Large-angle *X*-Ray Scattering Study and Magnetic Properties of Amorphous Complexes $[MM'(cdta)]\cdot nH_2O$ (M, M' = Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}; cdta = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate)

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Investigation by large-angle *X*-ray scattering of the amorphous complexes $[MM'(cdta)]\cdot nH_2O$ (M = M' = Ni^{II}, Co^{II}, or Cu^{II}; M = Zn^{II}, M' = Cu^{II}; M = Ni^{II}, M' = Cu^{II}; M = Co^{II}, M' = Cu^{II}; and M = Co^{II}, M' = Ni^{II}) has revealed that such complexes consist of binuclear entities, made up of cationic and anionic octahedral complexes bridged by a carboxylate group from the cdta ligand (*trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate). Their magnetic properties have been studied by assuming a Heisenberg exchange coupling between the two metal ions. All the compounds (except ZnCu) exhibit a weak antiferromagnetic interaction, with $2J$ values ranging from -1.6 to -4.7 cm^{-1}.

A systematic development of structurally ordered bimetallic compounds has been achieved in the last few years.[1] The families of crystalline and amorphous complexes $[MM'(edta)]\cdot 6H_2O$ (edta = ethylenediaminetetra-acetate) as well as crystalline $[MM'(cdta)]\cdot nH_2O$ (cdta = *trans*-cyclohexane-1,2-diaminetetra-acetate) (M and M' are bivalent first-row transition-metal ions) have provided nice examples of structural versatility in studies of a wide variety of low-dimensional ferrimagnetic systems[2–6] and antiferromagnetic dimers[7,8] respectively.

An investigation of the correlation between the local order and magnetic properties in the amorphous complexes $[MM'(cdta)]\cdot nH_2O$ (M and M' are bivalent first-row transition-metal ions) has now been carried out, in the light of their weak antiferromagnetic interactions (exchange coupling parameters ranging[7,8] from -2.2 to -14.7 cm^{-1}) and structural studies using large-angle *X*-ray scattering (LAXS).[9–12]

Experimental

Preparation of Complexes.—The crystalline compounds were first prepared[13] by reactions between aqueous solutions of $Na_4[cdta]$ and the corresponding metal nitrates dissolved in a minimum amount of water and in a 1:1 molar ratio. Crystals were formed upon slow addition of acetone and cooling in a refrigerator. After dissolving the crystals in a minimum amount of water, amorphous solids were obtained by slow evaporation. All the compounds $[Ni_2(cdta)]\cdot 8H_2O$ (**1**), $[Co_2(cdta)]\cdot 8H_2O$ (**2**), $[Cu_2(cdta)]\cdot 4H_2O$ (**3**), $[ZnCu(cdta)]\cdot 6H_2O$ (**4**), $[NiCu(cdta)]\cdot 7H_2O$ (**5**), $[CoCu(cdta)]\cdot 7H_2O$ (**6**), and $[CoNi(cdta)]\cdot 7.5H_2O$ (**7**) were prepared by using the same procedure [Found: C, 27.8; H, 5.7; N, 4.4; Ni, 19.4. $C_{14}H_{34}N_2Ni_2O_{16}$, (**1**), requires C, 27.8; H, 5.7; N, 4.6; Ni, 19.4. Found: C, 27.8; H, 5.5; Co, 19.4; N, 4.7. $C_{14}H_{34}Co_2N_2O_{16}$, (**2**), requires C, 27.8; H, 5.7; Co, 19.5; N, 4.6. Found: C, 30.5; H, 5.0; Cu, 23.4; N, 5.1. $C_{14}H_{26}Cu_2N_2O_{12}$, (**3**), requires C, 31.1; H, 4.8; Cu, 23.5; N, 5.2. Found: C, 29.5; H, 5.2; Cu, 10.9; N, 4.9; Zn, 11.0. $C_{14}H_{30}CuN_2O_{14}Zn$, (**4**), requires C, 29.0; H, 5.2; Cu, 11.0; N, 4.8; Zn, 11.3. Found: C, 28.0; H, 5.4; Cu, 10.5; N, 4.7; Ni, 9.8. $C_{14}H_{32}CuN_2NiO_{15}$ requires C, 28.5; H, 5.5; Cu, 10.8; N, 4.7; Ni, 9.9. Found: C, 28.2; H, 5.4; Co, 9.6; Cu, 10.9; N, 5.0. $C_{14}H_{32}CoCuN_2O_{15}$, (**6**), requires C, 28.5; H, 5.5; Co, 10.0; Cu, 10.8; N, 4.7. Found: C, 28.3; H, 5.7; Co, 9.7; N, 4.6; Ni, 9.6. $C_{14}H_{33}CoN_2NiO_{15.5}$ requires C, 28.3; H, 5.6; Co, 9.9; N, 4.7; Ni, 9.9%].

Large-angle X*-Ray Scattering* (*LAXS*) *Data Collection*.—The carefully crushed amorphous powders were pressed into pellets under 210 kg cm^{-2} and used for the registration of *X*-ray diffuse spectra (mean thickness of the pellets: 0.5 mm).

The diffuse spectrum scattered by the sample irradiated with graphite-monochromatized Mo-K_α radiation was obtained by using an automatic diffractometer. About 500 intensities corresponding to equidistant s points [$s = 4\pi(\sin\theta)/\lambda$] were collected in the range $0.617 < s < 16.615$ Å^{-1}. All the measurements were carried out at 22 °C.

Scattered intensities were corrected for polarization and absorption effects [namely $I_c(s)$] and then normalized by comparison with the sum of coherent and incoherent independent intensities in the vicinity of high θ angles.

The reduced intensities, $i(s)$, were calculated as in equation (1) where K is the normalization constant, $I_c(s)$ is the corrected

$$i(s) = KI_c(s) - \Sigma_i n_i\{[f_i(s) + \Delta f'_i]^2 + \Delta f''^2_i + I_{i(\mathrm{inch})}(s)\} \quad (1)$$

intensity, n_i is the number of atoms i in the chosen unit volume, $f_i(s)$ is the atomic scattering factor, $\Delta f'_i$ and $\Delta f''_i$ are the real and imaginary parts of the anomalous dispersion, and $I_{i(\mathrm{inch})}(s)$ is the total incoherent radiation for atom i. The radial distribution, $D(r)$, is then expressed in the form (2) where ρ^0 is the

$$D(r) = 4\pi r^2\rho^0 + 2r\pi^{-1}\int_{s_{\mathrm{min.}}}^{s_{\mathrm{max.}}} si(s)M(s)\sin(rs)\mathrm{d}s \quad (2)$$

average electron density of the sample and $M(s)$ is a modification function defined by $[f^2_i(0)/f^2_i(s)][\exp(-s^2/100)]$.

The corresponding theoretical intensities were calculated from the relation (3) where r_{ij} is the interatomic distance

$$i(s) = \Sigma_i\Sigma_j f_i(s)f_j(s)[\sin(r_{ij}s)/r_{ij}s]\exp(-b_{ij}s^2) \quad (3)$$

between atoms i and j and b_{ij} is a temperature factor affecting this interaction. Other details of the data processing are given elsewhere.[14,15]

Magnetic Measurements.—The magnetic susceptibilities were measured in the range 4—100 K with a pendulum-type apparatus[16] equipped with a helium cryostat. The uncertainty on the data is lower than 0.1 K for temperatures and 2×10^{-5} e.m. units mol^{-1} for susceptibilities (e.m. units = S.I. unit $\times 10^6/4\pi$). Corrections (in 10^{-6} cm^3 mol^{-1}) for the diamagnetism of the complexes were estimated from Pascal constants as 318.14, 318.14, 266.14, 292.14, 305.14 for complexes **(1)**, **(2)**, **(3)**, **(4)**, and **(5)** respectively.

Results and Discussion

LAXS Study.—The purpose of this structural study was a comparison between the structural order around the metal ions in these amorphous compounds and that observed in the corresponding crystalline complexes.

The modelling of the local order in the $[MM'(cdta)]\cdot nH_2O$ amorphous phases is based on: identification of the chelated metal ion from thermodynamic and spectroscopic studies; knowledge of the crystalline phases, the structures of which are plausible models; and study of the experimental radial distribution functions.

Five structural types (Figure 1) have been established by *X*-ray diffraction studies.

Type (**A**). This is represented by the structure of the homometallic $[Cu_2(cdta)]\cdot 4H_2O$ complex, which is made up of infinite chains with alternating cationic $[Cu(H_2O)_4O_2]^{2+}$ and anionic $[Cu(cdta)]^{2-}$ sites. The cdta ligand is co-ordinated through N(10), N(20), O(11), O(21), O(31), and O(41). The connection with the hydrated site (dimerization) and chain formation are made through oxygen atoms O(32) and O(42).[7]

Type (**B**). The $[MM'(cdta)]\cdot 6H_2O$ series with MM′ = ZnCu, NiCu, CoCu, MnCu, Ni_2, ZnNi, MnNi, CoNi, MgNi, MnZn, and MgZn crystallizes with this structural type which consists of binuclear units. The cdta co-ordination and the dimerization through O(32) are similar to the pattern observed in type (**A**).[17]

Type (**C**). The $[CuNi(cdta)]\cdot 7H_2O$ complex is the only example showing such a structure made up of binuclear units. The chelated metal ion environment is still the same as in (**A**) and (**B**) but the dimerization takes place through oxygen atoms O(21) and O(22).[18]

Type (**D**). This structure, formed by tetrameric units, is observed for the family $[MM'(cdta)]\cdot 9H_2O$ with MM′ = Co_2, MnCo, ZnCo, and Zn_2. The co-ordination of the cdta ligand is still the same as above but the M′–O(11) bond is considerably lengthened to connect the hydrated site. A water molecule is co-ordinated to the chelated metal ion. The oxygen atom O(32) is involved in formation of the tetranuclear unit.[19]

Type (**E**). The complex $[MnCd(cdta)]\cdot 7H_2O$ is the only one showing this structure, which is formed by infinite chains. The same ligand atoms are co-ordinated to the chelated metal ion. Seven-co-ordination of the cadmium atom is achieved, including O(32) which participates in the dimerization and in the chain formation.[20]

This summary of the structural knowledge on cdta complexes allows us to formulate four conclusions.

(*a*) The metal ion which occupies the chelate site always exhibits the greatest stability constant $K_{M(cdta)^{2-}}$ (thermodynamic control).[13] The only exception is the CuNi complex, type (**C**), but in this case a different synthetic procedure was used: kinetic control is operative [assistance offered by the inertness of Ni(cdta)] according to the order of addition of the metal-ion solutions to an aqueous solution of cdta ligand. Consequently, type (**C**) is not plausible as a model for the amorphous phases. The anionic site will be occupied by a copper atom in every MCu complex and by a nickel atom in CoNi.

(*b*) The copper and nickel atoms are always in an octahedral environment. The most plausible co-ordination of the cdta ligand involves the two nitrogen atoms and the oxygen atoms O(11), O(21), O(31), and O(41).

(*c*) The dimerization, or the chain formation, seems to take place preferably through O(32) or O(42), *i.e.* through oxygen atoms from glycinic rings perpendicular to the ethylenediamine ring.

(*d*) In the case of the Co_2 complex, the structural type (**D**) cannot be *a priori* discarded as it has been observed for the corresponding crystalline phase. On the contrary, type (**E**) which implies true seven-co-ordination is not plausible.

From the preceding points, it is possible to infer a short-range order which is common to most of the cdta complexes. Examination of the experimental radial distribution functions (r.d.f.s) confirms this idea and allows the amorphous phases to be classified into two groups based on the intensity of the third peak (4.2—4.3 Å). For the ZnCu, Cu_2, CoNi, and Ni_2 complexes, this peak is very low compared to the co-ordination peak (Figure 2). On the contrary, the NiCu and Co_2 r.d.f.s show a rather intense third peak (Figure 3). An intermediate situation is observed for CoCu but the comparison of the CoCu and NiCu r.d.f.s shows that these complexes have the same local order.

Theoretical r.d.f.s have been calculated from the five crystalline structural types. The modelling of the local order has been done on the basis of the geometry of the ZnCu complex, *i.e.* dimeric units. This choice is justified by the fact that this type (**B**) is observed, in the crystalline state, for every amorphous phase prepared except Co_2. The theoretical r.d.f., calculated from one binuclear unit, cannot fit the experimental functions, even in the short distances; the intensities of the third and fourth peaks are too low. This means that the local order is more extended and must be explained through a stacking of the dimers. The experimental function, until 6 Å, can be fitted only with the model shown on Figure 4. The other types failed to explain the experimental functions. In particular, types (**C**) and (**E**) lead to a wrong position for the third peak (3.6 Å).

Several remarks can be made.

(*i*) The slight shift between the experimental and calculated co-ordination peaks shows a relaxation in the amorphous state.

(*ii*) After 6 Å, the model cannot explain the experimental functions; particularly the peaks at 6 Å for the CoNi and 8.7 Å for the Ni_2 complex. So, it is necessary to expand the model. However, the number of parameters becomes very great and it is very difficult to define precisely the relative positions of the dimeric units. Besides, this extension is not necessary to explain the physical properties and especially the magnetic behaviour.

(*iii*) Comparison of the experimental r.d.f.s for the NiCu or CoCu, and CoNi complexes shows that there are no important differences between the local orders (Figure 5). However, the greater intensity at 4.2 Å for the NiCu complex suggests a metal–metal interaction at this distance. This can correspond to an asymmetrical co-ordination scheme as observed for the structural type (**D**).

(*iv*) No satisfactory model has been found for the Co_2 complex.

Magnetic Properties.—The magnetic behaviour of compounds **(1)**—**(5)** is shown in Figure 6. The magnetic behaviour of the ZnCu compound is obviously independent of temperature and the susceptibility follows a Curie law over the whole temperature range. The product $\chi_m T$ *versus* T (χ_M being the susceptibility for a binuclear unit) for the complexes exhibits a smooth decrease in the low-temperature region revealing the existence of a weak antiferromagnetic interaction between the metal ions.

The exchange in polynuclear units is usually expressed in terms of the exchange coupling constant J. For binuclear species

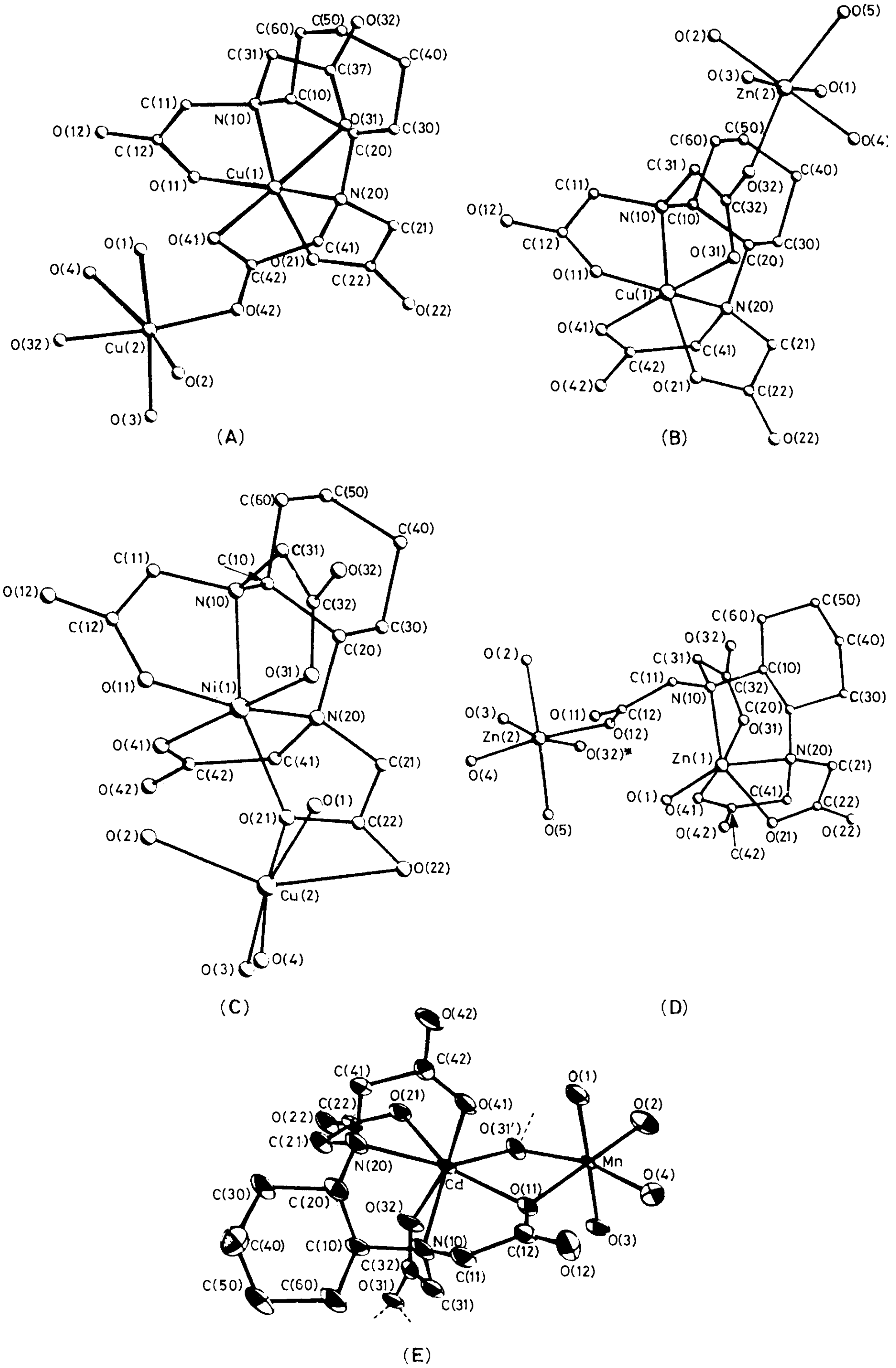


Figure 1. Perspective view of the five known structural types in the $[MM'(cdta)]\cdot nH_2O$ family

the Hamiltonian is $H = -2JS_1S_2$, at least when only exchange between nearest neighbours is considered. The magnetic susceptibility χ_M can be derived from this Hamiltonian.

The values of the parameters, where obtained by least-squares fitting by the theoretical equations to the experimental data is detailed here. The agreement between the experimental and calculated data is given by $R = [\Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi_{obs.}^2]^{\frac{1}{2}}$.

In the least-squares analysis for the Cu_2 system ($S_1 = S_2 = \frac{1}{2}$) the Bleaney–Bowers equation (4), for copper dimers,[21]

$$\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1} \quad (4)$$

was used where the symbols have their usual meaning. The fitting of the experimental data led to the values $2J = -4.7$ cm^{-1}, $g = 2.0$, and $R = 1.93 \times 10^{-4}$.

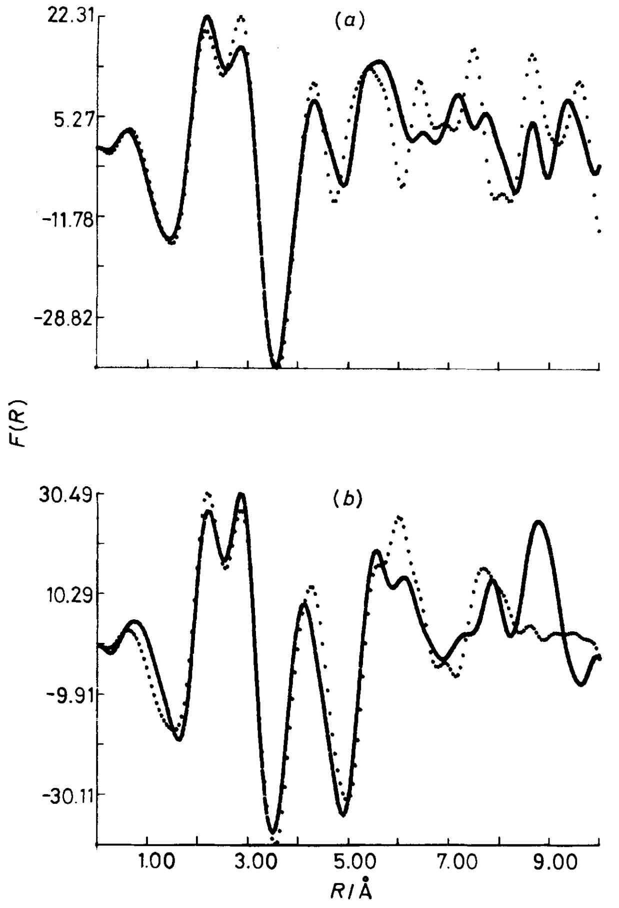


Figure 2. Experimental radial distribution curves for (*a*) ZnCu (full line) and Cu_2 (dotted line) complexes and (*b*) Ni_2 (full line) and CoNi (dotted line) complexes

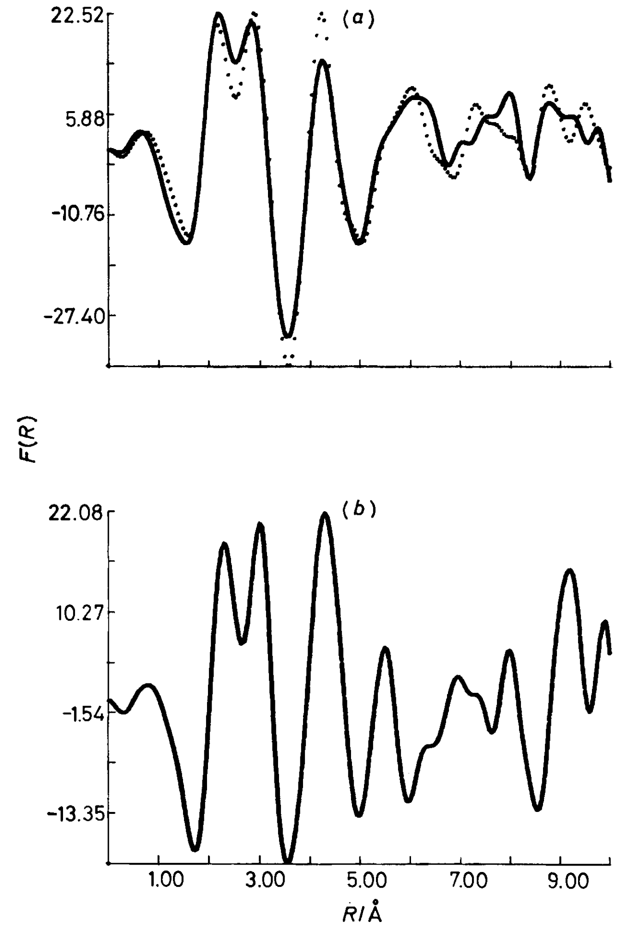


Figure 3. Experimental radial distribution curves for (*a*) CoCu (full line) and NiCu (dotted line) complexes and (*b*) the Co_2 complex

For the Ni_2 complex, $S_1 = S_2 = 1$, the parameters obtained were fitted by equation (5). Least-squares analysis yielded $2J =$

$$\chi_M = (2N\beta^2g^2/kT)[1 + 5\exp(4J/kT)]/[3 + 5\exp(4J/kT) + \exp(-2J/kT)] \quad (5)$$

-1.7 cm^{-1}, $g = 2.08$, and $R = 3.33 \times 10^{-4}$. The fit was not improved by inclusion of zero-field splitting (D)[22] ($2J = -1.6$ cm^{-1}, $g = 2.07$, $D = -2.0$ cm^{-1}, and $R = 3.56 \times 10^{-4}$).

The Co^{II} in a predominantly cubic environment has a twelve-fold degenerate ground state that corresponds to $^4T_1$. Spin–orbit coupling splits this term into a sextet, a quartet, and a Kramers doublet. The energy separation between the quartet and ground-state doublet is about 300 cm^{-1} [for $\lambda \approx -180$ cm^{-1}, κ (orbital reduction factor) ≈ 0.75], and it is clear that the upper levels cannot be neglected in calculating susceptibilities at temperatures corresponding to such a separation. The size of the problem is too great for expedient solution and is essentially unsolved in the sense that there is no widely accepted model.[23] We chose the 'Lines complete theory'[24,25] for a cobalt(II) dimer but with exchange splitting neglected in the higher single-ion levels ($a = 0, b = 0$), equation (6), where $g(T)$ is a temperature-

$$\chi_M = \{N\beta^2[g(T)]^2/kT\}\{2/[3 + \exp(-50J/9kT)]\} \quad (6)$$

dependent factor which takes into account the contribution of these levels [equation (7)]. The fitting of the experimental data led to $2J = -2.9$ cm^{-1}, $\kappa = 0.73$, $\lambda = -172$ cm^{-1}, and $R = 1.77 \times 10^{-4}$.

$$\{[g(T)]^2/4\}[1 + 2\exp(9\kappa\lambda/4kT) + 3\exp(6\kappa\lambda/kT)] = (1/36)(10 + 3\kappa)^2 - (10kT/81\kappa\lambda)(4 + 3\kappa)^2 + [(1/90)(22 - 6\kappa)^2 + (88kT/2\,025\kappa\lambda)(4 + 3\kappa)^2]\exp(9\kappa\lambda/4kT) + [(7/20)(6 - 3\kappa)^2 + (2kT/25\kappa\lambda)(4 + 3\kappa)^2\exp(6\kappa\lambda) \quad (7)$$

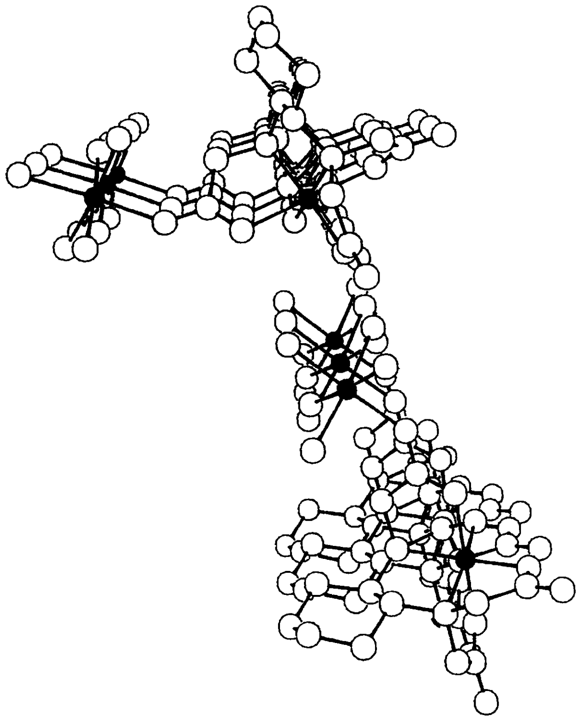
For the NiCu complex we used equation (8)[26] with local spins $S_{Cu} = \frac{1}{2}$ and $S_{Ni} = 1$, with $\delta = (g_{Cu} - g_{Ni})/3$. The fit gave $2J = -2.0$ cm^{-1}, $g_{Ni} = 2.12$, $g_{Cu} = 2.10$, and $R = 6.22 \times 10^{-5}$.

$$\chi_M = (N\beta^2/4kT)\{[(g_{Ni} - \delta)^2 + 10(g_{Ni} + \delta)^2\exp(3J/kT)]/[1 + 2\exp(3J/kT)]\} - (4N\beta^2\delta^2/3J)\{[1 - \exp(3J/kT)]/[1 + 2\exp(3J/kT)]\} \quad (8)$$

For the ZnCu system the Curie law ($S = \frac{1}{2}$) with g as the only adjustable parameter was used. A g value of 2.10 and $R = 1.23 \times 10^{-4}$ was obtained.

The strong overlap between the $x^2 - y^2$ type magnetic orbitals centred on the metal ions and delocalized towards the oxygen atoms of the carboxylate bridge leads to a large antiferromagnetic coupling. Such a situation occurs in copper acetate-type binuclear complexes.[27]

The special efficiency of Cu^{II} in antiferromagnetic interactions compared to Ni^{II}, Co^{II}, or Fe^{III} is easily evidenced when comparing J values in a series of μ-oxalato complexes[28] and a series of bimetallic complexes[29] of general formula $[CuMLCl_2]\cdot xH_2O$ where L is the binucleating Robson ligand.[30] To deal with comparable values we take into account the number of



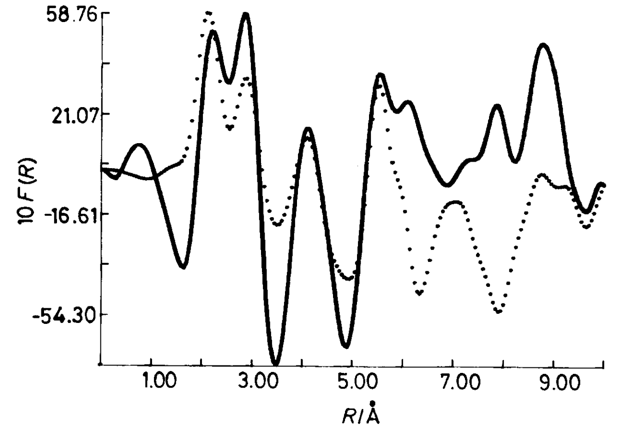


Figure 4. Comparison of the experimental radial distribution curve (full line) with the theoretical curve (dotted line) calculated from the model shown for the Ni_2 complex

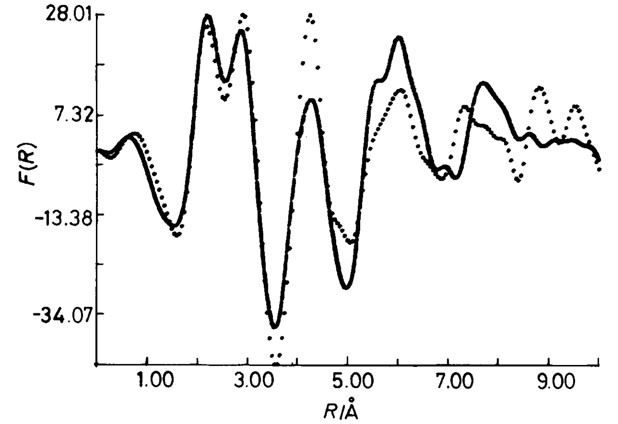


Figure 5. Experimental radial distribution curves for the CoNi (full line) and NiCu (dotted line) complexes

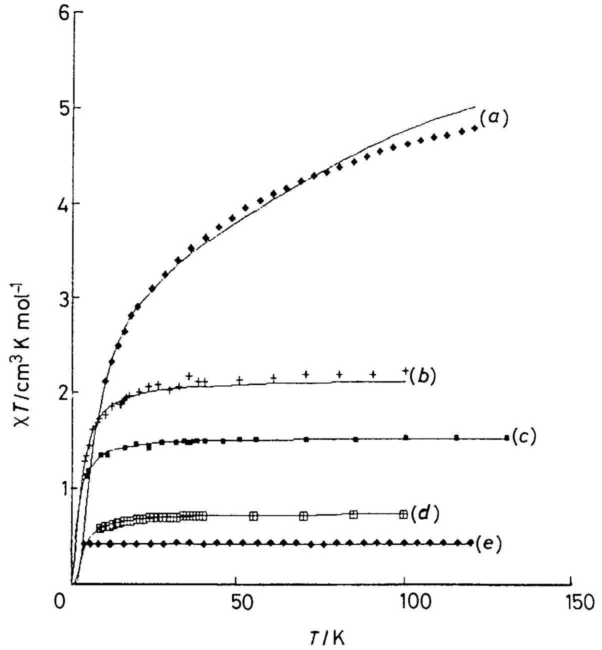


Figure 6. Magnetic behaviour of (*a*) the Co_2, (*b*) Ni_2, (*c*) NiCu, (*d*) Cu_2, and (*e*) ZnCu complex

unpaired electrons on each magnetic centre and compare the $(-n_An_B2J)$ values.[23,31] For the present compounds (geometries are assumed to be very similar) we obtained the following values. These values show, at least for the three first compounds, a rough decrease of the exchange parameter with increasing number of unpaired electrons. For the Co_2 system the Co^{II} is orbitally degenerate, so that the $2J$ value may be less reliable than for the other three compounds. Except for the NiCu system there is an increase in exchange magnitude $(-n_An_B2J)$ when we descend the series.

Complex	$-2J/cm^{-1}$	$-n_An_B2J/cm^{-1}$
Cu_2	4.7	4.7
NiCu	2.0	4.0
Ni_2	1.7	6.8
Co_2	2.9	26.1

The very low value of $2J$ obtained for the present compounds may be understood in terms of the nature of the magnetic orbital involved in the exchange interactions. Figure 7 shows the molecular structure for these compounds based on the knowledge of the molecular structure of the homologous crystalline compound whose structural results are presented in this paper. The extent of the antiferromagnetic interactions depends on the overlap between the 3*d* magnetic orbitals and the bridge symmetry-adapted molecular orbital and the energy difference between these orbitals. As can be seen from Figure 7, the $d_{x^2-y^2}$ magnetic orbitals of the Cu^{II} are unfavourably oriented for interaction with the carboxylate orbitals, and moreover the interaction parameter through the carboxylate bridge is expected to be very small, owing to the *anti-syn* configuration at this bridge.[32]

The d_{z^2} magnetic orbital (in the chelate ion) of the Ni_2 and Co_2 complexes is favourably oriented to interact, increasing the magnetic exchange magnitude $(-n_An_B2J)$ with respect to the Cu_2 species. For the NiCu complex the situation is similar to that of Cu_2, except that the Ni^{II} occupies the hydrate position.

We consider the very small $2J$ values as the maximum values expected for these compounds, since the dipolar interactions could have some importance.

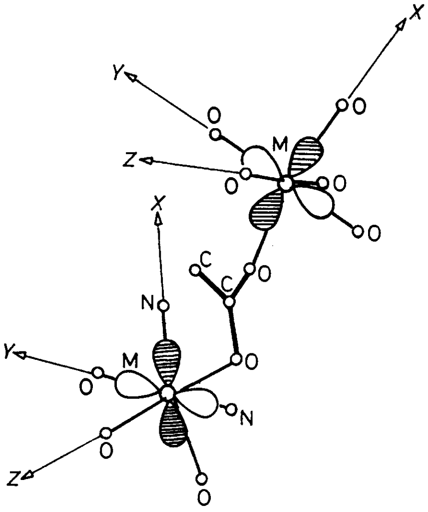


Figure 7. Superexchange mechanism in the $[MM'(cdta)]\cdot nH_2O$ dimers: projection in a bridging carboxylate plane

Conclusions

The goal of this study was to correlate the local structure of amorphous complexes to their magnetic behaviours. The LAXS studies have shown the great similarity of the short-range order of the structures.

The magnetic behaviour of these compounds support the structural hypothesis that these amorphous compounds are made up of dimer units, with a very weak antiferromagnetic coupling (except for the ZnCu complex) at low temperature according to the type of bidentate bridging carboxylate group.

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