4 × 10^{-3} cm^{-1} (asymmetric band). The elemental analysis was consistent with the given formula. Repeated preparations yielded essentially the same compound, differing only in the amount of solvent molecules incorporated in the crystal lattice.

Crystal Structure Determination and Refinement.—A clear light blue crystal of dimensions 0.2 × 0.2 × 0.3 mm was mounted in a Lindemann capillary. X-Ray data were collected at 298 K on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). Details of data collection and refinement are given in Table 1. The cell constants were determined from 25 reflections with $10 < \theta < 12°$. 4212 Reflections were collected of which 2079 were independent and 818 observed with $I > 2\sigma(I)$. Data were corrected for Lorentz and polarization effects and for anomalous scattering. An absorption correction was applied using Monte-Carlo methods.[28] The copper atoms were located by direct methods,[29] all non-hydrogen atoms by Fourier methods. Hydrogen atoms were fixed to their parent atoms at calculated positions that were positionally refined together with the corresponding non-hydrogen atoms. A unique common thermal parameter was refined for all hydrogens. Five lattice water molecules were located in the difference Fourier synthesis. Due to disorder four of these water molecules were given an occupancy of 0.5. Apart from the metal ions all atoms were isotropic. The refinement of the structure with a local least-squares program led to a final R value of 0.0694 and refinement with the complete data set yielded R' = 0.0969. All calculations were carried out on the Leiden University Computer (IBM 3083), using programs written or modified by Mrs. E. W. Rutten-Keulemans and Mr. R. A. G. de Graaff. Final atomic coordinates are given in Table 2. Bond distances and angles are listed in Tables 3 and 4. The illustrations were obtained using ORTEP.[30]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Description of the Structure.—Each double chain is a co-ordination polymer with crystallographically independent units (Fig. 1) consisting of the trinuclear copper(II) fragments $[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O$. Each copper(II) atom has a different co-ordination environment; Cu(1) is 0.25(1) Å from the least-squares plane formed by the triazole N^1 and carboxylate O atoms of two ligands L, and on the opposite side of the plane from the water molecule which occupies the apical position of the square pyramid, resulting in a Cu(1)(L-N^1,O)(L-$N^{1'}$,O')(H$_2$O) chromophore. The Cu(3) atom is attached to this unit as a dien chelate in which an N^2 atom of L occupies the fourth equatorial position of the approximately planar basal plane of the square pyramid. Another L N^2 is in the apical position at a relatively long distance [2.69(2) Å], forming a Cu(3)(dien)(L-N^2)(L-$N^{2'}$) chromophore. The basal planes of the Cu(1) and Cu(3) co-ordination pyramids form an angle of 90.5(6)° and the Cu(1) ··· Cu(3) distance is 4.014(6) Å. The 1,2,4-triazole N^1,N^2-bridging mode is quite well known in copper(II) co-ordination compounds.[15–21] Although in these cases a symmetric double triazole bridge is formed with Cu–N(triazole) distances in the range 1.936–2.087 Å, the Cu ··· Cu distances are in the same range. The Cu(2) atom is linked to this fragment *via* N(24) of the triazole ligand and a carboxylate O and is in a distorted octahedral environment with two triazole N^4 atoms, a carboxylato O and a water molecule occupying the equatorial positions and a second carboxylato O and a second water molecule (from another chain, see below) as axial ligands, yielding a Cu(2)(L-N^4,O)(L-$N^{4'}$,O')(H$_2$O)$_2$ chromophore. The equatorial plane forms angles of 112.2(8) and 127.6(5)° with the basal planes of the square pyramids around Cu(1) and Cu(3), respectively. The Cu(2) ··· Cu(1) and Cu(2) ··· Cu(3) distances are 5.937(4) and 5.906(5) Å, respectively, considerably shorter than those found for the N^2,N^4 triazole bridging mode in [Cu(tz)$_2$(NCS)$_2$] (tz = 1*H*-1,2,4-triazole) (Cu ··· Cu 6.36 Å).[22] This is due to the shorter Cu(2)–N(24) distance [2.03(2) Å compared to 2.477(2) Å in the latter compound[22]] and the

Table 2 Final atomic coordinates for the non-hydrogen atoms of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.3614(2)	−0.0042(3)	0.6292(1)	C(25)	0.394(2)	0.026(2)	0.743(1)
Cu(2)	0.4268(3)	0.0826(3)	0.8790(1)	C(211)	0.376(2)	−0.060(2)	0.745(2)
Cu(3)	0.4288(3)	0.2391(3)	0.6434(1)	O(211)	0.3471(10)	−0.0855(10)	0.6902(6)
O(11)	0.0226(1)	0.028(1)	0.627(1)	O(212)	0.3641(12)	−0.1106(11)	0.7880(7)
N(11)	0.3989(16)	0.0621(17)	0.5597(10)	C(212)	0.458(2)	0.226(3)	0.801(2)
N(12)	0.4068(16)	0.1443(16)	0.5467(9)	O(221)	0.4510(14)	0.2277(14)	0.8492(9)
C(13)	0.4180(15)	0.1383(16)	0.4892(9)	O(222)	0.468(1)	0.289(2)	0.763(1)
N(14)	0.4011(13)	0.0739(14)	0.4641(7)	N(31)	0.307(2)	0.273(2)	0.653(1)
C(15)	0.397(2)	0.020(2)	0.510(1)	C(4D)	0.581(2)	0.305(2)	0.594(2)
C(111)	0.372(2)	−0.072(2)	0.513(1)	C(3D)	0.528(2)	0.370(2)	0.596(1)
O(111)	0.3606(15)	−0.0964(15)	0.5679(9)	N(32)	0.4401(15)	0.3403(15)	0.5917(10)
O(112)	0.3777(15)	−0.1184(15)	0.4752(8)	C(2D)	0.377(2)	0.397(2)	0.608(1)
C(112)	0.425(2)	0.224(2)	0.453(1)	C(1D)	0.302(2)	0.344(2)	0.617(2)
O(121)	0.4278(10)	0.1965(12)	0.3932(7)	N(33)	0.5516(14)	0.2389(14)	0.6413(10)
O(122)	0.4383(13)	0.2916(13)	0.4704(7)	O(1w)	0.209(3)	0.208(3)	0.449(2)
O(21)	0.5521(9)	0.0715(11)	0.8779(8)	O(2w)	0.251(3)	0.249(3)	0.287(2)
N(21)	0.3964(12)	0.0674(13)	0.6923(7)	O(3w)	0.432(2)	0.309(2)	0.299(1)
N(22)	0.4209(14)	0.1450(14)	0.7023(7)	O(4w)	0.049(3)	0.135(3)	0.274(2)
C(23)	0.431(2)	0.159(2)	0.763(1)	O(5w)	0.348(4)	0.331(4)	0.207(3)
N(24)	0.4186(15)	0.0725(15)	0.7901(8)				

Table 3 Bond distances (Å) for $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ with e.s.d.s in the last significant digits in parentheses*

Cu(1)···Cu(2)	5.937(4)	Cu(1)···Cu(3)	4.014(6)	N(11)–N(12)	1.34(3)	N(21)–N(22)	1.31(3)
Cu(1)···Cu(1′)	4.393(7)	Cu(1)···Cu(2′)	6.715(4)	N(12)–C(13)	1.32(3)	N(22)–C(23)	1.41(3)
Cu(1)···Cu(3′)	5.001(5)	Cu(2)···Cu(3)	5.906(5)	C(13)–N(14)	1.20(3)	C(23)–N(24)	1.51(3)
Cu(2)···Cu(2′)	3.498(6)	Cu(3)···Cu(3′)	7.734(5)	N(14)–C(15)	1.34(3)	N(24)–C(25)	1.35(3)
Cu(1)–N(11)	1.99(2)	Cu(1)–N(21)	1.91(2)	C(15)–N(11)	1.32(3)	C(25)–N(21)	1.33(3)
Cu(1)–O(11)	2.20(2)	Cu(1)–O(221)	1.91(2)	C(13)–C(112)	1.59(3)	C(23)–C(212)	1.43(4)
Cu(1)–O(111)	2.02(2)			C(112)–O(121)	1.43(3)	C(212)–O(221)	1.11(3)
Cu(2)–O(21)	1.99(2)	Cu(2)–O(21′)	2.46(2)	C(112)–O(122)	1.16(3)	C(212)–O(222)	1.33(4)
Cu(2)–N(24)	2.03(2)	Cu(2)–O(221)	2.43(2)	C(15)–C(111)	1.52(4)	C(25)–C(211)	1.39(4)
Cu(2)–O(121″)	1.99(2)	Cu(2)–N(14″)	1.95(2)	C(111)–O(111)	1.31(3)	C(211)–O(211)	1.40(3)
Cu(3)–N(22)	2.01(2)	Cu(3)–N(12)	2.69(2)	C(111)–O(112)	1.15(3)	C(211)–O(212)	1.27(4)
Cu(3)–N(31)	2.02(2)	Cu(3)–N(32)	2.00(2)	N(31)–C(1D)	1.38(4)	N(32)–C(3D)	1.47(3)
Cu(3)–N(33)	1.95(2)			C(1D)–C(2D)	1.48(4)	C(3D)–C(4D)	1.32(4)
				C(2D)–N(32)	1.40(3)	C(4D)–N(33)	1.57(3)

* Primed atoms are generated by the symmetry operation $1 - x, -y, z$, double primed atoms by $\frac{1}{2} - y, \frac{1}{2} - x, -\frac{1}{2} + z$.

Table 4 Bond angles (°) for $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ with e.s.d.s for the last significant digits in parentheses*

O(11)–Cu(1)–N(11)	98(1)	N(11)–Cu(1)–N(21)	101.3(7)	Cu(3)–N(12)–N(11)	112(2)	Cu(3)–N(22)–N(21)	127(1)
O(11)–Cu(1)–O(111)	98.4(9)	N(11)–Cu(1)–O(211)	166.1(9)	Cu(3)–N(12)–C(13)	146(2)	Cu(3)–N(22)–C(23)	122(2)
O(11)–Cu(1)–N(21)	99.3(9)	O(111)–Cu(1)–N(21)	161.7(9)	Cu(3)–N(31)–C(1D)	102(3)	Cu(3)–N(32)–C(2D)	107(2)
O(11)–Cu(1)–O(211)	93.5(8)	O(111)–Cu(1)–O(211)	90.8(7)	Cu(3)–N(32)–C(3D)	108(2)	Cu(3)–N(33)–C(4D)	108(2)
N(11)–Cu(1)–O(111)	80.5(9)	N(21)–Cu(1)–O(211)	83.7(7)	N(11)–N(12)–C(13)	99(2)	N(21)–N(22)–C(23)	110(2)
O(21)–Cu(2)–N(24)	92.5(9)	N(24)–Cu(2)–O(21′)	85.5(8)	N(12)–C(13)–N(14)	120(2)	N(22)–C(23)–N(24)	104(2)
O(21)–Cu(2)–O(221)	85.6(7)	N(24)–Cu(2)–N(14″)	175.0(8)	C(13)–N(14)–C(15)	100(2)	C(23)–N(24)–C(25)	102(2)
O(21)–Cu(2)–O(21′)	77.1(6)	N(24)–Cu(2)–O(121″)	95.3(8)	N(14)–C(15)–N(11)	111(3)	N(24)–C(25)–N(21)	114(2)
O(21)–Cu(2)–N(14″)	91.7(9)	O(221)–Cu(2)–O(21′)	156.1(7)	C(15)–N(11)–N(12)	107(2)	C(25)–N(21)–N(22)	109(2)
O(21)–Cu(2)–O(121″)	166.9(7)	O(221)–Cu(2)–N(14″)	98.8(8)	N(11)–C(15)–C(111)	116(3)	N(21)–C(25)–C(211)	121(3)
N(24)–Cu(2)–O(221)	78.8(8)	O(221)–Cu(2)–O(121″)	106.2(7)	N(14)–C(15)–C(111)	132(3)	N(24)–C(25)–C(211)	124(3)
N(12)–Cu(3)–N(22)	97.0(7)	N(22)–Cu(3)–N(32)	174.2(9)	C(15)–C(111)–O(111)	112(2)	C(25)–C(211)–O(211)	108(3)
N(12)–Cu(3)–N(31)	96.4(9)	N(22)–Cu(3)–N(33)	94.4(9)	C(15)–C(111)–O(112)	124(3)	C(25)–C(211)–O(212)	133(3)
N(12)–Cu(3)–N(32)	88.8(8)	N(31)–Cu(3)–N(32)	86(1)	O(111)–C(111)–O(112)	122(3)	O(211)–C(211)–O(212)	117(3)
N(12)–Cu(3)–N(33)	96.3(9)	N(31)–Cu(3)–N(33)	164(1)	N(12)–C(13)–C(112)	117(2)	N(22)–C(23)–C(212)	138(3)
N(22)–Cu(3)–N(31)	94(1)	N(32)–Cu(3)–N(33)	84(1)	N(14)–C(13)–C(112)	120(2)	N(24)–C(23)–C(212)	118(2)
Cu(1)–N(11)–N(12)	136(2)	Cu(1)–N(21)–N(22)	141(1)	C(13)–C(112)–O(121)	104(2)	C(23)–C(212)–O(221)	126(4)
Cu(1)–N(11)–C(15)	115(2)	Cu(1)–N(21)–C(25)	111(2)	C(13)–C(112)–O(122)	129(2)	C(23)–C(212)–O(222)	102(3)
Cu(1)–O(111)–C(111)	116(2)	Cu(1)–O(211)–C(211)	115(2)	O(121)–C(112)–O(112)	127(2)	O(221)–C(212)–O(222)	129(4)
Cu(2)–O(21)–Cu(2′)	102.9(6)			N(31)–C(1D)–C(2D)	120(4)	N(32)–C(3D)–C(4D)	111(3)
Cu(2″)–N(14)–C(13)	117(2)	Cu(2)–N(24)–C(23)	109(2)	C(1D)–C(2D)–N(32)	104(3)	C(3D)–C(4D)–N(33)	108(3)
Cu(2″)–N(14)–C(15)	140(2)	Cu(2)–N(24)–C(25)	148(2)	C(2D)–N(32)–C(3D)	117(2)		
Cu(2″)–O(121)–C(112)	117(2)	Cu(2)–O(211)–C(212)	106(3)				

* Primed atoms are generated by the symmetry operation $1 - x, -y, z$; double primed atoms by $\frac{1}{2} - y, \frac{1}{2} - x, -\frac{1}{2} + z$.

chelating effect of the carboxylate groups. The least-squares planes through the two ligands L in one asymmetric unit form an angle of 10.4(4)°.

The trinuclear copper(II) units are linked together in zigzag chains (Figs. 2 and 3); upon each addition of a trinuclear fragment to the chain the least-squares planes through the

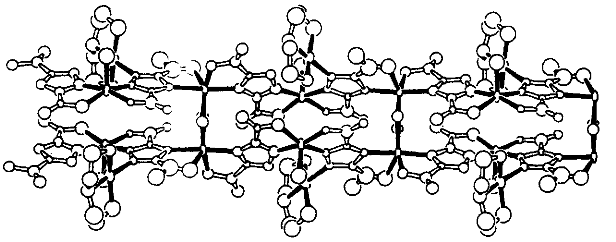

Fig. 2 An ORTEP[30] projection of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot3H_2O\}_\infty]$ showing the twisted antiparallel double chain structure

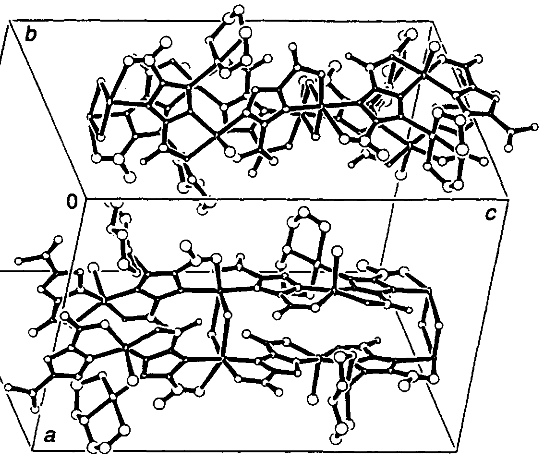

Fig. 3 An ORTEP[30] projection of the unit cell of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot3H_2O\}_\infty]$

Table 5 Interatomic distances (Å) for the hydrogen-bonding interactions in $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot3H_2O\}_\infty]$ with e.s.d.s for the last significant digits in parentheses*

O(11)···O(4w^{i})*	2.95(5)	O(122)···N(32)	2.86(3)
O(11)···O(5w^{ii})*	2.82(7)	O(2w)···O(5w)	2.72(8)
O(11)···O(211)	3.00(3)	O(3w)···O(5w)	2.51(6)
O(21^{iii})*···O(112)	2.58(3)	O(3w)···O(4w^{v})*	2.66(6)
O(21)···O(212^{iv})*	2.52(2)	O(3w)···O(121)	2.78(4)
O(21)···O(21^{iv})*	2.80(3)		

* Atoms generated by symmetry operations: i, $y, -x, 1 - z$; ii, $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} + z$; iii, $\frac{1}{2} - y, \frac{1}{2} - x, -\frac{1}{2} + z$; iv, $1 - x, -y, z$; v, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

two ligands L with symmetry operations (x,y,z) and $(\frac{1}{2} - y, \frac{1}{2} - x, -\frac{1}{2} + z)$ form an angle of 116.2(2)°. By addition of the next unit the chain continues in a backward twist. The zigzag chains are strongly linked together in pairs by stacking interactions between the ligands L; the mean distance between the least-squares planes of two ligands in different chains is 3.45 Å. In this way a ladder-like double chain is formed. In addition, two water molecules asymmetrically bridge the Cu(2) ions forming planar bridging $Cu(2)(H_2O)_2Cu(2')$ units with Cu(2)–O(21) 1.99(2), Cu(2)–O(21') 2.46(2) Å and Cu(2)–O(21)–Cu(2') 102.9(6)°. The distance between these Cu(2) atoms is 3.498(6) Å, which is in fact the shortest metal–metal distance found in this structure.

The double-chain structure is further stabilized by several hydrogen-bonding interactions. Short O···O and O···N contacts are summarized in Table 5. Although the hydrogen atoms could not be localized it is clear that there is hydrogen bonding from O(11) of the co-ordinating water molecule to the lattice water molecules, which themselves are involved in hydrogen bonding with other lattice water molecules. The other co-ordinating water molecule [O(21)] has short O···O contacts with the carboxylate groups of two different ligands L. The ligand oxygen O(122) appears to be involved in hydrogen bonding with N(31) of dien; van der Waals interactions complete the packing between the double chains.

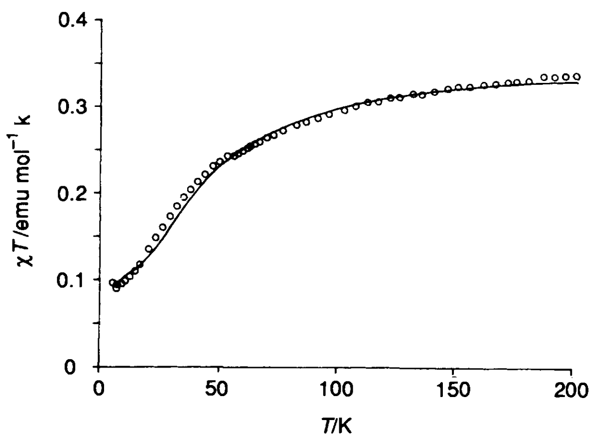

Fig. 4 A plot of χT *vs.* T for $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot3H_2O\}_\infty]$. The solid line represents the calculated curve $\{J_1[Cu(1)–Cu(3)] = -30.0$ cm^{-1}, $J_2[Cu(2)–Cu(2')] = -1.5$ cm^{-1} and $g = 2.0\}$

In summary the compound, which has a unique twisted antiparallel double-chain structure, self assembles starting from small nitrogen and oxygen donating ligands. The triazole L provides a large number of co-ordination modes, leading to a penta- and a hexa-dentate *N,O*-donating ligand. The dien ligand apparently blocks the formation of a three-dimensional network, by allowing chain growth only in the z direction.

EPR Spectra and Magnetic Properties.—The X-band EPR spectra recorded at 77 and 298 K show a featureless isotropic signal at $g = 2.06$. No fine splittings are resolved due to the close proximity of the Cu^{II} ions in the lattice.

The magnetic behaviour is shown in Fig. 4 by a plot of χT *vs.* T where χT is the magnetic susceptibility per copper(II) ion and T the temperature. At 284 K $\chi T = 0.323$ emu mol^{-1} K, which is about the value expected for a single, uncoupled copper(II) ion. The value of χT decreases upon cooling, reaching a value of 0.095 emu mol^{-1} K at 5.8 K. This behaviour is characteristic of compounds with an overall antiferromagnetic interaction between the metal ions, which is also illustrated by the θ value of −43 K obtained from the $1/\chi$ *vs.* T plot $(\chi_m^\infty\ 1/(T - \theta))$. In order to interpret the magnetic data the possible magnetic exchange pathways must be examined. Fig. 5 shows schematically the possible magnetic interactions between four pairs of copper(II) ions. At a first approximation the interaction between the pairs Cu(1), Cu(2) and Cu(2), Cu(3) can be ruled out, since the study of $[Cu(tz)_2(NCS)_2]$[22] has shown that the magnetic exchange *via* a single N^2,N^4 triazole bridge is very small. However, magnetic interaction *via* a single N^1,N^2 triazole bridge can be moderately strong.[15] Thus a reasonable antiferromagnetic coupling can be expected between Cu(1) and Cu(3), although the magnetic orbitals on these copper(II) ions are almost orthogonal. Since the magnetic orbitals on both copper(II) ions are pointing towards the co-ordinating triazole nitrogen atoms, a considerable electron delocalization may occur over these nitrogens and magnetic superexchange interaction is possible *via* mainly the σ orbitals of the triazole ligand. The interaction between Cu(2) and Cu(2') is estimated to be quite weak. The spin Hamiltonian (1) describes the magnetic properties; where $\hat{S}_{Cu1}$, $\hat{S}_{Cu2}$, $\hat{S}_{Cu2'}$ and $\hat{S}_{Cu2'}$ are

$$\hat{H} = \tfrac{2}{3}[-2J_1\hat{S}_{Cu1}\cdot\hat{S}_{Cu3}] + \tfrac{1}{3}[-2J_2\hat{S}_{Cu2}\cdot\hat{S}_{Cu2'}] \quad (1)$$

quantum spin operators and $2J_1$ and $2J_2$ are the singlet–triplet energy gaps for the two interaction pathways. The expression (2) for the magnetic susceptibility derived from (1) takes the form of a summation of two Bleaney–Bowers

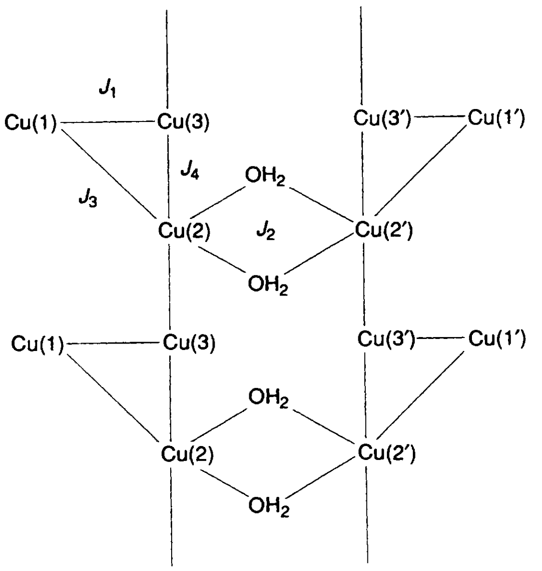

Fig. 5 Graphic representation of the model describing the magnetic properties of $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$

equations[31] describing the magnetic interaction in two different

$$\chi_m = \tfrac{2}{3}(2N\beta^2g^2/kT)[3 + \exp(-2J_1/kT)]^{-1} + \tfrac{1}{3}(2N\beta^2g^2/kT)[3 + \exp(-2J_2/kT)]^{-1} \quad (2)$$

$S = \frac{1}{2}$ dimers, where N, g, β, k and T have their usual meaning. The g-tensors for all individual metal ions are assumed to be equal. A very good fit has been obtained for the parameters J_1[Cu(1)–Cu(3)] (-30.0 cm^{-1}), J_2[Cu(2)–Cu(2′)] (-1.5 cm^{-1}) and g (2.0) (see Fig. 4). The exchange coupling constant J_1[Cu(1)–Cu(3)] is comparable with the J value of -34.5 cm^{-1} found for $[Cu(abpt)_2(SO_4)_2(H_2O)_4]\cdot H_2O_4$ [abpt = 4-amino-3,5-bis(pyridine-2-yl)-4*H*-1,2,4-triazole],[15] which is the only known dinuclear copper(II) compound with a single N^1,N^2 1,2,4-triazole bridge. Here the magnetic orbitals on both copper(II) ions are approximately in the plane of the triazole ligand with a Cu(1) ··· Cu(2) distance of 4.415(1) Å.

Conclusion

The compound $[\{[Cu_3L_2(dien)(H_2O)_2]\cdot 3H_2O\}_\infty]$ has a unique twisted antiparallel double-chain structure, where stacking interactions in combination with an asymmetric double aqua bridge between copper(II) ions and an important hydrogen-bonding network maintain the single chains. Magneto-structural correlations for 1,2,4-triazole bridged copper(II) compounds were used to interpret the magnetic data of the coordination polymer.

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