Crystal Structure and Magnetic Properties of the Alternating Chain $[Cu_2(cdta)]\cdot 4H_2O$†

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The crystal structure of the complex $[Cu(OH_2)_4][Cu(cdta)]$ (cdta = cyclohexane-1,2-diamine-*NNN′N′*-tetra-acetate) has been determined by *X*-ray methods. It crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ in a cell of dimensions $a = 10.863(3)$, $b = 12.074(4)$, and $c = 14.802(6)$ Å. Least-squares refinement of 1 281 reflections $[I > 2.5\sigma(I)]$ and 272 parameters gave a final $R = 0.039$. The complex exhibits a chain arrangement built up from alternating 'hydrated' and 'chelated' octahedral sites bridged by carboxylate groups. The ferrodistortive one-dimensional structural order observed arises from a co-operative Jahn–Teller effect between the two copper(II) co-ordination polyhedra. Magnetic susceptibility measurements, in the temperature range 4—50 K, are discussed in terms of a Heisenberg model involving alternating *g* values, the best yielding an antiferromagnetic exchange interaction of $J = -1.1$ cm^{-1}. Such a value is consistent with the proposed exchange mechanism.

The simplest class of one-dimensional magnetic systems are the linear spin $S = \frac{1}{2}$ chains built up by identical interacting magnetic sites. In co-ordination chemistry there are many examples of such systems.[1,2] Their experimental magnetic behaviour down to very low temperatures may be analyzed in terms of models involving two parameters: Landé factor (g), characterizing the magnetic site; exchange coupling (J) between nearest neighbours. The periodic variation of the distances between the magnetic sites results in a chain system with alternating J values which has been widely investigated both theoretically and experimentally.[2] In the 'design' of new one-dimensional materials these parameters should be correlated with structural and chemical data. In order to isolate a system with alternating g values it is necessary to construct a chain with two distinct environments for the paramagnetic ions. Recently we have shown[3,4] that an alternation of environments can be achieved by the interaction of a cationic site with an anionic one. When the two environments are occupied selectively by two different metal ions, this strategy allows the isolation of bimetallic ordered chains.[3,5] In such systems the non-compensation between the magnetic moments of the two sublattices results in one-dimensional ferromagnetic behaviour.[6-8]

In this paper we report the structure and magnetic behaviour of the compound $[Cu(OH_2)_4][Cu(cdta)]$ (cdta = cyclohexane-1,2-diamine-*NNN′N′*-tetra-acetate) which exhibits two copper(II) sites: an anionic 'chelated' site, formulated as $[Cu(cdta)]^{2-}$, and a cationic 'hydrated' one, formulated as $[Cu(OH_2)_4O_2]^{2+}$.

Experimental

Preparation.—The compound was prepared by reaction between aqueous solutions of $Cu(NO_3)_2\cdot 4H_2O$ and the tetrasodium salt of cdta in the molar ratio 2:1. Upon slow addition of propanone a light blue precipitate was formed. Refrigeration of the filtrate yielded well formed blue crystals. The microanalysis of both the precipitate and crystals gave the same results (Found: C, 30.0; H, 4.9; Cu, 23.1; N, 5.4. $C_{14}H_{26}Cu_2N_2O_{12}$ requires C, 31.0; H, 4.8; Cu, 23.5; N, 5.2%).

Table 1. Crystallographic data for $[Cu(OH_2)_4][Cu(cdta)]$

Crystal parameters

Formula	$C_{14}H_{26}Cu_2N_2O_{12}$	Z	4
M	541.4	D_c	1.84 Mg m^{-3}
a/Å	10.863(3)	D_m	1.83(1) Mg m^{-3}
b/Å	12.074(4)	U/Å^3	1 941.8
c/Å	14.802(6)	$F(000)$	1 112
Space group $P2_12_12_1$			

Measurement of intensity data

Radiation	Mo-K_α, $\lambda = 0.709\ 26$ Å
Reflections measured	$0 < h < 11$, $0 < k < 13$, $-16 < l < 16$
2θ Range/°	$1 < 2\theta < 47$
Standard reflections	$[0\bar{1}\bar{2}]$, $[\bar{1}\bar{2}\bar{5}]$, $[\bar{1}\bar{6}0]$

Crystallography.—The crystal data are summarized in Table 1. A well formed blue crystal with dimensions 0.12 × 0.15 × 0.08 mm was selected and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. The cell dimensions were derived from least-squares refinement of 23 well centered reflections ($7 < 2\theta < 43°$). Data collection showed systematic absences ($h00$, h odd; $0k0$, k odd; $00l$, l odd) which uniquely define orthorhombic space group $P2_12_12_1$. Examination of three standard reflections, monitored every hour, showed no substantial variations. 3 258 Intensity data were measured (ω—2θ scans) of which 1 281 unique intensities with $I > 2.5\sigma(I)$ were considered observed and used in the determination and refinement of the structure. Lorentz and polarization corrections were applied, but not for absorption, $\mu(\text{Mo-}K_\alpha) = 22.62$ cm^{-1}.

The positions of two copper and nine non-hydrogen atoms were determined by direct methods (MULTAN 11/82[9]). The remaining atoms were located from successive Fourier syntheses. The model obtained was refined with the SHELX 76

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† Tetra-aquacopper(II) (cyclohexane-1,2-diamine-*NNN′N′*-tetra-acetato)cuprate(II).

Supplementary data available (No. SUP 56539, 3 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 2. Fractional co-ordinates (H × 10^3, others × 10^4) for $[Cu(OH_2)_4][Cu(cdta)]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	3 525(1)	3 964(1)	7 083(1)
Cu(2)	8 604(1)	4 654(1)	6 704(1)
N(10)	3 997(6)	3 856(6)	5 782(5)
N(20)	3 408(7)	5 637(6)	6 958(5)
O(1)	9 036(6)	4 786(7)	5 414(5)
O(2)	7 402(7)	6 256(6)	6 508(5)
O(3)	7 950(6)	4 492(6)	7 955(5)
O(4)	9 811(7)	2 443(7)	6 708(6)
O(11)	3 213(6)	2 364(5)	6 952(4)
O(12)	2 577(6)	1 195(6)	5 902(4)
O(21)	3 456(7)	4 228(5)	8 384(4)
O(22)	4 032(6)	5 560(6)	9 350(4)
O(31)	5 729(6)	4 026(6)	7 210(4)
O(32)	7 271(6)	3 756(6)	6 222(4)
O(41)	1 412(7)	4 180(5)	6 744(5)
O(42)	10 051(6)	5 511(6)	7 063(5)
C(10)	3 824(9)	5 014(7)	5 380(6)
C(11)	3 160(8)	3 002(8)	5 408(6)
C(12)	2 974(8)	2 101(7)	6 136(6)
C(20)	4 143(8)	5 881(8)	6 106(6)
C(21)	4 055(8)	5 999(8)	7 799(7)
C(22)	3 829(8)	5 213(8)	8 579(6)
C(30)	4 056(10)	7 080(8)	5 770(7)
C(31)	5 290(8)	3 413(8)	5 690(6)
C(32)	6 137(7)	3 789(7)	6 434(6)
C(40)	4 804(11)	7 234(9)	4 913(8)
C(41)	2 118(9)	6 036(8)	6 942(8)
C(42)	1 146(8)	5 157(8)	6 930(6)
C(50)	4 385(10)	6 436(8)	4 209(7)
C(60)	4 505(10)	5 209(8)	4 515(6)
H(100)	285(5)	499(6)	533(5)
H(110)	332(5)	277(5)	489(4)
H(111)	244(5)	320(4)	537(5)
H(200)	508(6)	567(5)	618(4)
H(210)	352(4)	685(5)	794(6)
H(211)	487(5)	598(4)	771(5)
H(300)	307(4)	718(6)	566(5)
H(301)	433(4)	756(5)	634(6)
H(310)	560(6)	342(5)	501(4)
H(311)	527(4)	272(5)	574(5)
H(400)	582(4)	700(5)	502(4)
H(401)	477(5)	794(6)	471(5)
H(410)	197(4)	654(6)	752(4)
H(411)	201(6)	652(4)	633(5)
H(500)	465(5)	669(5)	365(5)
H(501)	341(4)	656(5)	414(6)
H(600)	554(5)	517(4)	462(6)
H(601)	416(4)	456(6)	400(5)

system[10] by weighted anisotropic full-matrix least squares to a *R* value of 0.045. After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, difference maps clearly indicated 14 H atoms of the cdta moiety. The co-ordinates of the four remaining H atoms of the ligand, H(300), H(301), H(410), and H(411), were calculated. The positions of the hydrogen atoms of the water molecules were difficult to calculate reliably, so they were omitted entirely. All these H atoms were included in the final refinement with common fixed isotropic thermal parameters (U = 0.0337 Å^2). The final *R* values were 0.039 and R' = 0.038 (272 parameters refined); $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + 0.00033 F_o^2]$ with $\sigma^2(F_o)$ from counting statistics.

Atomic scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref. 11. In the final difference map the residual maxima were less than 0.48 e Å^{-3}, except for one peak (0.63 e Å^{-3}) near the Cu(1) atom. The final positional parameters are given in Table 2.

Magnetic Measurements.—Magnetic susceptibility measurements were performed in the range 4—50 K by using a pendulum-type apparatus[12] equipped with a helium cryostat. The uncertainty in the data is less than 0.1 K for temperatures and 2 × 10^{-5} e.m. units mol^{-1} for susceptibilities (e.m. units = SI × $10^6/4\pi$). All magnetic measurements reported correspond to values corrected for the diamagnetic contribution estimated to be -281.5×10^{-6} e.m. units mol^{-1} from Pascal's tables.

Table 3. Hydrogen bonds in $[Cu(OH_2)_4][Cu(cdta)]$

A–B*	*d*	B–A–C*	Angle/°
$O(1)-O(12^{II})$	2.777(8)	$Cu(2^{I})-O(1)-O(12^{II})$	120.6(2)
$O(1)-O(22^{III})$	2.657(9)	$Cu(2^{I})-O(1)-O(22^{II})$	138.5(2)
		$O(12^{II})-O(1)-O(22^{III})$	88.2(3)
$O(2)-O(11^{IV})$	2.726(8)	$Cu(2^{I})-O(2)-O(11^{IV})$	115.9(2)
$O(3)-O(12^{IV})$	2.723(8)	$Cu(2^{I})-O(3)-O(12^{IV})$	125.3(2)
$O(3)-O(31^{I})$	2.712(8)	$Cu(2^{I})-O(3)-O(31^{I})$	87.7(2)
		$O(12^{IV})-O(3)-O(31^{I})$	102.9(3)
$O(4)-O(42^{V})$	2.962(9)	$Cu(2^{I})-O(4)-O(42^{V})$	136.9(2)

* The second atom (B or C) is related to the atom listed in Table 2 by the symmetry operations: I x,y,z; II $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; III $\frac{3}{2} - x, 1 - y, -\frac{1}{2} + z$; IV $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; V $2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$.

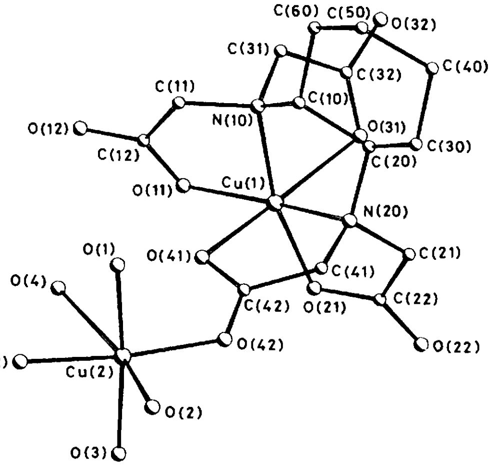

Figure 1. Perspective view and atomic numbering of $[Cu(OH_2)_4]$-$[Cu(cdta)]$

Results and Discussion

Crystal Structure.—Figure 1 shows a perspective view of the molecule and the atom numbering scheme and Figure 2 shows a stereoscopic view of the unit cell. The structure comprises infinite chains parallel to [100] built up by alternate anionic and cationic entities $[Cu(cdta)]^{2-}$ and $[trans\text{-}Cu(OH_2)_4O_IO_{II}]^{2+}$ (where O_I, O_{II} are oxygen atoms from carboxylate groups belonging to neighbouring anions). Adjacent chains interact only through van der Waals contacts and weak hydrogen bonds. Inter- and intra-chain oxygen–oxygen contacts short enough to be considered as corresponding to hydrogen bonds[13] are listed in Table 3. This kind of arrangement is similar to that found in the compounds $[cis\text{-}M(OH_2)_4O_IO_{II}][M'(edta)]\cdot 2H_2O$ (M = Mg, Mn, Co, Zn, or Ni; M′ = Co, Ni, Cu, or Zn;

edta^{4-} = ethylenediaminetetra-acetate).[3,14–17] Both copper(II) ions are six-co-ordinated: Cu(1), occupying the 'chelated' position, is bound to two nitrogen atoms and four oxygen atoms from the cdta ligand and Cu(2), which occupies the 'hydrated' position, is co-ordinated to four water molecules and two oxygen atoms belonging to bridging carboxylate groups from two adjacent [Cu(cdta)]$^{2-}$ entities. Interatomic distances and angles within the two co-ordination polyhedra and chelating ligand moiety are shown in Tables 4 and 5 respectively.

The co-ordination polyhedron around the Cu(1) atom can be described as a tetragonally elongated octahedron. The basal plane is comprised of the two nitrogen atoms and two oxygen atoms [O(11), O(21)] from type G carboxylates.[18] The Cu–N and Cu–O bond distances are normal and similar to those previously reported for this type of compound.[19] The axial sites are occupied by oxygen atoms belonging to type R carboxylates with Cu–O bonds significantly longer {$\bar{d}$[Cu(1)–O$_R$] = 2.383(9) Å} than the equatorial ones. The co-ordination of Cu(1) is then 4 + 2.[20] This kind of distortion is found habitually in six-co-ordinate copper(II) complexes, originating in the Jahn–Teller effect and modulated through crystal-packing forces and chelate effects.[20,21]

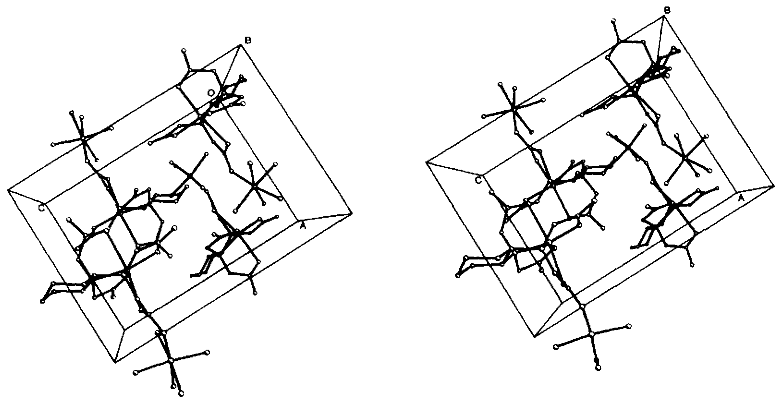

Figure 2. Stereoscopic view of the unit cell for [Cu(OH$_2$)$_4$][Cu(cdta)]

Table 4. Bond distances (Å) for non-H atoms in [Cu(OH$_2$)$_4$][Cu(cdta)] with e.s.d.s in parentheses

N(10)–Cu(1)	1.998(7)	C(12)–O(11)	1.276(10)
N(20)–Cu(1)	2.033(7)	C(12)–O(12)	1.226(10)
O(11)–Cu(1)	1.971(6)	C(22)–O(21)	1.289(10)
O(21)–Cu(1)	1.952(5)	C(22)–O(22)	1.236(10)
O(31)–Cu(1)	2.402(6)	C(32)–O(31)	1.263(10)
O(41)–Cu(1)	2.364(7)	C(32)–O(32)	1.272(10)
O(1)–Cu(2)	1.973(7)	C(42)–O(41)	1.244(10)
O(2)–Cu(2)	2.351(7)	C(42)–O(42)	1.280(10)
O(3)–Cu(2)	1.993(6)	C(20)–C(10)	1.540(12)
O(4)–Cu(2)	2.975(8)	C(60)–C(10)	1.497(12)
O(32)–Cu(2)	1.945(6)	C(12)–C(11)	1.544(12)
O(42)–Cu(2)	1.955(6)	C(30)–C(20)	1.535(12)
C(10)–N(10)	1.532(11)	C(22)–C(21)	1.515(13)
C(11)–N(10)	1.481(10)	C(40)–C(30)	1.518(14)
C(31)–N(10)	1.509(11)	C(32)–C(31)	1.506(12)
C(20)–N(20)	1.520(11)	C(50)–C(40)	1.491(15)
C(21)–N(20)	1.495(11)	C(42)–C(41)	1.497(12)
C(41)–N(20)	1.483(11)	C(60)–C(50)	1.554(13)

The cdta conformation is E,G/R, according to the classification established by Porai-Koshits,[22] in contrast with the *trans*-E or 'open' conformation observed for edta in the analogous compound [Cu$_2$(edta)]·4H$_2$O.[23] In the cdta compound the cyclohexane ring prevents full rotation of the two iminodiacetate segments of the ligand and these cannot face in opposite directions,[24] precluding the '*trans*-E' conformation. The angles and bond distances in the ligand are in general in agreement with those found in other cdta complexes.[25,26] The cyclohexane ring is in the chair form, its conformation being defined by the planes A[C(20)C(30)C(50)C(60)] [root mean

Table 5. Bond angles (°) in [Cu(OH$_2$)$_4$][Cu(cdta)] with e.s.d.s in parentheses

N(20)–Cu(1)–N(10)	89.6(3)	O(4)–Cu(2)–O(2)	169.5(2)	C(21)–N(20)–C(20)	112.8(6)	C(30)–C(20)–N(20)	114.7(7)
O(11)–Cu(1)–N(10)	83.4(3)	O(4)–Cu(2)–O(3)	93.8(3)	C(41)–N(20)–Cu(1)	112.5(5)	C(30)–C(20)–C(10)	113.7(7)
O(11)–Cu(1)–N(20)	162.6(3)	O(32)–Cu(2)–O(1)	82.4(3)	C(41)–N(20)–C(20)	114.9(7)	C(22)–C(21)–N(20)	112.1(7)
O(21)–Cu(1)–N(10)	166.2(3)	O(32)–Cu(2)–O(2)	90.0(3)	C(41)–N(20)–C(21)	111.2(7)	O(22)–C(22)–O(21)	125.2(9)
O(21)–Cu(1)–N(20)	85.7(3)	O(32)–Cu(2)–O(3)	91.2(3)	C(12)–O(11)–Cu(1)	111.8(5)	C(21)–C(22)–O(21)	117.3(7)
O(21)–Cu(1)–O(11)	104.5(3)	O(32)–Cu(2)–O(4)	80.1(2)	C(22)–O(21)–Cu(1)	111.1(5)	C(21)–C(22)–O(22)	117.5(8)
O(31)–Cu(1)–N(10)	79.7(2)	O(42)–Cu(2)–O(1)	91.7(3)	C(32)–O(31)–Cu(1)	105.8(5)	C(40)–C(30)–C(20)	110.7(8)
O(31)–Cu(1)–N(20)	92.2(3)	O(42)–Cu(2)–O(2)	92.6(3)	C(32)–O(32)–Cu(2)	127.8(6)	C(32)–C(31)–N(10)	113.3(7)
O(31)–Cu(1)–O(11)	102.1(2)	O(42)–Cu(2)–O(3)	94.9(3)	C(42)–O(41)–Cu(1)	106.4(6)	O(32)–C(32)–O(31)	124.9(7)
O(31)–Cu(1)–O(21)	87.5(3)	O(42)–Cu(2)–O(4)	96.9(2)	C(42)–O(42)–Cu(2)	121.9(6)	C(31)–C(32)–O(31)	121.3(7)
O(41)–Cu(1)–N(10)	92.9(2)	O(42)–Cu(2)–O(32)	173.4(3)	C(20)–C(10)–N(10)	108.8(6)	C(31)–C(32)–O(32)	113.6(7)
O(41)–Cu(1)–N(20)	79.0(3)	C(10)–N(10)–Cu(1)	106.5(5)	C(60)–C(10)–N(10)	114.5(7)	C(50)–C(40)–C(30)	110.0(8)
O(41)–Cu(1)–O(11)	85.4(2)	C(11)–N(10)–Cu(1)	104.4(5)	C(60)–C(10)–C(20)	112.2(7)	C(42)–C(41)–N(20)	115.8(7)
O(41)–Cu(1)–O(21)	98.8(3)	C(11)–N(10)–C(10)	114.5(6)	C(12)–C(11)–N(10)	108.1(6)	O(42)–C(42)–O(41)	124.5(8)
O(41)–Cu(1)–O(31)	168.7(2)	C(31)–N(10)–Cu(1)	110.4(5)	O(12)–C(12)–O(11)	124.1(8)	C(41)–C(42)–O(41)	120.7(8)
O(2)–Cu(2)–O(1)	86.9(3)	C(31)–N(10)–C(10)	113.8(6)	C(11)–C(12)–O(11)	117.3(7)	C(41)–C(42)–O(42)	114.6(8)
O(3)–Cu(2)–O(1)	172.8(3)	C(31)–N(10)–C(11)	106.9(6)	C(11)–C(12)–O(12)	118.5(7)	C(60)–C(50)–C(40)	112.7(8)
O(3)–Cu(2)–O(2)	89.8(2)	C(20)–N(20)–Cu(1)	103.6(5)	C(10)–C(20)–N(20)	109.2(7)	C(50)–C(60)–C(10)	111.0(8)
O(4)–Cu(2)–O(1)	88.2(3)	C(21)–N(20)–Cu(1)	100.6(5)				

Table 6. Mean asymmetry parameters of the unidentate and bridging CO_2 groups[a] and strain parameters of chelate rings for $[Cu(OH_2)_4][Cu(cdta)]$ and related compounds

	$\bar{\delta}$					d[M–O(bridging)]/Å		
Complex[b]	Unidentate	Bridging	t_E	$\bar{t}_G$	$\bar{t}_R$	M	M′	Ref.
$[Cu_2(cdta)]\cdot 4H_2O$	50	−23	−10.2	−13.0	−6.5	1.950	2.383	This work
$[ZnCu(cdta)]\cdot 6H_2O$	26	−11	−13.7	−14.7	−1.3	2.048	2.242	34
$[MnCu(edta)]\cdot 6H_2O$	14	−18	−13.5	−12.7	−2.1	2.149	2.252	16
$[Co_2(edta)]\cdot 6H_2O$	29	8	−13.8	−11.7	−2.6	2.095	2.105	15
$[Ni_2(edta)]\cdot 6H_2O$	25	30	−13.5	−13.3	−1.1	2.055	2.056	17

[a] The numbering of the atoms is equivalent for all the complexes. $10^{-3}\delta_i = d[C(i2)\text{–}O(i1)] - d[C(i2)\text{–}O(i2)]$ Å; $t = \sum_{i=1}^{5}(\alpha_i)_{obs.} - \sum_{i=1}^{5}(\alpha_i)_{ideal}$°. [b] The first listed (M) occupies the 'hydrated' site.

square deviation (r.m.s.d.) = 0.007 Å], B[C(30)C(40)C(50)], and C[C(10)C(20)C(60)]. The angles between planes A–B and A–C are 51.8 and 44.9° respectively, and the angular strain of the ring is low.

The carboxylate groups are all asymmetric, each showing two different C–O bond distances. In Table 6 we present the mean asymmetry parameter (δ), calculated as the difference between the two C–O bond distances for the bridging and unidentate carboxylate groups in the present compound and other edta and cdta bimetallic complexes. As expected, the absolute δ values of bidentate bridging carboxylate groups (of type a-2-a or a-2-s)[27] are generally smaller than for unidentate ones. On the other hand, the compounds having a copper occupying the 'chelated' position show δ values of opposite sign for the bridging COO_R and the unidentate COO_G. This inversion of the asymmetry is probably related to the Jahn-Teller effect and favours a stronger bond interaction of the bridging carboxylate groups with the metal that occupies the 'hydrated' position (see Table 6). The inversion is particularly acute in the title compound, in which a synergic action from hydrated Cu(2) is expected owing to the formation of strong equatorial Cu(2)–O bonds. This synergism is clearly revealed through a study of the strain in the five-membered chelate rings.

In Table 6 are also listed the mean values of the tension parameter, t, defined as the difference between the observed and idealized[18] sum of the angles of each ring, of the E, G, and R rings for the present compound and other similar complexes. Inspection of these values leads to the following conclusions. (*i*) The strains in the cdta and edta ligand rings are similar and the total strain values $t = \bar{t}_R + \bar{t}_G + t_E$ are roughly the same (*ca.* 30°) for all the compounds. (*ii*) The G rings are in all cases more strained than the R ones. This result is general in edta and edta-like complexes and arises from the cumulative bond-angle strains when forming a G ring.[18] (*iii*) the strains of the E and R rings seem to be correlated. Thus, small t_E values are associated with high t_R values. This fact can be related to the equilibrium system of E and R rings proposed by Weakliem and Hoard,[18] which allows closure of the G ring when forming the anion complex. (*iv*) There is no apparent correlation between the strain values and the nature of the 'chelated' ion. The last result allows us to conclude that the anomalous value of the R-ring strain [correlated with the large Cu(1)–O(bridging) bond length] for the present compound in Table 6 originates from the fact that the R carboxylates connect two Jahn-Teller active copper(II) atoms.

The six oxygen atoms around Cu(2) define an asymmetrically elongated octahedron. The equatorial co-ordination positions are occupied by two water molecules [O(1),O(3)] and two *trans* oxygen atoms from bridging R-carboxylates [O(32),O(42)]. The copper atom lies on the equatorial plane and the copper–oxygen bond distances are normal indicating a stronger interaction of bridging carboxylate groups with the 'hydrated' copper than the 'chelated' one. Two water molecules occupy the apical positions at distances longer than the equatorial ones and significantly different. One of these [O(4)] can be considered semi-co-ordinated to the central copper atom. The co-ordination of Cu(2) is then 4 + 1 + 1.[20]

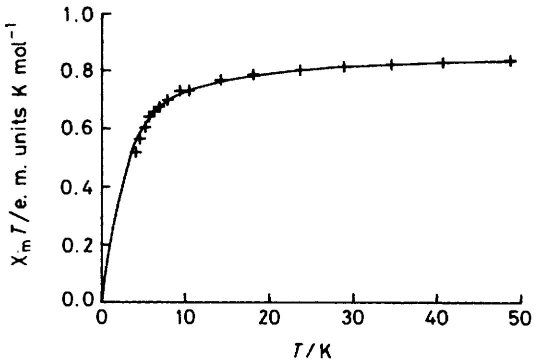

Figure 3. Magnetic behaviour of $[Cu(OH_2)_4][Cu(cdta)]$

The elongated octahedra centered on Cu(1) and Cu(2) are unequally oriented along the chain and their elongation axes form an angle of 58°. The Jahn–Teller induced distortion of each octahedron is static and there is a co-operative long-range order along [100]. The chain can be described as two one-dimensional ferrodistortive sublattices[28] (one for each type of copper) forming angles of 12.2° [Cu(1)] and 59.8° [Cu(2)] with [100]. In the case of chains formed by corner-connected identical octahedra, antiferrodistortion is energetically favoured. The same should be true for different alternating tetragonally elongated octahedra. However, in the present compound, the octahedron around Cu(1) shows a strong orthorhombic distortion which, besides the steric effects of the cdta ligand atoms, leads to the observed equilibrium configuration of the chain. There are two alternating and slightly different intrachain Cu(1)–Cu(2) distances [5.439(3) and 5.608(3) Å respectively] and the shortest interchain Cu–Cu distance is 5.971(3) Å [Cu(1)–Cu(2) $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$]. Thus from a structural point of view the compound can be regarded as built up from isolated dimerized linear chains.

Magnetic Properties.—The compound does not show a maximum in susceptibility in the studied temperature range (down to 4 K). A plot of $\chi_m T$ (proportional to $\mu_{eff.}^2$) *vs.* T(Figure 3) exhibits a significant decrease at $T < 10$ K [corresponding to a variation in $\mu_{eff.}$ between 1.21 (10 K) and 1.02 B.M. (4 K) per Cu atom] in agreement with the presence of very weak antiferromagnetic interactions between the copper ions.

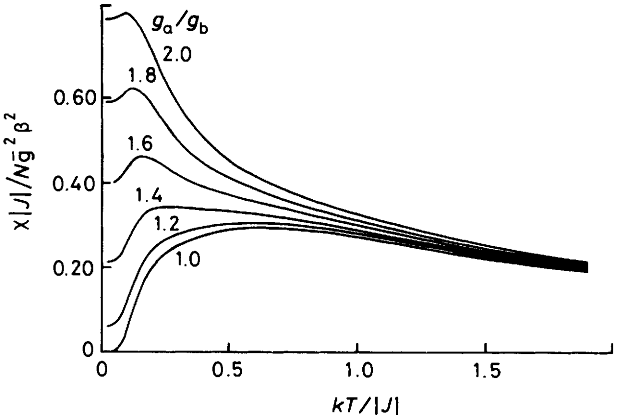

Figure 4. Influence of the g_a/g_b alternation in a 10-spin ($S = \frac{1}{2}$) closed Heisenberg chain system

The magnetic data can be satisfactorily analyzed in terms of a regular $S = \frac{1}{2}$ Heisenberg chain using the expression of Brown *et al.*[29] derived from the numerical results of Bonner and Fischer.[30] A good agreement with experiment is obtained by use of an exchange parameter $J = -1.1$ cm^{-1} and a Landé factor $g = 2.15$ (Figure 3). Owing to the different Cu(1)–Cu(2) distances and environments of this complex, the magnetic system should be viewed as $S = \frac{1}{2}$ chains, with alternating J values and g_a and g_b Landé factors. The fact that the

$$\cdots \underset{g_b}{\mathrm{Cu(1)}} \overset{J}{—} \underset{g_a}{\mathrm{Cu(2)}} \overset{J'}{—} \underset{g_b}{\mathrm{Cu(1)}} \overset{J}{—} \underset{g_a}{\mathrm{Cu(2)}} \cdots$$

experimental behaviour can be described without considering this alternation might indicate that its effect is too slight to be detectable over the reported temperature range.

In order to justify this we consider the influence on the susceptibility of a spin $S = \frac{1}{2}$ chain of alternating J and g factors. The alternating-J Heisenberg chain was first solved by Duffy and Barr[31] through a numerical treatment of a $S = \frac{1}{2}$ closed chain of increasing length. Their results indicate that the effect of the J alternation is only significant around and below the maximum of susceptibility,[32] being irrelevant above $kT \approx |J|$. The alternating-g Heisenberg chain was treated by us using a similar numerical procedure which takes into account the geometrical and spin space symmetries of the closed chain in order to reduce the amount of computation.[33] The calculation was limited to a ring of 12 spins. The g alternation leads to a divergence of the susceptibility when cooling, due to the presence of two non-compensated magnetic sublattices, similarly to the behaviour of alternating-spin chains ($S_a \neq S_b$).[6,7,33] This effect is particularly significant at low temperatures, and increases with the g_a/g_b ratio (Figure 4).

The e.s.r. powder spectrum of the present compound at room temperature exhibits a nearly isotropic signal centered around an average g value of 2.15. An estimation of g_a and g_b may be made from complexes with Cu^{II} located on similar ('hydrated' or 'chelated') sites. In this way, a g_b value of 2.13 can be evaluated from the e.s.r. spectrum of [ZnCu(cdta)]·6H$_2$O. Here, the Cu^{II} occupies the 'chelated' octahedral position.[34] On the other hand, g_a values around 2.16 have been commonly observed for Cu^{II} occupying similar 'hydrated' sites. This results in a ratio $g_a/g_b \approx 1.01$—1.02.

Figure 4 shows that the reduced susceptibility for a g_a/g_b ratio close to unity (*e.g.* 1.2) differs from that of the regular chain ($g_a/g_b = 1$) around the maximum, being superimposed above $kT/|J| = 0.7$—0.8. In our system, the estimated g_a/g_b ratio is close to unity and consequently the g-alternation effect is unobservable in the reported temperature range ($kT/|J| > 2.5$). Obviously, further investigations below 4 K are required in order to elucidate the role of these alternating factors.

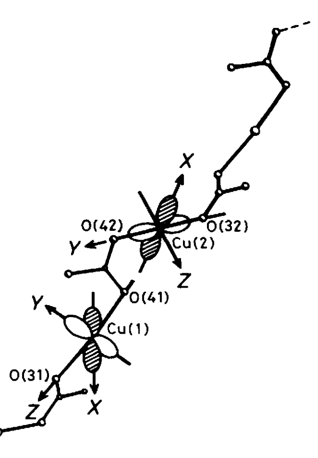

Figure 5. Superexchange mechanism in the [Cu(OH$_2$)$_4$][Cu(cdta)] chain. The figure corresponds to a projection in a bridging carboxylate plane

Magnetic exchange mechanism. The very low value of J may be understood in terms of the nature of the orbitals involved in the exchange interactions. The unpaired electron on each copper ion is described essentially by a $d_{x^2-y^2}$-type orbital, localized in a plane perpendicular to the bridging edge for the Cu(1) and pointing towards the bridging groups for Cu(2) (Figure 5). The extent of the antiferromagnetic interactions depends on the overlap between the magnetic orbitals. These, in turn, arise basically from the overlap among the spin-carrying orbitals of the metals and the symmetry-adapted orbitals of the bridging groups.

It is apparent from Figure 5 that the $d_{x^2-y^2}$ orbital of Cu(1) is unfavourably oriented to interact with the carboxylate orbitals. The idealized point groups of the Cu(2)O$_6$ and Cu(1)N$_2$O$_4$ chromophores are D_{4h} and C_{2v} respectively. The ground state of the former is well described by a $d_{x^2-y^2}$ orbital. Nevertheless, some admixture of the d_{z^2} orbital into the ground state is possible for the latter, owing to the opposite effects of the *cis* distortion, which destabilizes the d_{z^2} orbital, and the tetragonal elongation, which stabilizes it. The overlap of the Cu(1) ground state with molecular orbitals of the bridging carboxylates is then possible. Therefore the observed weak antiferromagnetic coupling can be explained by an exchange pathway involving interaction between the d_{z^2} [Cu(1)] and $d_{x^2-y^2}$ [Cu(2)] orbitals.

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