Bimetallic Compounds of *trans*-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate (cdta): Structural and Magnetic Characterization of $[(H_2O)_4Cu(cdta)Ni]\cdot 3H_2O$ † and $[(H_2O)_5Ni(cdta)Cu]\cdot H_2O$

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The crystal structure of the complex $[(H_2O)_4Cu(cdta)Ni]\cdot 3H_2O$ (**1**) (cdta = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate) has been determined by *X*-ray methods. It crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 8.685(4)$, $b = 11.415(6)$, $c = 12.841(4)$ Å, $\alpha = 96.43(4)$, $\beta = 96.60(3)$, $\gamma = 102.23(6)°$. Least-squares refinement of 2 368 reflections $[I > 2.5\sigma(I)]$ and 316 parameters gave a final $R = 0.036$. The molecular structure consists of heterobimetallic units in which the Cu^{II} ion occupies a 'hydrated' octahedral site and the Ni^{II} ion a 'chelated' one. The two metal ions are linked through a bridging oxygen belonging to a carboxylate group. The molecular structure of $[(H_2O)_5Ni(cdta)Cu]\cdot H_2O$ (**2**) is described, based on that determined previously for the isostructural zinc–copper compound. Magnetic properties of these compounds are analyzed in terms of isolated (Cu^{II}, Ni^{II}) ion pairs. Whereas there is no exchange coupling detected down to 4 K for the nickel–copper compound (**2**), an antiferromagnetic coupling ($J = -30.6$ cm^{-1}) is found for the copper–nickel one, (**1**). This difference is discussed based on comparison of the structural features of the bridging network and co-ordination sites.

Over the past few years a new approach has arisen in magnetism: instead of studying magnetic properties as available in nature, research workers started to look for and to synthesize the materials they needed for a given purpose.[1] Co-ordination chemistry offers a great flexibility in the design of a magnetic lattice. A great variety of ligands and complexes can be used to build up materials with the desired properties (magnetic dimensionality, strength and range of the interactions, spin values, *etc.*).

The ability of ethylenediamine-*NNN'N'*-tetra-acetate (edta) to form bimetallic ordered systems has been established.[2] Thus, a large family of alternating-heterometallic chain compounds of formula $[(H_2O)_4M(edta)M']\cdot 2H_2O$ (M = Mg, Mn, Co, Zn, or Ni; M' = Co, Ni, Cu, or Zn) exhibiting 'one-dimensional ferrimagnetism,' has been characterized.[3–6] Recently, by hydrothermal extrusion of co-ordinated water, a new series of materials formulated as $[MM'(edta)]\cdot 2H_2O$ (M = Mg, Co, or Zn; M' = Co or Ni) has been prepared and their structure determined.[7] In this case, the cationic alternation generates a novel quasi-two-dimensional network that may support the existence of 'two-dimensional ferrimagnetism.'

trans-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate (cdta) is a similar ligand which also forms bimetallic ordered complexes.[8] Nevertheless, the subtle competition between the ability of the carboxylate groups as bridging ligands and steric hindrance from the cyclohexane moiety allows a wide variety of structures to be obtained.[8–10] On the other hand, the inertness of some cdta complexes in solution makes these systems of particular interest due to the possibility of kinetic control of their synthesis.[11]

Using this strategy we have been able to prepare the two title compounds that may be formally considered as co-ordination isomers. We report here the structural and magnetic study of these bimetallic dimers.

Experimental

Preparation of the Complexes.—Both compounds $[(H_2O)_4Cu(cdta)Ni]\cdot 3H_2O$ (**1**) and $[(H_2O)_5Ni(cdta)Cu]\cdot H_2O$ (**2**) were separately prepared by the same procedure. To a solution of $Na_4(cdta)$ (pH *ca.* 11.7) an equimolar solution of the relevant metal nitrate (Ni or Cu, respectively) was added. After a short period (*ca.* 15 min) to ensure complexation of this metal ion, an equimolar aqueous solution of the second metal nitrate was added. Then, acetone was added dropwise with stirring until incipient turbidity. The resultant solutions were stored at *ca.* 5 °C and crystalline solids appeared after a few hours. The solids were vacuum filtered, washed with acetone–water (1:2), and stored in a desiccator over silica gel [Found for (**1**): C, 29.0; H, 5.3; Cu, 11.0, N, 4.7; Ni, 10.2. $C_{14}H_{32}CuN_2NiO_{15}$ requires C, 28.5; H, 5.4; Cu, 10.8; N, 4.7; Ni, 10.0. Found for (**2**): C, 29.6; H, 5.3; Cu, 11.1; N, 4.8; Ni, 10.3. $C_{14}H_{30}CuN_2NiO_{14}$ requires C, 29.3; H, 5.2; Cu, 11.1; N, 4.9; Ni, 10.3%].

Crystal Structure Determination of $[(H_2O)_4Cu(cdta)Ni]\cdot 3H_2O$.—*Crystal data.* Blue prismatic crystals of $C_{14}H_{32}CuN_2NiO_{15}$, $M = 590.7$, triclinic, space group $P\bar{1}$, $a = 8.685(4)$, $b = 11.415(6)$, $c = 12.841(4)$ Å, $\alpha = 96.43(4)$, $\beta = 96.60(3)$, $\gamma = 102.23(6)°$, $U = 1\,224(1)$ $Å^3$, $Z = 2$, $D_c = 1.60$ g cm^{-3}, $F(000) = 606$, $\mu(Mo\text{-}K_\alpha) = 16.8$ cm^{-1}.

Data collection. A crystal of dimensions 0.16 × 0.18 × 0.15 mm was selected and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The

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† 1,1,1,1-Tetra-aqua-μ-[*trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetato-*NN'OO'O''O'''*(Ni); μ-*O''';O''''*(Cu)]-copper(II)nickel(II) trihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

cell dimensions were obtained by a least-squares fit to 18 well centred reflections ($10 < 2\theta < 21°$), using Mo-K_α radiation (λ = 0.709 26 Å). The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by the successful refinement of the structure. 3 978 Reflections were measured ($2 < 2\theta < 47°$; $-9 < h < 9$, $-12 < k < 12$, $0 < l < 14$) using the variable-speed ω–2θ technique. During the data collection, four standard reflections [($1\bar{1}3$), ($1\bar{2}5$), ($2\bar{1}3$), (210)] were monitored to check the stability and orientation of the crystal. No appreciable decay was observed. A total of 2 368 reflections having $I > 2.5\sigma(I)$ were considered observed and used in the determination and refinement of the structure. Lorentz-polarization corrections were applied, but not for absorption.

Structure solution and refinement. The positions of copper, nickel, and ten non-hydrogen atoms were determined by direct methods (MULTAN 11/82[12]). The remaining non-hydrogen atoms were located from successive Fourier syntheses. Refinement of the structure was carried out with the SHELX 76 system[13] by weighted anisotropic full-matrix least-squares methods. Positions of all hydrogen atoms present in the molecule were determined by Fourier difference syntheses and included in the final refinement with common fixed isotropic thermal parameters (U = 0.05 Å^2). Final values of R and R' were 0.036 and 0.040 respectively (316 parameters refined). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 0.3425/[\sigma^2(F_o) + 0.004\,35F_o^2]$ with $\sigma^2(F_o)$ from counting statistics. In the final difference map the residual maxima were less than 0.62 e Å^{-3}. Atomic scattering factors and corrections for anomalous dispersion for Cu and Ni atoms were taken from ref. 14. The geometrical calculations were performed with XANADU[15] and DISTAN[16] and molecular illustrations were drawn with PLUTO.[17]

Magnetic Measurements.—Magnetic susceptibility measurements were performed with a pendulum-type magnetometer[18] and were corrected for diamagnetic contributions. The uncertainty in the data is <0.1 K for temperature and $<2 \times 10^{-5}$ e.m.u. mol^{-1} (e.m.u. = S.I. × $10^6/4\pi$) for susceptibility.

Results and Discussion

Molecular Structure of the Compounds.—[$(H_2O)_4Cu(cdta)Ni$]·$3H_2O$. Final atomic co-ordinates are given in Table 1. Figure 1 shows a perspective view of the molecule and the

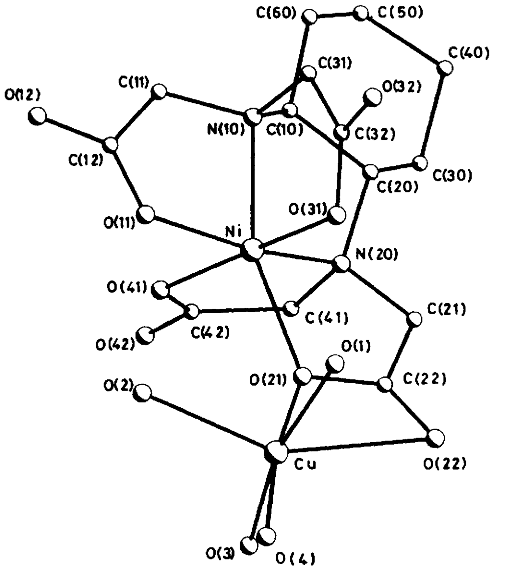

Figure 1. Perspective view and atomic numbering of [$(H_2O)_4Cu(cdta)Ni$]·$3H_2O$

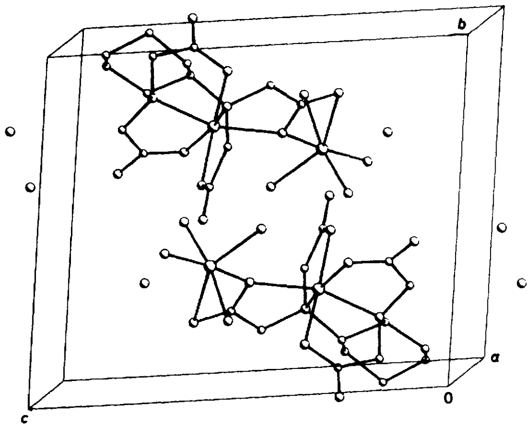

Figure 2. View of the unit-cell contents of [$(H_2O)_4Cu(cdta)Ni$]·$3H_2O$

Table 1. Fractional atomic co-ordinates (× 10^4) for complex (1) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni	6 970(1)	2 459(1)	3 812(1)	O(41)	6 676(5)	4 134(4)	3 581(4)
Cu	8 858(1)	3 130(1)	6 567(1)	O(42)	4 878(5)	5 254(4)	3 510(4)
N(10)	6 362(5)	1 606(4)	2 264(4)	C(10)	4 601(7)	1 590(5)	1 978(5)
N(20)	4 526(6)	2 102(4)	3 898(4)	C(11)	7 414(7)	2 379(6)	1 672(5)
O(1)	9 216(6)	1 524(4)	6 092(4)	C(12)	9 044(7)	2 966(5)	2 340(5)
O(2)	10 611(6)	3 978(6)	5 546(4)	C(20)	3 767(7)	1 215(5)	2 922(5)
O(3)	8 063(6)	4 484(4)	7 178(4)	C(21)	4 328(7)	1 583(6)	4 890(5)
O(4)	10 469(6)	3 431(5)	7 797(4)	C(22)	5 756(7)	2 062(5)	5 748(5)
O(5)	6 643(5)	6 830(4)	2 345(4)	C(30)	1 931(7)	1 023(7)	2 678(5)
O(6)	6 435(11)	2 330(7)	−1 086(6)	C(31)	6 730(7)	391(5)	2 243(5)
O(7)	9 598(11)	3 703(9)	−268(6)	C(32)	7 552(6)	143(5)	3 285(5)
O(11)	9 162(5)	2 984(4)	3 324(3)	C(40)	1 310(8)	127(7)	1 678(6)
O(12)	10 130(5)	3 417(4)	1 853(3)	C(41)	4 058(7)	3 288(5)	3 935(5)
O(21)	7 002(5)	2 752(4)	5 457(3)	C(42)	5 281(7)	4 303(5)	3 652(5)
O(22)	5 700(5)	1 795(4)	6 624(3)	C(50)	2 019(8)	644(8)	743(6)
O(31)	7 517(5)	865(4)	4 113(3)	C(60)	3 842(8)	819(6)	920(5)
O(32)	8 146(5)	−748(4)	3 258(4)				

Table 2. Selected bond distances (Å) and angles (°) in complex (**1**) with e.s.d.s in parentheses

N(10)–Ni	2.070(4)	O(41)–Ni	2.031(3)	O(21)–Cu	1.964(3)	C(22)–O(22)	1.201(6)
N(20)–Ni	2.093(4)	O(1)–Cu	1.965(4)	O(22)–Cu	2.855(4)	C(32)–O(31)	1.278(6)
O(11)–Ni	2.062(4)	O(2)–Cu	2.257(5)	C(12)–O(11)	1.255(6)	C(32)–O(32)	1.232(6)
O(21)–Ni	2.097(3)	O(3)–Cu	1.946(4)	C(12)–O(12)	1.244(7)	C(42)–O(41)	1.279(6)
O(31)–Ni	2.041(4)	O(4)–Cu	1.933(4)	C(22)–O(21)	1.315(6)	C(42)–O(42)	1.234(6)

N(20)–Ni–N(10)	86.6(2)	O(31)–Ni–O(21)	83.2(2)	O(3)–Cu–O(2)	103.8(3)	O(22)–Cu–O(2)	146.2(2)
O(11)–Ni–N(10)	82.4(2)	O(41)–Ni–N(10)	99.2(2)	O(4)–Cu–O(1)	93.3(2)	O(22)–Cu–O(3)	83.3(2)
O(11)–Ni–N(20)	163.4(2)	O(41)–Ni–N(20)	83.6(2)	O(4)–Cu–O(2)	93.1(2)	O(22)–Cu–O(4)	120.3(2)
O(21)–Ni–N(10)	159.1(2)	O(41)–Ni–O(11)	86.0(2)	O(4)–Cu–O(3)	89.2(2)	O(22)–Cu–O(21)	51.2(1)
O(21)–Ni–N(20)	79.8(2)	O(41)–Ni–O(21)	95.0(2)	O(21)–Cu–O(1)	87.1(2)	O(12)–C(12)–O(11)	125.1(6)
O(21)–Ni–O(11)	114.1(2)	O(41)–Ni–O(31)	173.6(2)	O(21)–Cu–O(2)	95.5(2)	O(22)–C(22)–O(21)	123.7(6)
O(31)–Ni–N(10)	84.3(2)	O(2)–Cu–O(1)	90.4(2)	O(21)–Cu–O(3)	88.4(2)	O(32)–C(32)–O(31)	125.4(6)
O(31)–Ni–N(20)	102.0(2)	O(3)–Cu–O(1)	165.5(2)	O(21)–Cu–O(4)	171.4(2)	O(42)–C(42)–O(41)	123.9(6)
O(31)–Ni–O(11)	89.2(2)			O(22)–Cu–O(1)	83.1(2)		

atomic numbering scheme; a view of the unit-cell contents is given in Figure 2. Selected bond distances and angles are listed in Table 2.

There are two different co-ordination sites for the metal atoms in the molecule. The nickel atom occupies the 'chelated' position being bonded to two nitrogen atoms and four oxygen atoms from the cdta which acts as a sexidentate ligand. The copper atom, which lies in the 'hydrated' site, is co-ordinated to four water molecules and two oxygen atoms belonging to a carboxylate group from the $[Ni(cdta)]^{2-}$ moiety. Thus, the molecular structure consists of dinuclear units in which the two metal atoms are linked through a carboxylate bridge.

The co-ordination geometry around the nickel atom is an octahedron slightly compressed along the $Ni-O_R$ direction [Ni–N (av.) 2.082(6), $Ni-O_G$ (av.) 2.080(5), $Ni-O_R$ (av.) 2.036(5) Å]. (The subscripts R and G indicate the chelate rings whose mean plane is nearly perpendicular or parallel, respectively, to the N–M–N′ plane, as established by Weakliem and Hoard.[19]) The largest Ni–O bond corresponds to the O(21) atom, which is also bonded to the copper atom. The equatorial ligands [N(10), N(20), O(11), O(21)] present a mean deviation of 0.225 Å from their least-squares plane and the nickel atom is nearly in this plane (0.029 Å apart). Tetragonal distortion from octahedral geometry is not usual for those nickel(II) complexes containing six electronically similar ligands. Sometimes such a distortion is imposed by crystal packing factors, as occurs in $K_2[NiF_4]$.[20] However, in compound (**1**), the slight shortening of $Ni-O_R$ bonds probably arises from the fact that O(21) is also bonded to the copper atom [Cu–O(21) 1.964(3) Å]. Thus, a comparatively large Ni–O(21) bond [2.097(3) Å] results. This argument is supported by the fact that related compounds such as $[Ni_2(edta)]\cdot6H_2O$,[6] $[Ni(OH_2)(H_2edta)]$,[21] and $[(en)_2Cu(edta)Ni]\cdot2H_2O$ (en = ethylenediamine),[22] in which such a bridge is absent, do not show this kind of distortion. The mean deviation of the bond angles in the $[Ni(cdta)]^{2-}$ complex from the octahedral values is 9.3°. Interatomic distances and angles within the chelating ligand are normal and similar to those exhibited by other cdta complexes.[9,10,23,24] The ligand configuration is *E,G*/*R*[25] and the cyclohexane ring shows the chair conformation defined by the planes A [C(20), C(30), C(50), C(60)], 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 56.5 and 42.7° respectively.

The unidentate carboxylate groups are asymmetric and the C–O bond distances satisfy the relation C–O(*n*1) > C–O(*n*2), as expected from the polarization of the charge density towards the metal-bonded oxygen atoms. Thus, the more asymmetric is a carboxylate group, the shorter is the Ni–O bond. The bridging carboxylate group is very asymmetric owing to the presence of two metals bonded to the same oxygen atom. The structural function of this COO group is intermediate between 3_2-a and $2-sa$.* This type of bridge is infrequent in edta-like compounds and may reflect the attack of the Cu^{II} ions on the inert sexidentate $[Ni(cdta)]^{2-}$ complex in aqueous solution.†

The co-ordination polyhedron of the copper(II) ion may be regarded as a square pyramid. The basal plane is formed by three oxygen atoms from co-ordinated water molecules [O(1), O(3), O(4)] and a fourth oxygen atom [O(21)] belonging to the bridging carboxylate group from the chelated nickel moiety. The copper–oxygen bond distances are similar and normal [av. 1.952(8) Å] and the copper is displaced 0.18 Å from the basal plane. The apex of the pyramid is occupied by an oxygen atom of a water molecule (2.257(5) Å from the metal). If the second oxygen atom of the bridging carboxylate [O(22)] is considered as 'semico-ordinated' [Cu–O(22) 2.855(4) Å] the environment of the copper would be described as an elongated and strongly distorted octahedron [O(21)–Cu–O(22) 51.2(1)°].

Crystal packing is allowed by hydrogen bonding between water molecules and the carboxylate groups.

$[(H_2O)_5Ni(cdta)Cu]\cdot H_2O$. This bimetallic compound belongs to a large family of isostructural complexes of general formula $[(H_2O)_5M(cdta)M']\cdot H_2O$ in which the metal pairs (M, M′) are: (Mn, Ni), (Zn, Ni), (Ni, Ni), (Ni, Cu), (Mn, Cu), (Mg, Zn), (Co, Ni), (Co, Cu), and (Zn, Cu). The structures of the last two complexes have been reported.[10,27] As in the (Cu, Ni) compound the bimetallic molecules show two different co-ordination sites for the metal ions (Figure 3). We have recently shown that preferential occupation of them occurs leading to ordered compounds.[11] The cationic 'hydrated' site, occupied in (**2**) by the nickel(II) ion, is defined by six oxygen atoms disposed quasi-octahedrally around the metal ion. Five of them, belonging to water molecules, define a square pyramid. The

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* In this notation, established by Porai-Koshits,[26] principal number = total co-ordination capacity of carboxylate, subscript = number of metal atoms attached to RCOO, *a* = *anti*, and *s* = *syn*.

† Labile metal–cdta complexes may form bimetallic units in solution through attack of the $M^{2+}(aq)$ ions on the free carboxylate group of quinquedentate $[M'(OH_2)(cdta)]^{2-}$ species. However, the Ni^{II} ion forms with the cdta a very inert complex towards both substitution and metal-exchange reactions, and the presence of quinquedentate species is unlikely. Furthermore, the affinity of the Cu^{II} ions for the COO groups is around ten-fold greater than that of the Ni^{II} ion. On the other hand it is known that equatorial glycinate, $-N-CH_2-COO_G$, cdta groups are more sensitive to electrophilic attack than axial, $-N-CH_2-COO_R$, ones. Based on these arguments, the isolated bimetallic compound may represent the normal mode of attack of the Cu^{II} ions on cdta-chelated complexes in metal-exchange reactions.

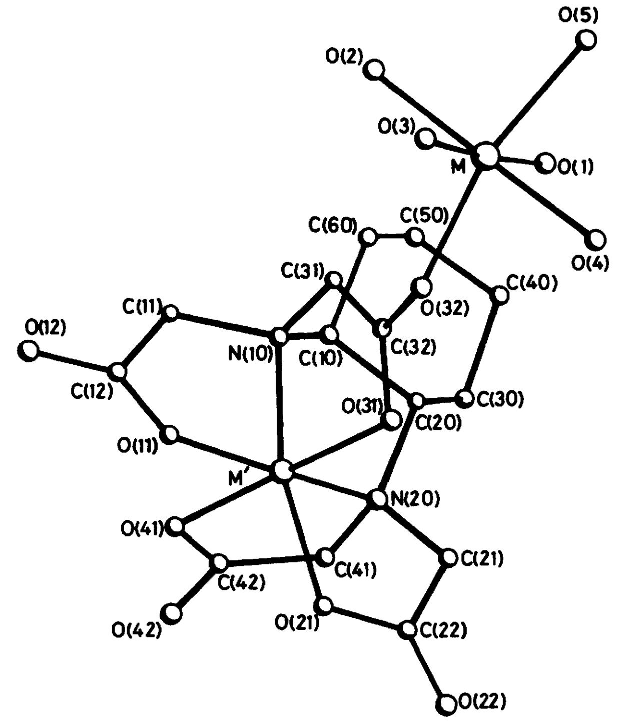

Figure 3. Molecular structure of $[(H_2O)_5M(cdta)M']\cdot H_2O$

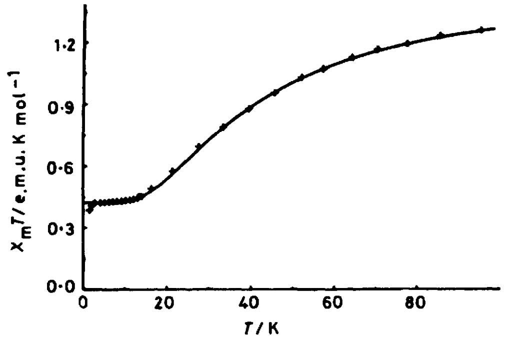

Figure 4. Magnetic behaviour of $[(H_2O)_4Cu(cdta)Ni]\cdot 3H_2O$

sixth, belonging to a bridging carboxylate of structural function *a*–2–*a*, completes the octahedron.

The 'chelated' site shows a distorted octahedral geometry and is occupied by the Cu^{II} ion, leading to a CuN_2O_4 chromophore. As occurs in the isotructural (Zn, Cu) compound a Jahn–Teller distortion along the *trans*-COO_R direction can be expected for the copper site. This assumption is supported by the results of the visible spectral analysis, which requires such a distortion. The same set of transitions is obtained for the copper chromophore in both compounds, (Ni, Cu) and (Zn, Cu).[11]

Magnetic Properties.—Variable-temperature magnetic measurements have been performed down to 2.5 K for compound (**1**) and 4.2 K for compound (**2**). While the magnetic data of (**1**) indicate a significant intramolecular antiferromagnetic coupling (Figure 4), for (**2**) there are no exchange interactions detectable to 4.2 K. The magnetic behaviour of the latter follows a Curie law with a constant value of the magnetic moment ($\mu_{eff.} = 3.6$). For (**1**) the plot of $\chi_m T$ (proportional to $\mu_{eff.}^2$) *vs.* T exhibits a rapid decrease down to $T = 15$ K followed by a plateau ($\chi_m T = 0.4$ e.m.u. K mol^{-1}). Such a feature agrees with a doublet ground state for the Cu^{II}/Ni^{II} pair, which is evidence of antiferromagnetic coupling between the two metal ions.

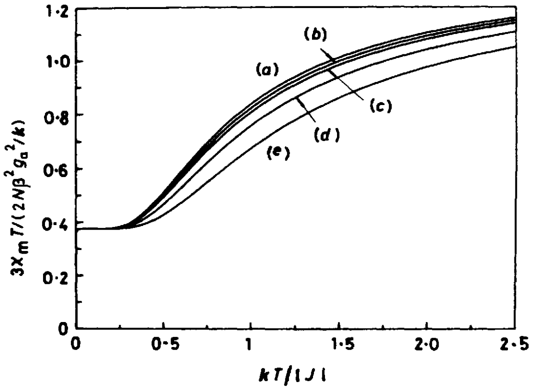

Figure 5. Influence of the zero-field splitting of Ni^{II} ion on the magnetic susceptibility of an antiferromagnetically coupled ion pair with $S_a = \frac{1}{2}$ and $S_b = 1$: $D/|J| = 0$ (*a*), 0.1 (*b*), 0.2 (*c*), 0.5 (*d*), and 1.0 (*e*). (N = Avogadro's number, k = Boltzmann constant)

Analysis of the Magnetic Data.—For a system in which pairs of Cu^{II}/Ni^{II} ions are interacting, the spin Hamiltonian describing their magnetic properties can be expressed as given below. Here,

$$\mathcal{H} = -J\hat{S}_a\hat{S}_b - (g_a\hat{S}_{az} + g_b\hat{S}_{bz})\beta H + D\hat{S}_{bz}^2$$

J is the exchange constant, β is the Bohr magneton, H is the applied magnetic hold, g_a and g_b are the Landé parameters of the Cu^{II} and Ni^{II} ions respectively, and D is the zero-field splitting parameter of the Ni^{II} ion; $\hat{S}_a$ and $\hat{S}_b$ are the local spin operators of the two ions [$S_a = \frac{1}{2}$ (Cu^{II}), $S_b = 1$ (Ni^{II})].

Magnetic data for the (Cu, Ni) compound (**1**) can be very satisfactorily fitted assuming an exchange coupling $J = -30.6$ cm^{-1} and a mean $g = 2.12$. It does not seem necessary to introduce further parameters into the fit. This fact may indicate that g alternation and local anisotropy effects are too small to be observable in the reported temperature range. This assumption can be justified as described below.

With regard to the g alternation, it should be pointed out that the description of the experimental behaviour is not improved by fitting with two different g parameters. Sets of two g values ranging from 2.1 to 2.3 give similar agreements with the experimental data; variations of the J values are $<3\%$. An accurate e.s.r. determination of the two g values on magnetically diluted compounds containing Ni^{II} and Cu^{II} ions in similar environments may provide more insight. However, it is evident from the above results that introduction into the fit of these values will not alter significantly the J value.

With regard to the nickel ion anisotropy, the influence on the magnetic susceptibility of an antiferromagnetically coupled ion pair with $S_a = \frac{1}{2}$ and $S_b = 1$ is plotted in Figure 5. Only positive D values, which are the most frequently observed for octahedral Ni^{II} environments, have been considered. As the spin Hamiltonian is written, D is positive when the splitting of the $^3A_2$ Ni^{II} ground state gives rise to a singlet ($M_s = 0$) which is at lower energy than the doublet state ($M_s = \pm 1$).

Convergence to a constant value of $\chi_m T$, corresponding to a $S = \frac{1}{2}$ ground state, is observed in all the curves. This ground state can be explained when $D = 0$ as arising from an antiferromagnetic coupling between the two local spins; when $D > 0$ it arises from the spin doublet of the Cu^{II} ion (in such cases the ground state of the Ni^{II} ion is non-magnetic). At

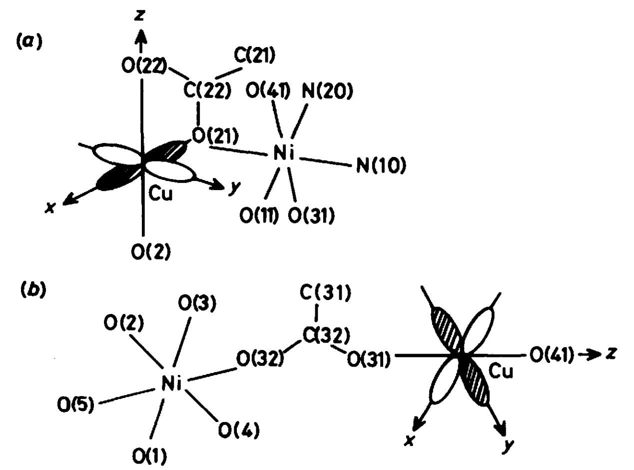

Figure 6. Orientation of the copper $d_{x^2-y^2}$ orbital: (*a*) in (**1**), (*b*) in (**2**)

intermediate temperatures (above $kT/|J| = 0.3$), the increase of the $D/|J|$ ratio leads to a decrease of the magnetic moment. Obviously, in the high-temperature limit all the curves approach the same χ_mT value (corresponding to the sum of the Curie constants of both ions).

In the case under consideration, taking into account that D values ranging from 2 to 6 cm^{-1} are commonly observed for Ni^{II} ions,[28] an upper limit of $D/|J| = 0.2$ can be assumed. For Ni^{II} located in similar sites {the 'chelated' site of [MM′(edta)]·6H_2O, for example}, D values of *ca.* 6 cm^{-1} have been estimated from specific heat measurements.[29] An inspection of Figure 5 shows that the curve with $D/|J| = 0.2$ is practically superimposed on that with $D = 0$. Such an observation justifies neglecting D in the reported fit of the data, and allows us to predict that magnetic measurements at lower temperatures will not be useful in order to obtain a precise value of this parameter.

Magnetostructural Correlations.—Analysis of the magnetic data has shown a very different exchange coupling in the two compounds. This fact can be understood in terms of the structural differences in the bridging network and in the two co-ordination sites.

In the (Ni, Cu) complex (**2**), the bridging carboxylate acts as a bidentate ligand adopting an *a*-2-*a* structural function.[26] In general, bridging carboxylate groups provide poor support for the propagation of exchange, leading to weak interactions;[30] only when the structural function is *s*-2-*s*, as for example, in copper(II) acetate, have large magnetic couplings been detected.[31] On the contrary, in the (Cu, Ni) complex (**1**), the topology of the bridge gives rise to a coupling essentially controlled by an oxygen atom, which constitutes a good support for the exchange.[32]

The relative orientation of the co-ordination polyhedra with regard to the bridging group determines the orientation of the metal orbitals involved in the exchange interactions. If these are favourably oriented to interact with orbitals of the bridging group, a significant exchange coupling can be achieved. For Cu^{II} in octahedral sites, the $d_{x^2-y^2}$ orbital essentially contains the unpaired electron. In the present case this orbital points toward the bridging group in (**1**), being localized in a plane perpendicular to the bridge in (**2**) (Figure 6). Thus, an effective overlap between the exchange-propagating orbitals of the bridge and the $d_{x^2-y^2}$ metal orbital is only possible in the (Cu, Ni) bimetallic complex (**1**). This, together with the better support of the exchange provided by the oxygen atom, explains the large antiferromagnetic coupling detected in (**1**). On the other hand, both the bridging network and the orientation of the copper polyhedron do not favour the exchange in (**2**). This argument explains the lack of magnetic interactions observed for the latter compound.

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