Synthesis, Molecular Structure, and Magnetic Properties of $[CuLNi(H_2O)_2LCu][ClO_4]_2\cdot 4H_2O$ [H_2L = *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamide] and its Trinickel Homologue†

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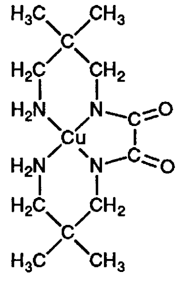
The compounds $[MLNi(H_2O)_2LM][ClO_4]_2\cdot 4H_2O$ [M = Cu or Ni; H_2L = *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamide] were prepared and characterized by means of structural, magnetic and spectroscopic measurements. The crystals of both compounds are triclinic, space group $P\bar{1}$ and $Z = 2$, with $a = 12.080(1)$, $b = 13.054(1)$, $c = 14.775(2)$ Å, $\alpha = 101.97(1)$, $\beta = 90.82(1)$ and $\gamma = 101.88(1)°$, for M = Cu and $a = 12.099(5)$, $b = 13.060(4)$, $c = 14.750(7)$ Å, $\alpha = 101.98(3)$, $\beta = 90.28(4)$ and $\gamma = 102.25(3)°$ for M = Ni. The structural unit of both complexes consists of trinuclear dipositive cations, two perchlorate anions and four lattice water molecules. The central and terminal metal ions are antiferromagnetically coupled, $J = 90(1)$ cm^{-1} in the case of M = Cu.

Copper(II) complexes with various ligands derived from oxalates, oxamidates, oxamates (CuL) are known to act as paramagnetic ligands towards other metal ions.[1] In the last few years they have been actively investigated especially when bound to paramagnetic metal ions, with the purpose of designing molecular-based materials exhibiting spontaneous magnetization. In particular it has been found that strong antiferromagnetic coupling is operative when CuL is bound to M ions ($M = Cu^{2+}$, Ni^{2+} or Mn^{2+}) in a pseudo-octahedral (square planar in the case of copper) environment.[2–5] The extent of the isotropic coupling decreases in the order $J_{Cu} > J_{Ni} > J_{Mn}$. This has been attributed[1] to the fact that the CuL moiety has a magnetic orbital which can overlap very efficiently with an *xy* magnetic orbital on M thus providing a strong antiferromagnetic pathway. The decrease of J along the series is justified by both intrinsic differences between the metal ions, and by the fact that the exchange coupling constant can be expressed as $J = \frac{1}{n}\sum_k J_{xy,k}$ where n is the number of magnetic orbitals, k, on M, if the only efficient pathway involves the *xy* orbitals. Kahn and co-workers[6–8] have found that CuL can form ferrimagnetic chains with $M = Ni^{2+}$ or Mn^{2+}, and that these chains can order magnetically at sufficiently low temperature. The critical temperature is determined by the extent of the intrachain coupling and of the weak interchain interactions.

We have now used as paramagnetic ligand the copper compound [CuL] which forms with nickel(II) the trinuclear complex $[CuLNi(H_2O)_2LCu][ClO_4]_2\cdot 4H_2O$. The peculiarity of this compound, compared with those previously reported, is that the central octahedrally co-ordinated nickel(II) ion has two water molecules in *cis* rather than in *trans* configuration. We report here the structure and the magnetic properties of the complex together with those of the trinickel homologue in which the two external NiL units are diamagnetic.

Experimental

All chemicals were reagent grade and used as received. The complexes were obtained by a two-step reaction.[9] The dicoppernickel complex was prepared by treating at 0 °C diethyl oxalate (1 mol) in absolute ethanol (140 cm^3) with 2,2-dimethyl propane-1,3-diamine (2 mol) in ethanol (240 cm^3). The mixture was kept at 100 °C for 30 min. A solution of $CuSO_4\cdot 5H_2O$ (1 mol) in water (5 cm^3) was added and the mixture treated with NaOH (2 mol) in water (50 cm^3). A violet precipitate formed, which was filtered off and washed with water. A suspension of the compound in water was then dissolved in the minimum amount of CH_3CO_2H; a solution (0.1 mol dm^{-3}) of NaOH was added until the violet solution turned red; a precipitate slowly formed (Found: C, 45.75; H, 7.65; N, 17.40. Calc. for $C_{12}H_{24}CuN_4O_2$: C, 45.05; H, 7.55; N, 17.50%). The stirred precipitate (1 mol) suspended in water was treated with solid $Ni(ClO_4)_2\cdot 6H_2O$ (2 mol). The solution was filtered and left under vacuum with P_2O_5. Within 2 d ruby-violet crystals were formed (Found: C, 28.75; H, 5.65; N, 11.30. Calc. for $C_{24}H_{60}Cl_2Cu_2N_8NiO_{18}$: C, 28.95; H, 5.45; N, 11.15%). The same preparation procedure was used for the yellow trinickel complex. The first step gave the yellow product (Found: C, 45.70; H, 7.70; N, 17.60. Calc. for $C_{12}H_{24}N_4NiO_2$: C, 45.75; H, 7.70; N, 17.80%). Final product (Found: C, 28.75; H, 5.65; N, 11.30. Calc. for $C_{24}H_{60}Cl_2N_8Ni_3O_{18}$: C, 28.95; H, 5.45; N, 11.15%).



CuL

Magnetic Susceptibility Measurements.—Magnetic suscepti-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Relevant bond lengths (Å) and angles (°) for the complexes $[MLNi(H_2O)_2LM][ClO_4]_2{\cdot}4H_2O$

	M = Cu	M = Ni
Ni–O(1w)	2.070(5)	2.050(7)
Ni–O(2w)	2.085(5)	2.093(6)
Ni–O(1a)	2.066(5)	2.055(7)
Ni–O(2a)	2.053(5)	2.059(6)
Ni–O(1b)	2.084(4)	2.064(6)
Ni–O(2b)	2.041(4)	2.073(5)
M(a)–N(1a)	1.960(6)	1.880(8)
M(a)–N(2a)	1.952(6)	1.889(7)
M(a)–N(3a)	1.994(8)	1.930(9)
M(a)–N(4a)	1.995(6)	1.929(8)
M(b)–N(1b)	1.953(6)	1.890(7)
M(b)–N(2b)	1.969(5)	1.919(6)
M(b)–N(3b)	2.012(7)	1.900(9)
M(b)–N(4b)	2.006(6)	1.951(7)
O(1w)–Ni–O(2b)	90.3(2)	90.1(2)
O(1w)–Ni–O(1b)	92.7(1)	93.4(2)
O(2w)–Ni–O(2a)	88.5(2)	88.5(2)
O(1w)–Ni–O(1a)	171.1(2)	171.0(2)
O(1b)–Ni–O(2b)	81.6(1)	81.4(2)
O(2a)–Ni–O(2b)	96.9(1)	97.4(2)
O(2a)–Ni–O(1b)	177.1(1)	176.7(2)
O(1a)–Ni–O(2b)	91.3(2)	90.8(2)
O(1a)–Ni–O(1b)	96.1(1)	95.6(2)
O(1a)–Ni–O(2a)	81.4(2)	81.4(2)
O(2w)–Ni–O(2b)	174.4(2)	174.1(2)
O(1w)–Ni–O(2w)	88.6(2)	88.7(3)
N(3a)–M(a)–N(4a)	88.3(2)	84.8(3)
N(1a)–M(a)–N(2a)	83.6(2)	85.0(3)
N(2a)–M(a)–N(4a)	175.9(2)	176.7(3)
N(1a)–M(a)–N(3a)	71.0(2)	76.6(3)
N(3b)–M(b)–N(4b)	87.6(3)	85.1(4)
N(1b)–M(b)–N(2b)	83.2(2)	84.4(3)
N(2b)–M(b)–N(4b)	171.2(2)	175.1(3)
N(1b)–M(b)–N(3b)	177.2(2)	175.9(4)

bilities were measured in the range 4.2–300 K with a fully automatized AZTEC DSM5 susceptometer equipped with an Oxford Instruments CF 1200S continuous-flow cryostat and a Brüker BE15 electromagnet, operating at *ca.* 1.2 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

Crystallography.—Ruby-violet crystals of $[CuLNi(H_2O)_2LCu][ClO_4]_2{\cdot}4H_2O$ and yellow crystals of $[NiLNi(H_2O)_2LNi][ClO_4]_2{\cdot}4H_2O$ were obtained by slow crystallization of the reaction mixture. The crystals consisting of well shaped individuals defined by three pairs of pinacoids were stored under the mother-liquor and those chosen for the diffraction experiments were sealed in glass capillaries together with some saturated solution in order to prevent deterioration. X-Ray data were collected at room temperature on Enraf-Nonius CAD 4 diffractometers with Mo-Kα radiation. During the measurements the crystal decay was tested by detecting the intensity of standard reference reflections at intervals. Unit-cell parameters, obtained from least-squares treatment of the orienting reflections, the conditions for the intensity data collection, and numerical details of the structure determination are listed in Table 2. The refined non-hydrogen atomic coordinates are listed in Table 3.

The structure of the dicoppernickel complex was solved by direct methods, which afforded the positions of the metal atoms; all the remaining non-hydrogen atoms were located by subsequent Fourier difference syntheses. The refinement was carried out by least-squares calculations including the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. Geometrical constraints were applied to the perchlorate anions by imposing equal Cl–O and O···O distances within 0.01 Å. The average Cl–O and O–Cl–O values were 1.388(9) Å and 109.5(5)°. The hydrogen atoms bonded to C and N atoms were placed in calculated positions, while those bonded to the co-ordinated oxygen atoms were found in the Fourier maps. The refinement of the hydrogen atoms was completed as follows: (*i*) all the atoms in the ligands were given a constant thermal parameter (U = 0.1 Å^2) and allowed to ride with respect to their carrier atoms; (*ii*) atoms belonging to the two co-ordinated water molecules were refined with a constrained model by imposing equal O–H and H···H distances within 0.01 Å; (*iii*) atoms belonging to the lattice water were not considered because they were not detected.

The structure of the trinickel analogue was refined straightforwardly using the dicopper structure as a model because the crystals are strictly isomorphous.

For both compounds the final Fourier difference map showed maximum peaks of residual electron density not exceeding 1 e Å^{-3}. The SHELX[10] package of crystallographic programs was used for the computations, and the ORTEP[11] plotting program. Absorption corrections were made according to Walker and Stuart.[12] The final agreement indices turned out to be quite high in both structures, in spite of the good quality of the crystals used. This originated from unfavourable counting statistics of the diffraction measurements caused by the high background radiation produced by the saturated solution in which the crystals had to be kept.

In spite of the isomorphism of the two species the trinickel cation exhibits some evidence of disorder that has no counterpart in the dicopper analogue. The disorder shows up as abnormally elongated thermal ellipsoids of C(1b) and adjacent atoms. It is explainable in terms of low conformational rigidity of the six-membered rings, as confirmed by the presence of two conformations of these rings. Three rings have the same conformation while the fourth is different (see discussion of the structures). The disorder affects the unique ring showing that it is not as stable as the other three. Very probably its conformation is a compromise between ring stability and packing efficiency. Attempts at refining separate positions of the affected atoms were unsuccessful because of insufficient resolution.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structure.—The structural unit of both complexes consists of trinuclear dipositive complex cations, two perchlorate anions and four lattice water molecules involved in a network of hydrogen bridges. An analysis of the crystal packing revealed no features of chemical relevance. Selected bond distances and angles are listed in Table 1.

The stereogeometry of the $[CuLNi(H_2O)_2LCu]^{2+}$ cation is depicted in Fig. 1, that of the trinickel cation is strictly equivalent and, unless otherwise stated, the discussion refers to both species. The central Ni^{2+} ion is octahedrally co-ordinated by two pairs of oxamidate oxygens and two water molecules in *cis* positions. The idealized symmetry of the co-ordination polyhedron is C_2 and the crystals contain a racemic mixture of the chiral cations.

The constraints of the five-membered chelate rings impose deviations of the O–Ni–O angles from 90°, the actual bite angles being 81.4°. The chelate rings are planar with the maximum deviation from the average planes not exceeding 0.08 Å. The Ni–O distances are in the range 2.041(4)–2.093(6), with average values Ni–O(aqua) 2.074 and Ni–O(oxamidate) 2.062 Å. Although the spread of individual values is quite high the average values indicate different strengths of the chemically non-equivalent Ni–O interactions. The *cis* co-ordination geometry around the central nickel ion in each complex is

Table 2 Crystal data and details of structure determinations[a] for $[MLNi(H_2O)_2LM][ClO_4]_2\cdot 4H_2O$

	M = Cu	M = Ni
Formula	$C_{24}H_{60}Cl_2Cu_2NiN_8O_{18}$	$C_{24}H_{60}Cl_2Ni_3N_8O_{18}$
M_r	1005.49	995.78
Crystal colour	Ruby-violet	Yellow
Crystal dimensions/mm	0.3 × 0.4 × 0.6	0.4 × 0.4 × 0.6
a/Å	12.080(1)	12.099(5)
b/Å	13.054(1)	13.060(4)
c/Å	14.775(2)	14.750(7)
α/°	101.97(1)	101.98(3)
β/°	90.82(1)	90.28(4)
γ/°	101.88(1)	102.25(3)
U/Å^3	2226.4(5)	2233(2)
D_c/g cm^{-3}	1.50	1.53
μ(Mo-Kα)/cm^{-1}	15.6	14.5
F(000)	1048	1044
Transmission factor range	64–100	68–100
θ range/°	2.5–25	2–26
Scan width, (+ 0.35 tan θ)/°	0.8	1.15
Required counting $\sigma(I)/I$	0.02	0.01
Prescan speed/° min^{-1}	5.3	4
Maximum scan time/s	100	120
Data collected	8867	9060
Data used [$I > 2\sigma(I)$]	5542	4329
R, R'	0.079, 0.087	0.074, 0.080
k, g[b]	5.9, 1 × 10^{-4}	1.0, 1.03 × 10^{-2}

[a] Details in common: crystal system triclinic; space group $P\bar{1}$ (no. 2); $Z = 2$; scan mode, ω; prescan acceptance criterion, $\sigma(I)/I = 0.5$; octants collected $\pm h$, $\pm k$, $+l$. [b] The weighting scheme employed was $w = k/[\sigma^2(F) + |g|F^2]$, where both k and g were independently determined.

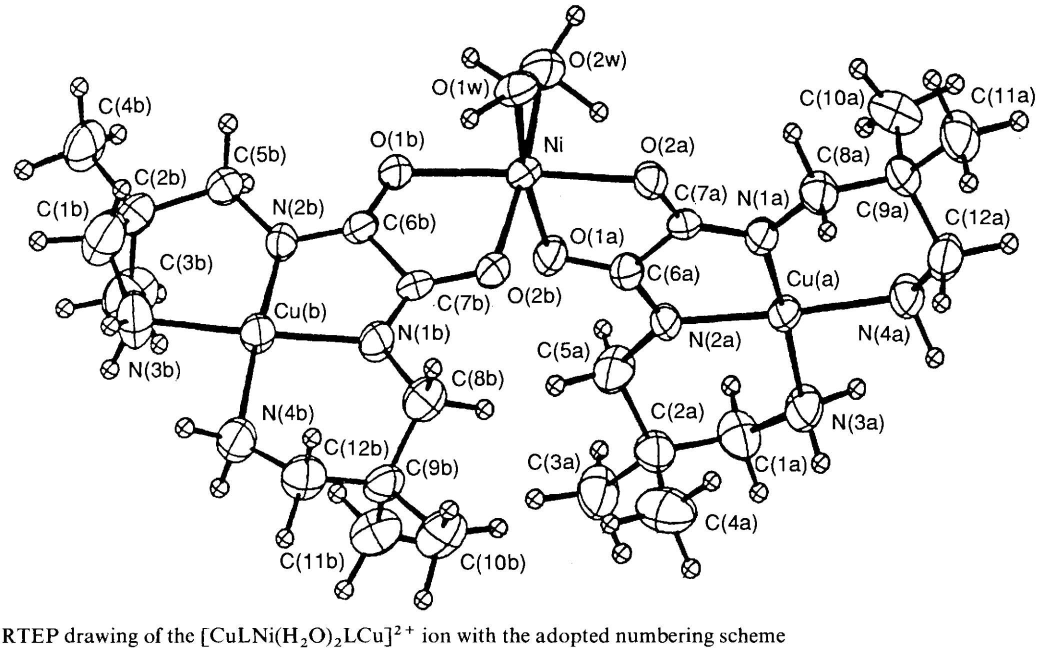

Fig. 1 An ORTEP drawing of the $[CuLNi(H_2O)_2LCu]^{2+}$ ion with the adopted numbering scheme

indicative of the greater stability of this isomer with respect to the *trans* one. A possible explanation is that bonding interactions between oxamidate oxygens and nickel orbitals are favoured when the weaker water donor oxygens are placed *trans* to them.

Two oxamidate anions act as bridges between the central and the outer metal ions. They are flat and the bridged metal ions are contained in the same plane (maximum deviation from the average plane 0.08 Å). The distances between contiguous metal centres are Ni···Cu 5.316, 5.315(1) and Ni···Ni 5.263, 5.304(2) Å. The oxamidate anions are functionalized by two N-bonded three-carbon chains substituted by two methyl groups at the central carbon and terminating in amine groups. The resulting N-tetradentate ligands co-ordinate in planar geometry two copper(II) or nickel(II) ions, respectively. Each complex unit $M^{II}N_2$(amidate)N_2(amine) contains three chelate rings: a five-membered ring which is part of the flat system metal(octahedral)–oxamidate–metal(square) and two puckered six-membered rings. Three out of the four six-membered rings in each cation exhibit a half-chair conformation in which the substituted carbon atom (*para* to the metal atom) is out of the average plane described by the other five atoms (*ca.* 0.75 Å). The fourth ring has the same conformation, but the out-of-plane carbon is now *meta* to the metal atom C(1b) (see also Experimental section). As a consequence, the local idealized symmetries at the outer metal centres are different, *i.e.* C_2 (moiety labelled a) and C_1 (moiety labelled b). This feature deprives the molecule as a whole of any symmetry.

Table 3 Fractional atomic coordinates for $[MLNi(H_2O)_2LM][ClO_4]_2{\cdot}4H_2O$

	M = Cu			M = Ni		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ni	0.427 51(7)	0.522 17(7)	0.845 07(6)	0.429 03(9)	0.520 42(9)	0.844 96(8)
O(1w)	0.530 2(4)	0.425 9(3)	0.880 3(3)	0.531 9(5)	0.425 8(5)	0.880 2(4)
O(2w)	0.543 1(4)	0.655 3(4)	0.919 7(4)	0.541 9(5)	0.654 2(5)	0.919 3(4)
M(a)	0.448 01(7)	0.727 84(7)	0.568 61(6)	0.445 76(9)	0.718 87(9)	0.567 57(8)
N(1a)	0.530 0(4)	0.633 2(4)	0.616 0(4)	0.529 4(5)	0.632 2(5)	0.614 0(5)
C(1a)	0.258 5(6)	0.846 8(6)	0.563 4(6)	0.261 5(8)	0.840 1(8)	0.564 3(8)
C(2a)	0.182 1(6)	0.765 5(7)	0.612 0(6)	0.183 2(7)	0.756 8(9)	0.606 5(7)
C(3a)	0.085 0(8)	0.815 5(9)	0.649 3(7)	0.086(1)	0.806(1)	0.645(1)
C(4a)	0.137 3(8)	0.662 0(8)	0.543 3(8)	0.137 7(9)	0.654 4(9)	0.534 2(9)
C(5a)	0.245 8(7)	0.743 6(7)	0.693 4(6)	0.245 4(8)	0.733 7(9)	0.688 1(7)
N(2a)	0.346 2(4)	0.699 6(4)	0.666 1(4)	0.346 6(6)	0.692 6(6)	0.662 4(5)
C(6a)	0.380 8(5)	0.643 1(5)	0.719 1(4)	0.382 2(6)	0.637 0(6)	0.717 4(5)
O(1a)	0.341 2(4)	0.620 8(4)	0.793 3(3)	0.341 0(5)	0.615 9(5)	0.791 6(4)
O(2a)	0.517 4(3)	0.536 6(3)	0.729 8(3)	0.520 3(4)	0.534 6(4)	0.729 2(4)
C(7a)	0.485 9(5)	0.600 7(5)	0.686 5(4)	0.487 8(6)	0.597 9(6)	0.685 3(5)
N(3a)	0.347 5(5)	0.803 1(5)	0.510 9(5)	0.355 2(6)	0.800 1(7)	0.515 2(6)
C(8a)	0.630 0(6)	0.595 8(6)	0.581 5(5)	0.630 2(7)	0.595 1(8)	0.577 7(7)
C(9a)	0.706 3(5)	0.670 7(6)	0.532 3(5)	0.706 8(6)	0.672 6(8)	0.530 7(6)
C(10a)	0.803 1(7)	0.614 6(8)	0.491 6(7)	0.802 8(8)	0.618 3(9)	0.489 6(8)
C(11a)	0.758 8(7)	0.776 0(7)	0.600 7(7)	0.755 4(9)	0.777 9(9)	0.598 2(9)
C(12a)	0.644 5(7)	0.690 4(7)	0.448 8(5)	0.641 0(8)	0.692(1)	0.448 3(7)
N(4a)	0.560 9(5)	0.761 1(5)	0.475 9(4)	0.551 0(6)	0.753 4(7)	0.475 4(5)
M(b)	0.064 83(7)	0.261 06(7)	0.931 25(6)	0.063 1(1)	0.266 8(1)	0.928 80(8)
N(1b)	0.148 1(5)	0.284 8(4)	0.822 5(4)	0.145 5(6)	0.283 5(6)	0.822 5(4)
C(1b)	0.049 0(9)	0.296 1(8)	1.137 1(6)	0.058(2)	0.296(1)	1.137(1)
C(2b)	0.086 5(6)	0.413 7(6)	1.148 2(5)	0.087 7(8)	0.409 8(8)	1.145 1(7)
C(3b)	−0.017 4(9)	0.459 6(9)	1.114 5(8)	−0.022(1)	0.413(3)	1.110(1)
C(4b)	0.117 4(8)	0.469 2(7)	1.248 9(5)	0.112(1)	0.466(1)	1.245 6(7)
C(5b)	0.185 0(6)	0.449 1(6)	1.092 3(5)	0.178(1)	0.448 3(9)	1.088 4(7)
N(2b)	0.173 6(4)	0.391 7(4)	0.993 8(4)	0.169 7(6)	0.391 4(6)	0.989 8(5)
C(6b)	0.248 8(5)	0.427 5(5)	0.938 9(4)	0.247 2(6)	0.425 5(6)	0.936 2(5)
O(1b)	0.329 1(3)	0.508 4(3)	0.958 4(3)	0.330 0(4)	0.508 3(4)	0.957 2(4)
O(2b)	0.308 6(3)	0.389 5(3)	0.784 0(3)	0.310 9(4)	0.385 5(4)	0.784 5(3)
C(7b)	0.233 7(5)	0.361 4(5)	0.838 9(4)	0.236 0(6)	0.360 8(6)	0.839 0(5)
N(3b)	−0.013 7(6)	0.237 8(6)	1.046 8(5)	−0.014(1)	0.242 5(8)	1.037 0(6)
C(8b)	0.130 0(6)	0.214 0(6)	0.728 4(5)	0.132 3(8)	0.210 3(8)	0.731 5(7)
C(9b)	0.007 5(6)	0.159 7(5)	0.702 0(5)	0.010 6(7)	0.159 1(7)	0.703 1(6)
C(10b)	−0.065 4(8)	0.243 1(7)	0.698 7(7)	−0.062(1)	0.241(1)	0.699 2(9)
C(11b)	0.002 9(8)	0.090 8(7)	0.604 7(6)	0.005(1)	0.085(1)	0.604 4(7)
C(12b)	−0.039 7(7)	0.084 7(6)	0.762 9(6)	−0.038 4(8)	0.087 0(7)	0.769 3(7)
N(4b)	−0.057 8(5)	0.143 3(5)	0.859 5(4)	−0.052 0(7)	0.148 3(6)	0.862 7(5)
O(3w)	0.446 6(8)	0.217 2(6)	1.888 2(7)	0.442 9(9)	0.217 3(7)	1.894 5(8)
Cl(1)	0.419 6(2)	−0.019 9(1)	0.331 1(2)	0.420 2(3)	−0.029 9(2)	0.332 2(2)
O(5)	0.471 7(4)	0.080 9(2)	0.319 1(4)	0.472 2(8)	0.064 4(5)	0.305 7(7)
O(6)	0.345 9(7)	−0.009 6(5)	0.401 9(5)	0.365(1)	−0.004 9(8)	0.413 6(8)
O(7)	0.500 9(5)	−0.072 7(6)	0.353 8(8)	0.501 8(8)	−0.086(1)	0.347(1)
O(8)	0.359 5(9)	−0.078 1(6)	0.249 7(4)	0.342(1)	−0.093(1)	0.262 3(8)
Cl(2)	0.194 9(2)	0.030 4(1)	0.948 0(1)	0.196 4(3)	0.017 3(2)	0.945 1(3)
O(9)	0.220 6(7)	0.004 0(5)	1.030 8(3)	0.221 0(9)	−0.006 7(8)	1.029 6(4)
O(10)	0.084 2(3)	−0.019 4(5)	0.917 3(6)	0.083 3(4)	−0.027 9(8)	0.917 6(8)
O(11)	0.267 7(7)	−0.003 6(6)	0.882 2(5)	0.265 3(9)	−0.024 3(8)	0.878 4(7)
O(12)	0.207 2(5)	0.140 5(2)	0.961 4(5)	0.216 1(8)	0.128 1(3)	0.954 8(8)
O(4w)	0.265 3(7)	0.750 2(7)	0.950 7(7)	0.272(1)	0.752(1)	0.944 4(9)
O(5w)	0.381 2(5)	0.651 2(5)	0.319 1(5)	0.378 6(6)	0.650 7(6)	0.322 1(5)
O(6w)	0.381(1)	0.173 2(7)	1.165 1(7)	0.377(1)	0.178(1)	1.165 5(9)

The square-planar co-ordination polyhedrons are substantially flat with deviations from the average planes in the range −0.07 to +0.17 for the dicopper complex and −0.10 to +0.09 Å for the trinickel complex. These slight deviations from planarity are tetrahedral-like and the N(amidate)–M–N(amine) angles are 171, 177° and 175, 177° respectively. The average bond distances are M–N(amidate) 1.959, 1.895 and M–N(amine) 2.002, 1.928 Å for copper and nickel respectively. These figures indicate that the copper(II) cation is 0.07 Å larger than nickel(II), probably as a consequence of the antibonding character of its unpaired electron. The M–N(amidate) interactions are stronger than the M–N(amine) ones in both species, being 0.04 Å shorter.

The simultaneous presence in the trinickel complex of four- and six-co-ordinate nickel(II) ions deserves a comment. It should be noted that the neutral donor oxygens stabilize six-co-ordination at the central metal atom, while four nitrogen atoms, two of which negatively charged, are enough to saturate the acceptor ability of the outer metal ions. Similar considerations apply to the square copper(II) ions in the dicopper complex.

Magnetic Properties.—The room-temperature value of μ_{eff} for the dicopper compound is 3.65 μ_B, much lower than the value 4.11 μ_B expected for two spins of $\frac{1}{2}$ and one spin of 1 with average $g = 2.2$. On lowering the temperature μ_{eff} decreases regularly approaching almost zero. A plateau of ≈0.56 μ_B is

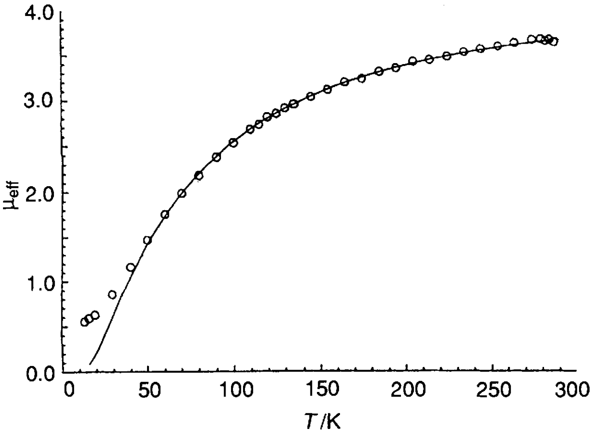

Fig. 2 Temperature dependence of the effective moment of the dicopper complex. The solid line represents the best fit (see text)

reached at about 20 K. For the trinickel complex the room-temperature value of μ_{eff} is 3.28 μ_B, and remains constant on decreasing the temperature. Below 20 K a decrease is observed. The temperature behaviour of the magnetic susceptibility of the dicopper complex clearly indicates that the $S = 1$ state of nickel(II) is antiferromagnetically coupled to the terminal $S = \frac{1}{2}$ of the copper(II) ions. The susceptibility was calculated using the standard formulae[13] for three coupled spins having the symmetry of an isosceles triangle. The spin Hamiltonian was taken in the form $H = J_{Cu-Ni}(S_{Cu^1} \cdot S_{Ni} + S_{Cu^2} \cdot S_{Ni})$. No correction for temperature-independent paramagnetism (t.i.p.) was made. The best-fit parameters are $J_{Cu-Ni} = 90(1)$ cm^{-1}, $g_{Ni} = 2.36(2)$, $g_{Cu} = 2.15(1)$ with $R = 2.2 \times 10^{-4}$. The agreement with the observed magnetic susceptibility is good, as can be seen in Fig. 2, except at low temperature where the calculated values are much lower than the experimental ones. The discrepancy is probably due to paramagnetic impurities (less than 2%), whose contribution becomes relevant when the compound is practically diamagnetic.

We did not introduce any corrections to take into account the presence of such impurities because they do not add any useful information to the analysis of the data. Also the zero-field splitting of the $S = 1$ state was neglected because, as shown by the magnetic data for the trinickel complex, it affects the susceptibility only at low temperature, where the compound is almost diamagnetic. The calculated J value is very close to those previously reported for other Cu(L)Ni complexes.[14,15] The fact that the data can be well fitted with a single coupling constant, and the similarity of the value obtained with those previously reported, suggests that indeed there are not two different J constants. This is easily understood, because in an octahedral environment the positions of the CuL ligands are equivalent whether they occupy two *trans* or two *cis* positions. Taking the z axis as normal to the Ni(H$_2$O)$_2$ plane, the z^2 orbital has identical non-zero overlaps with both CuL ligands, and the same is true of x^2–y^2. In other words the overlap between the magnetic orbital on nickel and that on CuL is essentially σ in nature, and the extent of the coupling is independent of the orientation in the octahedral co-ordination polyhedron. This result confirms both the essentially σ nature of the nickel CuL interaction, and the assumption that the exchange contributions in CuNiCu chromophores are essentially additive.

Conclusion

The main interest in the magnetic properties of [CuLNi(H$_2$O)$_2$LCu][ClO$_4$]$_2$·4H$_2$O lies in the connectivity of the lateral CuL ligands to the central nickel(II). In fact in all the ferrimagnetic chains reported so far using the CuL derivative, the nickel or manganese ions are bonded to two CuL ligands which occupy the four equatorial positions in a tetragonally elongated co-ordination octahedron.

We have now shown that it is possible to connect the CuL ligands occupying three equatorial and one axial positions, without varying significantly the extent of the antiferromagnetic coupling between CuL and nickel(II). If it were possible to synthesise mixed-metal chains with such an arrangement, differences in the critical temperature for magnetic ordering could be anticipated, as observed in the case of manganese-radical chains.[16,17] The possibility of varying the connectivity of the copper and nickel ions in polynuclear systems shows the versatility of molecular chemistry in designing magnetic materials.

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