

Rational Design of Homo and Hetero Hexanuclear Coordination Compounds: Syntheses and Magnetic Properties of $[\text{Cu}_2^{\text{II}}\text{M}_4^{\text{II}}]$ ($\text{M} = \text{Cu}, \text{Ni}$) Species and the Crystal Structure of $\{\text{Cu}(\text{tmen})(\text{H}_2\text{O})\}_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}](\text{H}_2\text{O})\}(\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$

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New homo- and heterometallic hexanuclear complexes of formula $\{\text{Cu}(\text{tmen})(\text{H}_2\text{O})\}_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}](\text{H}_2\text{O})\}(\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$ [**Cu₆-tmen**] $\{\text{Cu}(\text{pmdien})\}_4[\text{Cu}_2\text{L}](\text{ClO}_4)_4 \cdot 4 \text{H}_2\text{O}$ [**Cu₆-pmdien**] and $\{\text{Ni}(\text{cyclam})\}_4[\text{Cu}_2\text{L}](\text{ClO}_4)_4 \cdot 4 \text{H}_2\text{O}$ [**Cu₂Ni₄-cyclam**] [H_8L = tetrakis(aminomethylene)methane-tetrakis(oxamic acid), tmen = *N,N,N',N'*-tetramethylethylenediamine, pmdien = *N,N,N',N',N''*-pentamethyldiethylenetriamine, and cyclam = 1,4,8,11-tetraazacyclotetradecane] have been synthesized. The crystal structure of [**Cu₆-tmen**] has been determined by single-crystal X-ray diffraction. The structure consists of cationic $\{\text{Cu}(\text{tmen})(\text{H}_2\text{O})\}_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}](\text{H}_2\text{O})\}^{4+}$ hexanuclear units. The hexanuclear cation is made up of two symmetry-related oxamato-bridged trinuclear units connected through the central carbon atom C(6) of the L^{8-} ligand. Variable-temperature magnetic susceptibility

measurements (1.8–300 K) have been performed for these series of complexes including the dinuclear precursors of formula $\text{Na}_4[\text{Cu}_2\text{L}] \cdot 10.5 \text{H}_2\text{O}$ [**Cu₂-Na**], $(\text{NMe}_4)_4[\text{Cu}_2\text{L}] \cdot 4 \text{H}_2\text{O}$ [**Cu₂-NMe₄**] and $(\text{PPh}_4)_4[\text{Cu}_2\text{L}] \cdot 6 \text{H}_2\text{O}$ [**Cu₂-PPh₄**]. The magnetic data have been interpreted. Evidence of a weak intramolecular ferromagnetic interaction between the two Cu^{II} ions in $[\text{Cu}_2\text{L}]^{4-}$ has been observed. For the hexanuclear species, the interaction through the oxamato bridge was found to be equal to −6790, −2650, and −1643 μJ (−342, −133, and −82 cm^{-1}) for [**Cu₆-tmen**], [**Cu₆-pmdien**], and [**Cu₂Ni₄-cyclam**], respectively. In these complexes, the weak intramolecular ferromagnetic coupling between the two Cu^{II} ions within the dinuclear synthon was masked by intermolecular interactions or local anisotropy.

Introduction

One of the current challenges for inorganic chemists is the design and synthesis of high nuclearity complexes of the first row transition metal ions in a controlled fashion.^[1–2] The pathways used to obtain these intriguing species are based, essentially, on the following synthetic schemes: i) the self-assembly method,^[3–10] ii) the use of polynucleating ligands,^[11–12] or iii) the use of complexes as ligands.^[13–18] In the former case, the nature of the final products cannot be determined a priori. In contrast, the latter two methods proceed step by step. Hence they provide an alternative route to gain control of both the nuclearity and the dimensionality of the polymetallic edifice and, furthermore, allow the preparation of species containing metal ions of different natures, i.e. heterometallic complexes.

In a previous paper,^[19] we described the synthesis of a new dinuclear copper(II) complex $[\text{Cu}_2\text{L}]^{4-}$ (Figure 1), where L^{8-} is the bis-tetradentate chelating ligand *N,N',N'',N'''*-tetramethylenemethanetetrakis(oxamato).

This dinuclear complex can be used as a building block for the synthesis of high nuclearity complexes or extended networks, following the strategy of “complexes as ligands”. The design of this molecular synthon fulfils several important criteria. Firstly, $[\text{Cu}_2\text{L}]^{4-}$ is potentially a tetrakis-bidentate ligand that can coordinate to four other metal ions through the external oxygen atoms. The use of ancillary ligands on these metal ions avoids polymerisation, and leads to polynuclear species instead of extended networks. Also, the chelating nature of the oxamate groups ensures high values for the stability constants of the polynuclear complexes. Secondly, from a topological point of view, the connectivity number of four of this ligand is favourable for the construction of high-spin dendrimer-like molecules, and also for the synthesis of molecular-based magnets, since the critical temperature T_C is related to the number of neighbours of each magnetic centre.^[20] Furthermore, the geometry of the ligand with non-coplanarity between the two planes containing the copper ions, as shown in Figure 1, has been designed with the aim of inducing a ferromagnetic coupling between the two Cu^{II} ions.^[21] Such a coupling should, therefore, lead to a molecular synthon with an $S = 1$ ground state. Polynuclear complexes or extended networks built with this dinuclear complex are expected to have attractive magnetic properties.

This “complexes as ligands” strategy has been successfully applied in the preparation of the homometallic hexanuclear complexes $\{\text{Cu}(\text{tmen})(\text{H}_2\text{O})\}_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}]\}$ -

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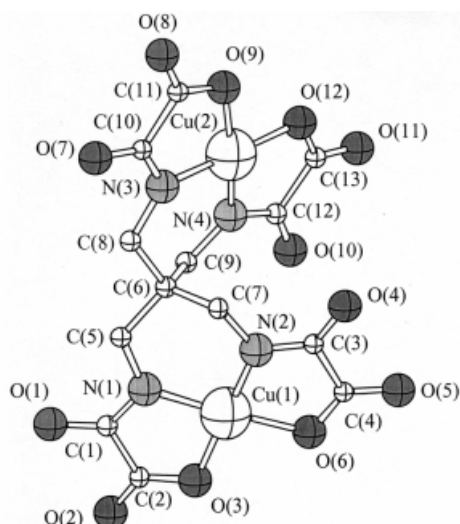


Figure 1. Perspective view of the anionic dinuclear unit $[\text{Cu}_2\text{L}]^{4-}$ of $[\text{Cu}_2\text{-Na}]$ (hydrogen atoms have been omitted for clarity); crystallographic data of this compound are reported in reference^[19]

$(\text{H}_2\text{O})\{\text{ClO}_4\}_4 \cdot 2 \text{H}_2\text{O}$ $[\text{Cu}_6\text{-tmen}]$ (tmen = *N,N,N',N'*-tetramethylethylenediamine) and $\{[\text{Cu}(\text{pmdien})]_4[\text{Cu}_2\text{L}]\}(\text{ClO}_4)_4 \cdot 4 \text{H}_2\text{O}$ $[\text{Cu}_6\text{-pmdien}]$ (pmdien = *N,N,N',N',N''*-pentamethyldiethylenetriamine), and a heterometallic hexanuclear complex $\{[\text{Ni}(\text{cyclam})]_4[\text{Cu}_2\text{L}]\}(\text{ClO}_4)_4 \cdot 4 \text{H}_2\text{O}$ $[\text{Cu}_2\text{Ni}_4\text{-cyclam}]$. We report herein their synthesis and magnetic characterisations as well as the magnetic properties of their dinuclear precursors $\text{Na}_4[\text{Cu}_2\text{L}] \cdot 10.5 \text{H}_2\text{O}$ $[\text{Cu}_2\text{-Na}]$, $(\text{NMe}_4)_4[\text{Cu}_2\text{L}] \cdot 4 \text{H}_2\text{O}$ $[\text{Cu}_2\text{-NMe}_4]$ and $(\text{PPh}_4)_4[\text{Cu}_2\text{L}] \cdot 6 \text{H}_2\text{O}$ $[\text{Cu}_2\text{-PPh}_4]$, and the X-ray structural determination of $[\text{Cu}_6\text{-tmen}]$.

Results and Discussion

Synthesis of the Complexes

The dinuclear precursors were obtained by reaction of the tetraethyl ester derivative of the ligand ($\text{Et}_4\text{H}_4\text{L}$) with NaOH or NMe_4OH , for $[\text{Cu}_2\text{-Na}]$ and $[\text{Cu}_2\text{-NMe}_4]$ respectively, followed by addition of Cu^{2+} . The tetraphenylphosphonium derivative $[\text{Cu}_2\text{-PPh}_4]$ was then obtained by successive metatheses with Ag^+ and PPh_4^+ . The hexanuclear compounds were synthesised by adding four equivalents of an external complex to the dinuclear $[\text{Cu}_2\text{-Na}]$ precursor and isolated as microcrystalline powders after slow evaporation of the solvent. External complexes were $\text{Ni}(\text{cyclam})\cdot(\text{ClO}_4)_2(\text{H}_2\text{O})_2$, or in situ generated $\text{Cu}(\text{tmen})(\text{ClO}_4)_2$ or $\text{Cu}(\text{pmdien})(\text{ClO}_4)_2$.

Crystal Structure Analysis

The structure of $[\text{Cu}_6\text{-tmen}]$ consists of hexameric copper(II) complex cations, $\{[\text{Cu}(\text{tmen})(\text{H}_2\text{O})]_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}](\text{H}_2\text{O})\}^{4+}$ (Figure 2), perchlorate anions and crystallisation water molecules. The hexanuclear cation is made up of two symmetry-related oxamato-bridged trinuclear units ($I = 1 - x, y, -z$) connected through the central carbon

atom C(6) which lies on a crystallographic twofold axis, in accordance with the C_2 space group.

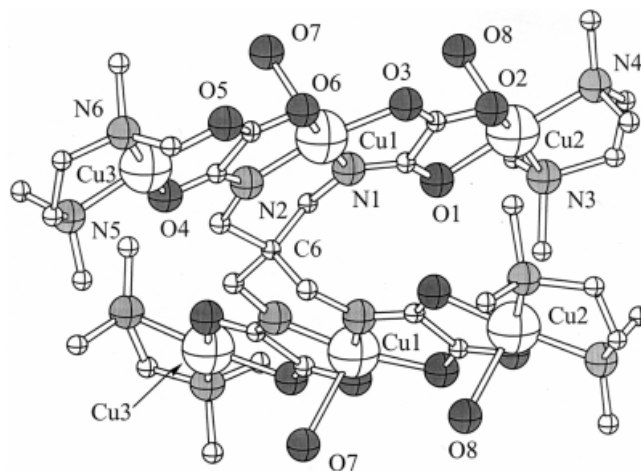


Figure 2. Perspective view of the cationic hexanuclear unit $\{[\text{Cu}(\text{tmen})(\text{H}_2\text{O})]_2[\text{Cu}(\text{tmen})]_2[\text{Cu}_2\text{L}(\text{H}_2\text{O})]\}^{4+}$ of $[\text{Cu}_6\text{-tmen}]$ with the atom-numbering scheme (hydrogen atoms have been omitted for clarity); selected bond lengths [pm] and angles [°] with standard deviations in parentheses: Cu(1)–N(1) 192.6(5), Cu(1)–N(2) 191.7(5), Cu(1)–O(3) 196.1(4), Cu(1)–O(6) 196.3(4), Cu(2)–N(3) 192.9(5), Cu(2)–N(4) 191.9(5), Cu(2)–O(9) 196.6(4), Cu(2)–O(12) 198.2(4); N(2)–Cu(1)–N(1) 96.7(2), O(3)–Cu(1)–N(1) 84.3(2), O(6)–Cu(1)–N(1) 173.4(2), N(2)–Cu(1)–O(3) 176.8(2), N(2)–Cu(1)–O(6) 84.2(2), O(6)–Cu(1)–O(3) 95.1(2), N(3)–Cu(2)–N(4) 95.2(2), O(9)–Cu(2)–N(3) 84.4(2), O(12)–Cu(2)–N(3) 179.0(2), N(4)–Cu(2)–O(9) 172.4(2), N(4)–Cu(2)–O(12) 83.9(2), O(12)–Cu(2)–O(9) 96.4(2)

Within each trinuclear fragment, the terminal Cu(2) and Cu(3) atoms are (4 + 1) and (4 + 2) coordinated, respectively. Their basal planes are formed by two amino nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamato bridge. The apical positions are filled by the oxygen atom O(8) from the water molecule (234 pm) in the former, and the O(10) and O(13) atoms from two weakly bound perchlorate anions (272 pm) in the latter. The central Cu(1) atom has a (4 + 1) coordination environment, with an equatorial plane occupied by two deprotonated amido nitrogen atoms and two carboxylate oxygen atoms from the oxamato groups. The fifth axial position is occupied by the water oxygen atom O(7) (250 pm). The metal atoms Cu(1) and Cu(2) are displaced from the least-square basal plane toward the apical water molecule by 15 and 20 pm, respectively, while the Cu(3) atom shows no deviation from the mean plane. The basal planes of the three copper(II) ions in the trinuclear unit are almost coplanar [dihedral angles of 7(2), 6(2), and 5(2)° for Cu(1)–Cu(2), Cu(1)–Cu(3), and Cu(2)–Cu(3), respectively], in contrast to those of the central copper(II) ions from the $[\text{Cu}_2\text{L}]$ fragment [43.2(8)° for Cu(1)–Cu^I(1)].

In the crystal, two neighbouring hexanuclear entities ($II = 1 - x, y, 1 - z$) are linked through the oxygen atom O(7) from apical water which acts as a bridge between the central copper(II) ions, thus leading to a chain along the *c* axis (Figure 3). The Cu(1)–O(7)–Cu^{II}(1) angle is 124(2)°. The intramolecular metal–metal separations Cu(1)···Cu(2), Cu(1)···Cu(3), Cu(2)···Cu(3), and Cu(1)···Cu^I(1) are 514,

513, 1024, and 591 pm, respectively, whereas the intermolecular one $\text{Cu}(\text{I})\cdots\text{Cu}(\text{II})$ is 442 pm.

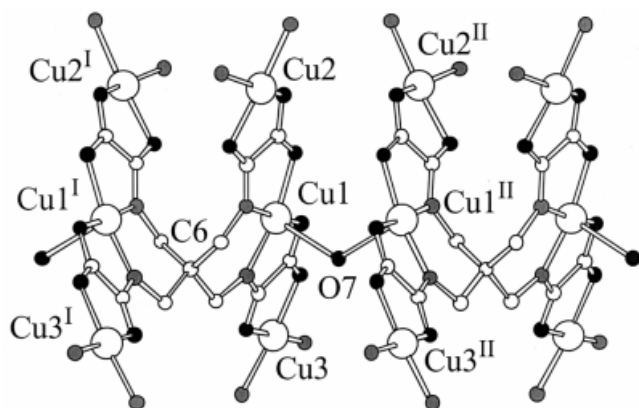


Figure 3. View of two symmetry-related hexanuclear complexes (II: $1-x, y, 1-z$) belonging to the chain which runs along the c axis; the carbon atoms of the tmen ligands and the oxygen atoms of coordinated water and perchlorate molecules have been omitted for clarity

Magnetic Properties of Dinuclear Precursors

The magnetic properties of $[\text{Cu}_2\text{-Na}]$, $[\text{Cu}_2\text{-NMe}_4]$ and $[\text{Cu}_2\text{-PPh}_4]$ (SQUID, 1.8–300 K) are depicted in Figure 4. The magnetic properties of the dinuclear copper(II) complexes strongly depend on the nature of the counter-cation. As can be seen for $[\text{Cu}_2\text{-Na}]$, the $\chi_M T$ curve smoothly decreases upon cooling below 5 K, showing that the dominant interaction between $\text{Cu}(\text{II})$ ions is antiferromagnetic. On the contrary, upon cooling $[\text{Cu}_2\text{-NMe}_4]$ and $[\text{Cu}_2\text{-PPh}_4]$, the increase of the $\chi_M T$ product indicates that the coupling between the $\text{Cu}(\text{II})$ ions is ferromagnetic. The best fits are obtained using the following parameters $J = -4.6$ yJ (-0.23 cm^{-1}), $g = 2.10$, 5.4 yJ (0.27 cm^{-1}), $g = 2.05$ and 23.8 yJ (1.2 cm^{-1}), $g = 2.02$ for $[\text{Cu}_2\text{-Na}]$, $[\text{Cu}_2\text{-NMe}_4]$ and $[\text{Cu}_2\text{-PPh}_4]$, respectively ($H = -JS_I \cdot S_2$).^[22] The agreement factors R defined as $\Sigma(\chi_M T_{\text{exp}} - \chi_M T_{\text{theo}})^2 / \Sigma(\chi_M T_{\text{exp}})^2$ are then equal to $4.6 \cdot 10^{-5}$, $7 \cdot 10^{-6}$, and $4 \cdot 10^{-5}$ for $[\text{Cu}_2\text{-Na}]$, $[\text{Cu}_2\text{-NMe}_4]$, and $[\text{Cu}_2\text{-PPh}_4]$, respectively.

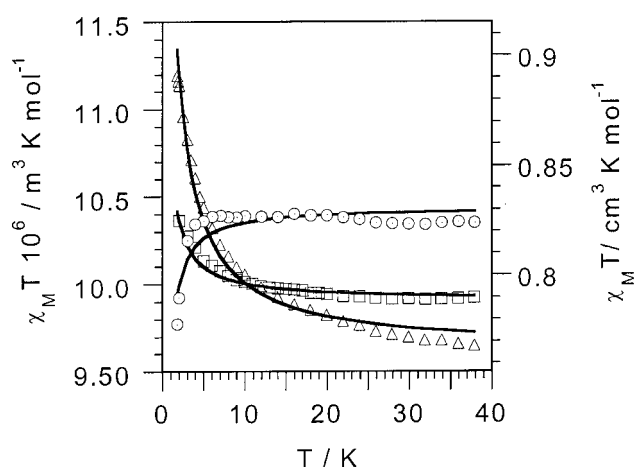


Figure 4. Thermal variation of the magnetic susceptibility of $[\text{Cu}_2\text{Na}]$ (○), $[\text{Cu}_2\text{NMe}_4]$ (□) and $[\text{Cu}_2\text{PPh}_4]$ (Δ) in the form of $\chi_M T$ versus T plot; the lines are the calculated curves

The antiferromagnetic interaction obtained for $[\text{Cu}_2\text{Na}]$ can be explained in light of its crystal structure. The dinuclear units are not isolated within the crystal, as the oxygen atoms of oxamato groups of $[\text{Cu}_2\text{L}]^{4+}$ are coordinated to the Na^+ ions leading to an extended 3D network.^[19] The antiferromagnetic coupling between the $\text{Cu}(\text{II})$ ions is probably due to the interaction through the Na^+ ions and not from the interaction through the carbon atoms linking the two $\text{Cu}(\text{II})$ ions. This analysis is reinforced by the magnetic behaviour of $[\text{Cu}_2\text{-NMe}_4]$ and $[\text{Cu}_2\text{-PPh}_4]$. For these two compounds, where organic cations are present and cannot be coordinated to the external oxygen atoms of the oxamato group, the coupling is, as expected, ferromagnetic. Moreover, the magnitude of the coupling seems to be related to the size of the counter-cation, i.e. the bulkier the counter-cation, the more pronounced the coupling. Even though no crystallographic structures of these compounds are yet available, the stronger ferromagnetic interaction is observed for the PPh_4^+ salt where the intermolecular interactions are expected to be the smallest.

Magnetic Properties of Hexanuclear Species

The magnetic properties of the hexanuclear complexes $[\text{Cu}_6\text{-tmen}]$ and $[\text{Cu}_6\text{-pmdien}]$ are shown in Figure 5. At room temperature, $\chi_M T$ is equal to 14.9 μm^3 K mol^{-1} (1.19 cm^3 K mol^{-1}) and 24.6 μm^3 K mol^{-1} (1.96 cm^3 K mol^{-1}) for $[\text{Cu}_6\text{-tmen}]$ and $[\text{Cu}_6\text{-pmdien}]$, respectively. These values are lower than expected for six noninteracting copper(II) ions (31.2 μm^3 K mol^{-1}). For both compounds, $\chi_M T$ decreases upon cooling to reach a constant value of 10.0 μm^3 K mol^{-1} (0.798 cm^3 K mol^{-1}) around 100 K for $[\text{Cu}_6\text{-tmen}]$ and 10.2 μm^3 K mol^{-1} (0.811 cm^3 K mol^{-1}) around 20 K for $[\text{Cu}_6\text{-pmdien}]$. Upon further cooling, $\chi_M T$ decreases abruptly below 20 K for $[\text{Cu}_6\text{-tmen}]$ and 8 K for $[\text{Cu}_6\text{-pmdien}]$. At 1.8 K, $\chi_M T$ values are equal to 6.36 μm^3 K mol^{-1} (0.506 cm^3 K mol^{-1}) and 9.31 μm^3 K mol^{-1} (0.741 cm^3 K mol^{-1}) for $[\text{Cu}_6\text{-tmen}]$ and $[\text{Cu}_6\text{-pmdien}]$, respectively. In the high temperature region, these observed trends are typical of strongly coupled trinuclear $\text{Cu}(\text{II})$ complexes and the plateaux correspond to temperature ranges where the $S = 1/2$ ground states of the trinuclear units are the only populated states.

The rapid decrease in the $\chi_M T$ products at low temperature is interpreted as arising from a weak interaction between the trinuclear units. To take this into account, the effective spin Hamiltonian shown in Equation 1 has been used where $S_A = S_B = 1/2$ correspond to the two ground-state doublets of the Cu_3^{II} trimeric units, defined as A and B in this perturbational treatment.^[23]

$$H = -J(S_{A1}S_{A2} + S_{A1}S_{A3} + S_{B1}S_{B2} + S_{B1}S_{B3}) - j_{\text{eff}}S_A S_B + g\beta(S_{A1} + S_{A2} + S_{A3} + S_{B1} + S_{B2} + S_{B3}) \cdot B \quad (1)$$

Over the whole temperature range, the theoretical curves derived from the above Hamiltonian closely follow the experimental data for both compounds. The best fits are obtained using the following parameters $J = -6790$ yJ (-342 cm^{-1}), $j_{\text{eff}} = -31.8$ yJ (-1.6 cm^{-1}), $g = 2.07$ and $J = -2650$ yJ (-133 cm^{-1}), $j_{\text{eff}} = -10.7$ yJ (-0.54 cm^{-1}), $g =$

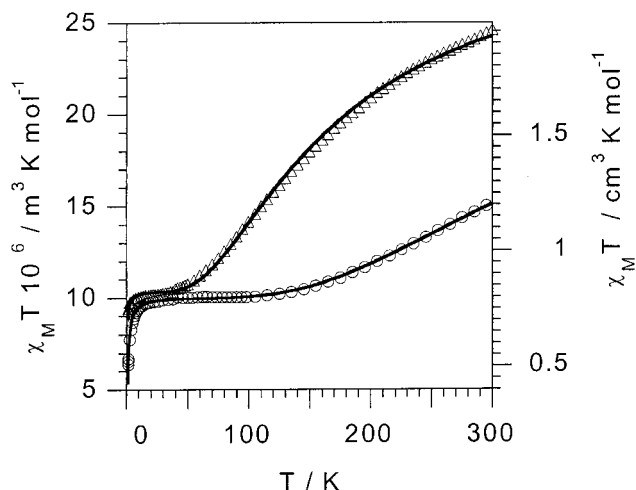


Figure 5. Thermal variation of the magnetic susceptibility of **[Cu₆-tmen]** (Δ) and **[Cu₆-pmdien]** (O) in the form of $\chi_M T$ versus T plot; the lines are the calculated curves

2.10 for **[Cu₆-tmen]** and **[Cu₆-pmdien]**, respectively (solid lines in Figure 5). The agreement factors R are then equal to $1.91 \cdot 10^{-4}$ and $7.4 \cdot 10^{-5}$, respectively. In **[Cu₆-tmen]**, the exchange interaction parameter J between Cu(1) and Cu(2) or equivalently, Cu(1) and Cu(3) ($J = J_{12} = J_{13}$) through the oxamato bridge is in excellent agreement with that of the related trinuclear complex $\{[\text{Cu}(\text{tmen})]_2\text{Cu}(\text{pba})\}(\text{ClO}_4)_2$,^[24] where J is equal to -7530 yJ (-379 cm⁻¹). As for the effective interaction parameter j_{eff} between the two trinuclear units, it may be related to the exchange parameter $J_{\text{Cu-Cu}}$ between the two central Cu^{II} ions by the expression $j_{\text{eff}} = 1/9 \cdot J_{\text{Cu-Cu}}$, i.e. $J_{\text{Cu-Cu}} = -278$ yJ (-14 cm⁻¹).^[25] This value may be associated with two different pathways for the interaction between the trinuclear units. The first is an intramolecular coupling between the two trinuclear units of the same molecule, through the N-C-C-C-N σ -bond moiety. The other takes place between units of two different molecules, due to the Cu(1) ions which are connected by the apical O(7) oxygen (Figure 3). The latter pathway takes preference as coupling occurs through only one atom. This preference is also supported by a comparison between the value of -278 yJ for this interaction and those of the dinuclear units **[Cu₂-NMe₄]** and **[Cu₂-PPh₄]** ($+5.4$ and $+23.8$ yJ). It is noteworthy that there is no improvement in the quality of the fit for the low temperature data by using an alternating $S = 1/2$ chain model. In other words, it is not possible to determine from the magnetic data the respective contribution of the intra- and intermolecular interactions.

The lack of crystallographic structure renders the thorough analysis of the magnetic behaviour of **[Cu₆-pmdien]** difficult. Nevertheless, the J value through the oxamato bridge (-2650 yJ) is also in very good agreement with that of the related trinuclear complex $\{[\text{Cu}(\text{pmdien})]_2\text{Cu}(\text{pba})\}(\text{PPh}_4)_2$,^[24] where J is equal to -3020 yJ (-152 cm⁻¹). In **[Cu₆-pmdien]**, the j_{eff} value of -10.7 yJ is likewise associated to intermolecular interaction. The weaker interaction through the oxamato bridge for **[Cu₆-pmdien]** than for **[Cu₆-tmen]** stems from the relative orientation of the magnetic

orbitals in these complexes. In the latter compound, all magnetic orbitals lie almost in the same plane, ensuring a maximum overlap between them. On the contrary, in **[Cu₆-pmdien]** the magnetic orbitals of the Cu^{II} ions are not coplanar, and hence leads to a decrease in the orbital overlap.^{[24][26][27]}

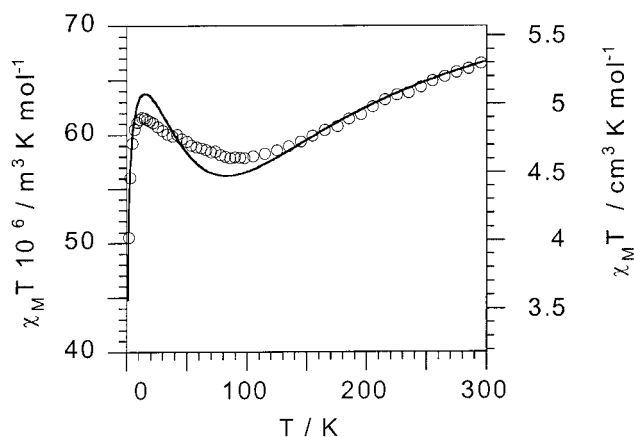


Figure 6. Thermal variation of the magnetic susceptibility **[Cu₂Ni₄-cyclam]** in the form of $\chi_M T$ versus T plot: (O) experimental data, calculated curve (line)

The magnetic properties of **[Cu₂Ni₄-cyclam]** are depicted in Figure 6. At room temperature $\chi_M T$ is equal to $66.6 \mu\text{m}^3 \text{ K mol}^{-1}$ ($5.3 \text{ cm}^3 \text{ K mol}^{-1}$) which is close to $71.3 \mu\text{m}^3 \text{ K mol}^{-1}$, the expected value for noninteracting ions (for $g_{\text{Cu}} = 2.1$ and $g_{\text{Ni}} = 2.2$). The $\chi_M T$ product first decreases upon cooling, reaches a minimum around 80 K, then increases to a maximum at about 15 K with $\chi_M T$ equal to $66.6 \mu\text{m}^3 \text{ K mol}^{-1}$, and finally decreases again upon cooling to 2 K.

The expected behaviour of **[Cu₂Ni₄-cyclam]** is that of **[NiCuNi]** heterotrinuclear species, with a weak interaction between the trinuclear units in the low temperature region. In fact, the experimental curve can be fitted using the theoretical law of a trinuclear **[NiCuNi]** complex.^{[13][28]} In this model, the decrease of $\chi_M T$ at low temperature is attributed to the zero field splitting in the $S = 3/2$ ground state of the **[NiCuNi]** trinuclear unit. The best fit of the experimental data is obtained using the following parameters $J = -1704$ yJ (-85 cm⁻¹), $D = -69.6$ yJ (-3.5 cm⁻¹), $g_{\text{Ni}} = 2.30$ and $g_{\text{Cu}} = 2.15$. The agreement factor R is then equal to $5.2 \cdot 10^{-4}$. On the other hand, the experimental data can also be fitted to a hexanuclear model using the effective spin Hamiltonian (1) with $S_A = S_B = 3/2$ being the two quadruplets ground states of the **[NiCuNi]** trimeric units, defined as A and B . For this model, the best fit of the data is obtained with the following parameters $J = -1643$ yJ (-82 cm⁻¹), $j_{\text{eff}} = -1.4$ yJ (-0.068 cm⁻¹), $g_{\text{Ni}} = 2.30$ and $g_{\text{Cu}} = 2.15$. The agreement factor R is then equal to $4.5 \cdot 10^{-4}$. The effective interaction parameter j_{eff} between the two trinuclear units may be related to the exchange parameter $J_{\text{Cu-Cu}}$ between the two central Cu^{II} ions by the expression $j_{\text{eff}} = 1/25 \cdot J_{\text{Cu-Cu}}$

i.e. $J_{Cu-Cu} = -34$ yJ (-1.7 cm $^{-1}$). For both models, the interaction through the oxamato bridge is smaller than that of the related [NiCuNi] trinuclear complexes. Recently, the role of peripheral ligand on the coupling constant has been studied in oxalato-bridged nickel(II) complexes.^[29] With four nitrogens as donor atoms, the peripheral cyclam ligand is expected to induce a coupling close to that of the cth ligand (cth = 2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane), that is -2470 yJ (-124.5 cm $^{-1}$).^[13] This is not observed experimentally, but in the absence of an X-ray analysis of the compound, it is not possible to give a satisfactory explanation to this relatively small value of the exchange interaction through the oxamato bridge.

It should be noted that the theoretical curves for the two alternative models are almost indistinguishable, showing that the D and j_{eff} parameters are strongly correlated. This renders impossible an unambiguous determination of D and j_{eff} by a fit of the magnetic data with a theoretical model including the two parameters. Nevertheless, [Cu₂Ni₄-cyclam] is EPR silent indicating that both effects are not negligible. First, the weak interaction j_{eff} between two trinuclear subunits leads to integer spin values for the hexanuclear species. Second, the large value for the Ni^{II} single ions zero field splitting makes the low lying integer spin states EPR silent. Unfortunately, neither the magnetic data nor the EPR spectra are able to give the relative values of D and j_{eff} . Hence, we cannot rule out the possibility of the weak ferromagnetic coupling between the trinuclear subunits associated with large values of the zero field splitting in the low lying states in [Cu₂Ni₄-cyclam].

Conclusion

We have obtained three new hexanuclear species with a new dinuclear Cu^{II} molecular synthon. The non-coplanarity of the Cu^{II}'s coordination environment favours a ferromagnetic coupling between the two ions as shown by the magnetic properties of [Cu₂NMe₄] and [Cu₂PPh₄]. However, the ferromagnetic coupling between the two Cu^{II} ions within the dinuclear synthon is weak and often masked by intermolecular interactions, as in [Cu₂-Na] and [Cu₆-tmen], or local anisotropy as in [Cu₂Ni₄-cyclam]. To overcome this problem, we are presently working on new polynuclear synthons with different spacers that should induce larger ferromagnetic couplings. To the best of our knowledge, only ligands allowing the synthesis of homo-hexanuclear^[12] or hetero-tetranuclear species have been described in the literature.^{[30][31]} The tetrakis-bidentate molecular synthon [Cu₂L]⁴⁺ reported here, is a unique example of a building block allowing the synthesis of homo- and heterometallic hexanuclear complexes in a rational fashion. Taking advantage of the design of [Cu₂L]⁴⁺, high-spin ($S = 9$) heterometallic hexanuclear species with Mn^{II} or Fe^{III} ions are in the process of being synthesised. We are also using this tetrakis-bidentate complex as a ligand to obtain extended networks. The non-coplanar connectivity of four should

lead to both a graphite-like hexagonal 2D array and a diamond like 3D network, and possibly to high-temperature molecular-based magnets.

Experimental Section

General: All reagents were obtained from commercial sources and used as received. The tetraethyl ester derivative Et₄H₄L of the ligand was synthesised following a literature procedure.^[19] – Elemental analyses were performed by the Microanalytical Service of ICNS (CNRS). – IR spectra were carried out on a Spectrum 1000 FT-IR spectrophotometer (Perkin-Elmer). – Magnetic measurements in the 1.8–300 K temperature range were carried out with a MPMS5 SQUID susceptometer (Quantum Design Inc). – EPR measurements were performed at 100 K on a Bruker ER 200 E at X-band on solid samples.

Syntheses and General Physical Properties of the Dinuclear Complex: The dicopper(II) complex was obtained by reaction of the tetraethyl ester derivative of the ligand (Et₄H₄L) with Cu²⁺ in basic aqueous media and isolated as its sodium, tetramethylammonium, and tetraphenylphosphonium salts.

[Cu₂-Na]: The synthesis and characterisation of the sodium salt Na₄[Cu₂L] · 10.5 H₂O have previously been described.^[19]

[Cu₂-NMe₄]: The tetramethylammonium derivative (NMe₄)₄[Cu₂L] · 4 H₂O was synthesised and isolated in a similar manner to that of [Cu₂-Na]: To a suspension of the tetraethyl ester derivative Et₄H₄L (1.33 g, 2.5 mmol) in water (50 mL) was added NMe₄OH (8.9 mL of a 25% methanolic solution, 22 mmol). After stirring for 5 min at room temperature, an aqueous solution (25 mL) of Cu(NO₃)₂ · 3 H₂O (1.20 g, 5 mmol) was added dropwise. The deep-blue solution was then filtered and the solvent volume was reduced to 10 mL on a rotary evaporator. Slow addition of absolute ethanol to the mother liquor gave a hygroscopic purple solid which was collected by filtration, washed with ethanol and ether, and dried under vacuum (74%). – C₁₃H₈Cu₂N₄O₁₂[N(C₄H₉)₄]₄ · 4 H₂O (1629.7): calcd. C 38.36, H 7.10, Cu 13.9, N 12.34; found C 37.88, H 6.79, Cu 13.6, N 12.26. – IR (KBr): $\tilde{\nu} = 1635$ and 1602 cm $^{-1}$ (C=O).

[Cu₂-PPh₄]: The tetraphenylphosphonium derivative (PPh₄)₄[Cu₂L] · 6 H₂O was synthesised from [Cu₂-Na] by successive metalations with Ag⁺ and PPh₄⁺: To a solution of [Cu₂-Na] (140 mg, 0.17 mmol) in water (10 mL) was added solid silver nitrate (31 mg, 0.18 mmol). After stirring for 5 min, the purple precipitate that formed in a quantitative yield was collected by filtration, washed successively with water, ethanol and ether, and then dried under vacuum. To a suspension of this solid (152 mg, 0.16 mmol) in water (5 mL) was added an aqueous solution (10 mL) of tetraphenylphosphonium chloride (235 mg, 0.63 mmol). Silver chloride appeared as a white solid. After stirring for 15 min, the purple blue solution was filtered and evaporated to dryness. The solid residue was dissolved in the minimum amount of acetonitrile and 5 mL of acetone was added. Addition of ether allowed the isolation of a hygroscopic purple precipitate which was collected by filtration, washed with ether and kept in a desiccator (94%). – C₁₃H₈Cu₂N₄O₁₂[P(C₆H₅)₄]₄ · 6 H₂O (2005): calcd. C 65.30, H 5.03, Cu 6.34, N 2.79; found C 65.54, H 5.04, Cu 6.26, N 2.87. – IR (KBr): $\tilde{\nu} = 1634$ and 1603 cm $^{-1}$ (C=O).

Syntheses and General Physical Properties of the Hexanuclear Complexes: These compounds were synthesised in a straightforward

manner from the dinuclear copper(II) complex **[Cu₂-Na]** and the appropriate external complex.

[Cu₆-tmen]: The hexacopper complex {[Cu(tmen)(H₂O)]₂-[Cu(tmen)]₂[Cu₂L](H₂O)}(ClO₄)₄ · 2 H₂O was synthesised in the following way with [Cu(tmen)]²⁺ prepared in situ from a 1:1 mixture of Cu²⁺ and the corresponding diamine: To a solution of copper(II) perchlorate (0.74 g, 2.0 mmol) and *N,N,N',N'*-tetramethylethylenediamine (302 µL, 2 mmol) in water (20 mL) was added under stirring an aqueous solution (10 mL) of **[Cu₂-Na]** (0.39 g, 0.5 mmol). Slow evaporation at room temperature of the deep-blue filtered solution gave, after a few days, a microcrystalline deep-blue powder which was filtered off and air-dried. – C₃₇H₈₂Cl₄Cu₆N₁₂O₃₃ (1746.2): calcd. C 25.45, H 4.73, N 9.63; found C 25.72, H 4.83, N 9.58. – IR (KBr): $\tilde{\nu}$ = 1634 and 1600 cm⁻¹ (C=O), 1120 and 1086 cm⁻¹ (Cl–O; ClO₄⁻). A single crystal of **[Cu₆-tmen]** of low quality but good enough for a complete structure determination was selected. Up to now, attempts to obtain single crystals of higher quality by recrystallization from various solvents (water, methanol, acetonitrile) have been unsuccessful.

[Cu₆-pmdien]: The other hexacopper complex {[Cu(pmdien)]₄-[Cu₂L]}(ClO₄)₄ · 4 H₂O was formed by the same procedure with *N,N,N',N',N''*-pentamethyldiethylenetriamine (418 µL, 2 mmol) in place of *N,N,N',N'*-tetramethylethylenediamine. After slow evaporation, a deep-blue microcrystalline powder formed, but no well-shaped crystals of a sufficient quality for X-ray analysis were obtained. – C₄₉H₁₀₀Cl₄Cu₆N₁₆O₂₈ · 4 H₂O (1956.6): calcd. C 30.08, H 5.56, Cl 7.25, N 11.45; found C 29.92, H 5.58, Cl 7.33, N 11.41. – IR (KBr): $\tilde{\nu}$ = 1620 cm⁻¹ (C=O), 1121 and 1089 cm⁻¹ (Cl–O; ClO₄⁻).

[Cu₂Ni₄-cyclam]: The polymetallic complex {[Ni(cyclam)]₄[Cu₂L]}(ClO₄)₄ · 4 H₂O was obtained as follows: To a solution of Ni(cyclam)(H₂O)₂(ClO₄)₂ (198 mg, 0.4 mmol) in 1:1 water/acetonitrile (6 mL) was added solid **[Cu₂-Na]** (82 mg, 0.1 mmol). After stirring for 30 min at 40 °C the solid had dissolved to give a purple-red solution. Slow evaporation at room temperature afforded crystalline material of very low quality for X-ray analysis. All attempts at isolating crystals of good quality by recrystallisation were unsuccessful. – C₅₃H₁₀₄Cl₄Cu₂N₂₀Ni₄O₂₈ · 4 H₂O (2045.3): calcd. C 31.12, H 5.52, Cl 6.93, N 13.70; found C 30.98, H 5.51, Cl 7.06, N 13.73. – IR (KBr): $\tilde{\nu}$ = 1614 cm⁻¹ (C=O), 1114 and 1086 (Cl–O; ClO₄⁻), 2925 and 2869 (N–H; cyclam).

X-ray Crystallographic Study: Crystal structure analysis of the selected crystal of **[Cu₆-tmen]**: Enraf–Nonius CAD-4 diffractometer, Mo-*K*_α radiation, λ = 71.069 pm, graphite monochromator, 293 K. Data collection solution and refinement: *w*-2 θ , Lorentz and polarisation effects and absorption correction, standard Patterson methods with subsequent full-matrix least-squares method refinement SHELX86, SHELX93.^[32,33] C₃₇H₈₂Cl₄Cu₆N₁₂O₃₃, monoclinic, space group C₂, *a* = 2807.1(10), *b* = 1430.4(6), *c* = 872.1(7) pm, β = 95.28(2)°, *V* = 3.487(3) nm³, *Z* = 4, *r*_{calcd} = 1.65 g cm⁻³, *m* = 2.04 mm⁻¹, $1 \leq \theta \leq 25^\circ$, crystal size 0.10 × 0.10 × 0.10 mm. 2395 Unique reflections, and 2344 assumed as observed with *I* > 2σ(*I*). The hydrogen atoms were not found or calculated. Refinement of 363 variables with anisotropic thermal parameters for all atoms except for the O(5) atom which was refined with an overall isotropic thermal parameter gave *R* = 0.105 and *R*_w = 0.251 with $\Sigma = 1.09$. The crystal drawings were carried out with the CRYSTAL MAKER^[34] program. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101561. Copies of the data can be obtained free of charge on application to CCDC, 12 Union

Road, Cambridge CB21EZ, UK [fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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$$j_{eff} = J_{ij} \frac{S(S+1) + S_i(S_i+1) - S^*(S^*+1)}{2S(S+1)} \cdot \frac{S(S+1) + S_j(S_j+1) - S^*(S^*+1)}{2S(S+1)}$$

- where J_{ij} is the interaction between the ions i and j belonging to the two different trinuclear units, S^* and $S^\#$ are the intermediate spin values in the trinuclear unit in the chosen coupling scheme.
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