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# Nonmagnetic ground state in the molecular material $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$ (pba = 1,3-propylenebis(oxamato))

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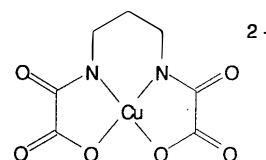
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**Abstract.** – The crystal structure of  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$  with pba = 1,3-propylenebis(oxamato) was first described two years ago. It consists of tube-like motifs of the formula  $\text{Nd}_2[\text{Cu}(\text{pba})]_3(\text{H}_2\text{O})_9$  and noncoordinated water molecules. Each Nd(III) ion is surrounded by three nearest-neighbor Cu(II) ions, and in turn each Cu(II) ion is situated between two Nd(III) ions. The magnetic properties of the compound have been investigated. The magnetic susceptibility presents a rounded maximum around 2.5 K, and the product of the magnetic susceptibility and the temperature tends to zero as the temperature approaches absolute zero. This indicates that the ground state of the compound is quasinonmagnetic, which at a first view is quite an unexpected result. This situation is attributed to a compensation between the local magnetic moments of the two Nd(III) ions and the three Cu(II) ions at low temperature. This idea has been tested with a theoretical model in which the local Kramer's doublets for Nd(III) and Cu(II) interact antiferromagnetically. A compensation of the magnetic moments may be expected for a value of the ratio  $g'_{\text{Nd}}/g_{\text{Cu}}$  close to 1.73  $g'_{\text{Nd}}$  and  $g_{\text{Cu}}$  being the average values of the Zeeman factor for the ground Kramer's doublet of Nd(III) and Cu(II), respectively.

## Introduction

A few years ago, we initiated a new project of research dealing with molecular materials containing both  $4f^n$  lanthanide(III) and  $3d^n$  transition metal ions<sup>1-4</sup>. Our objectives at that time could be summed up as follows: (i) we were looking for new molecular-based architectures, with one-, two-, or three-dimensional structures; (ii) we expected to observe original magnetic properties arising from the interaction between the two types of spin carriers; and (iii) we thought that interesting optical properties could result from the simultaneous presence of lanthanide and transition metal ions in the structure.

Up to now our main activity in this new field of research has consisted of exploring the  $[\text{Cu}(\text{pba})]^{2-}/\text{Ln}(\text{III})$  system;  $[\text{Cu}(\text{pba})]^{2-}$  is the copper(II) precursor:



where pba is 1,3-propylenebis(oxamato), and Ln(III) is a lanthanide(III) ion. Three different architectures have already been characterized, depending on the nature of Ln(III) and/or the conditions of synthesis. These architectures have been compared in a short review<sup>3</sup>.

As far as the magnetic properties of these Ln(III)Cu(II) compounds are concerned, until now we have focused on systems in which Ln(III) is Gd(III). Whatever the details of the structure may be, the Gd(III)-Cu(II) interaction through the oxamato bridge is ferromagnetic, and the Gd(III)Cu(II) compounds exhibit a three-dimensional

(3D) ferromagnetic ordering around  $T_c = 1\text{K}$ <sup>5</sup>. These Gd(III)Cu(II) compounds may be considered as the first genuine molecular-based magnets involving rare earth ions. A theoretical model accounting for the ferromagnetic nature of the Gd(III)-Cu(II) interaction has been proposed<sup>6,7</sup>.

In this paper we would like to investigate the quite unexpected magnetic properties of the Nd(III)Cu(II) compounds. We will focus on one compound of this kind, namely  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$ . The other Nd(III)Cu(II) compounds characterized so far behave in the same manner.

## Experimental section

The synthesis of  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$  was performed as previously described<sup>2,3</sup>. The isomorphism of the compound with  $\text{Sm}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$  was checked by Debye-Scherrer photographs and cell determinations. The crystal structure was solved for the Sm(III) derivative<sup>3</sup>.

The magnetic susceptibility measurements were carried out using a Faraday type magnetometer working in the 4.2–300K temperature range, and a SQUID magnetometer working down to 1.8K. Special care was taken to avoid the orientation of the crystallites along the field direction.

## Structure

The crystal structure of  $\text{Sm}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$  has been described previously. It can be viewed as resulting from the condensation of two puckered ladders with a redistribution of the rungs, which leads to infinite tube-like motifs with an essentially square section and quasifourfold symmetry as schematized in Figure 1 where only the Ln(III) ions are represented. A schematic view down the pseudofourfold axis is shown in Figure 2. The ladder rungs are intertwined by alternately switching from one edge of one ladder to that of its nearest orthogonal neighbor, which creates an helicoidal pattern. Along both the edges of the ladders running along the pseudo-fourfold axis and the rungs between these edges, two adjacent Ln(III) ions are bridged by a Cu(pba) group with Ln...Cu separations ranging from 5.67 to 5.76 Å. The Ln(III) ion adopts a distorted monocapped square antiprism coordination of nine oxygen atoms as shown in Figure 3, with six of the oxygen atoms coming from three Cu(pba) groups, and three from water molecules. The Cu(II) ion adopts a square pyramid coordination, with a water molecule occupying the apical position. It turns out that the actual formula of the tube-like compound is  $\text{Nd}_2[\text{Cu}(\text{pba})]_3(\text{H}_2\text{O})_9$ . The noncoordinated water molecules very efficiently isolate the tubes from each other in the crystal lattice.

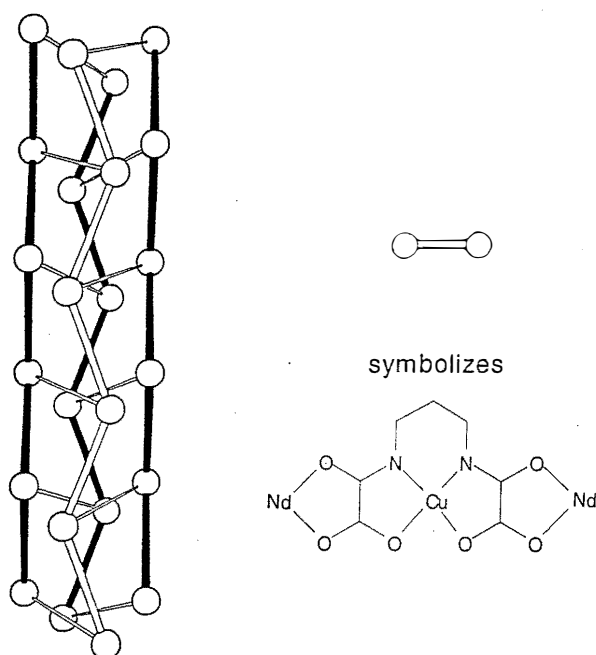


Figure 1. – Schematic view perpendicular to the pseudo-fourfold rotation axis of a tube-like motif in  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$ .

## Magnetic properties

The magnetic susceptibility data for  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{H}_2\text{O}$  are represented in the form of the  $\chi_M T$  versus  $T$  curve in Figure 4, and the  $\chi_M$  versus  $T$  curve in Figure 5, where  $\chi_M$  is the molar magnetic susceptibility (per  $\text{Nd}_2\text{Cu}_3$  unit) and  $T$  the temperature. At room temperature  $\chi_M T$  is equal to  $4.50\text{ cm}^3\text{ K mol}^{-1}$ , which approximately corresponds to what is expected for two Nd(III) and three Cu(II) isolated ions. Indeed,  $\chi_M T$  for an isolated Nd(III) ion at room temperature is roughly equal to  $1.64\text{ cm}^3\text{ K mol}^{-1}$ , and for an isolated Cu(II) ion it is  $0.4\text{ cm}^3\text{ K mol}^{-1}$ <sup>8,9</sup>. As the temperature is lowered,  $\chi_M T$  continuously decreases, and tends to zero as  $T$  approaches absolute zero. As for  $\chi_M$ , it shows a well-pronounced maximum at 2.5K, and then rapidly decreases as  $T$  is lowered further below this temperature.

In principle the maximum of  $\chi_M$  along with the shape of the  $\chi_M T$  versus  $T$  curve may have two origins: either it characterizes a three-dimensional (3D) antiferromagnetic ordering, or it corresponds to a nonmagnetic ground state for the tube-like motif  $\text{Nd}_2[\text{Cu}(\text{pba})]_3(\text{H}_2\text{O})_9$ . The profile of the  $\chi_M$  versus  $T$  plot in the low temperature range is rather in favor of the latter hypothesis. This maximum is rather rounded, and not very sharp as would be expected for a long-range ordering. Two other experimental results allow us to rule out definitively the former hypothesis. First, the *ac* magnetic susceptibility does not show any peak around 2.5K while such a peak should be present

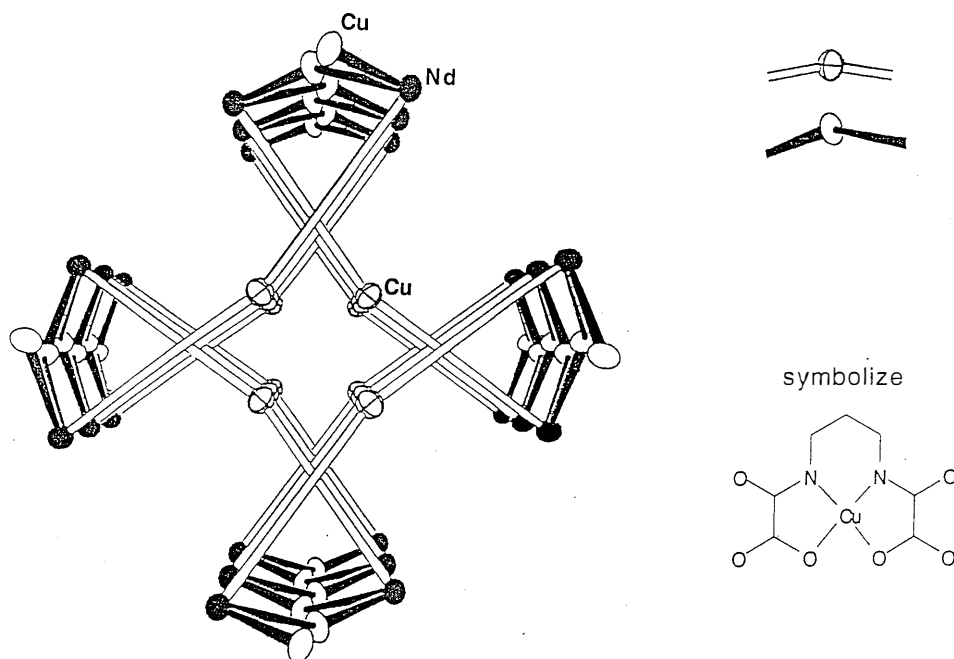


Figure 2. – Schematic view along the pseudo-fourfold rotation axis of a tube-like motif in  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23 \text{H}_2\text{O}$ .

in the case of long-range magnetic ordering. Secondly, the temperature dependence of the heat capacity does not exhibit the  $\lambda$ -type discontinuity characterizing a 3D magnetic ordering. In contrast, the heat capacity of the  $\text{Gd}_2[\text{Cu}(\text{pba})]_3 \cdot 23 \text{H}_2\text{O}$  isomorphous compound exhibits such a well-shaped  $\lambda$  peak at  $T_c = 1 \text{K}$ <sup>5</sup>.

It follows from what precedes that the ground state of the  $\text{Nd}_2[\text{Cu}(\text{pba})]_3(\text{H}_2\text{O})_9$  motif is (quasi-) nonmagnetic. We are then faced with the interpretation of this quite surprising result. Let us justify why we qualify this result as surprising. The interaction between two adjacent spin carriers is usually antiferromagnetic; the  $\text{Gd}(\text{III})$ - $\text{Cu}(\text{II})$  situation is rather exceptional. Therefore, the fact that the  $\text{Nd}(\text{III})$ - $\text{Cu}(\text{II})$  interaction is antiferromagnetic in itself is not a surprise. On the other hand, the fact that the  $\text{Nd}(\text{III})$ - $\text{Cu}(\text{II})$  antiferromagnetic interactions lead to

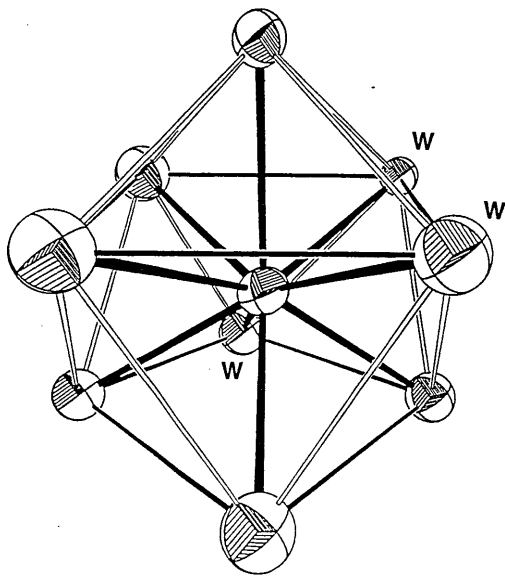


Figure 3. – Coordination polyhedron around the neodymium atom in  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23 \text{H}_2\text{O}$ . The oxygen atoms of water molecules are indicated by the letter W.

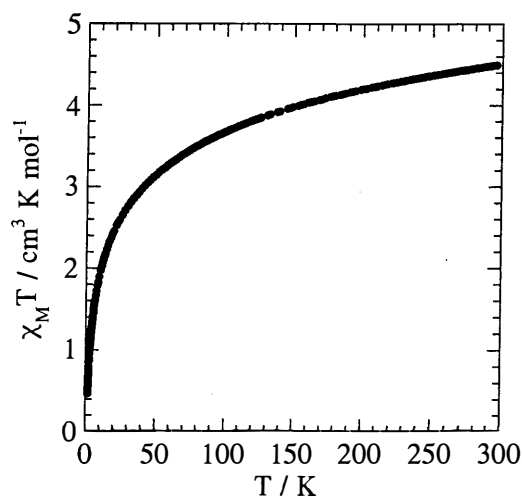
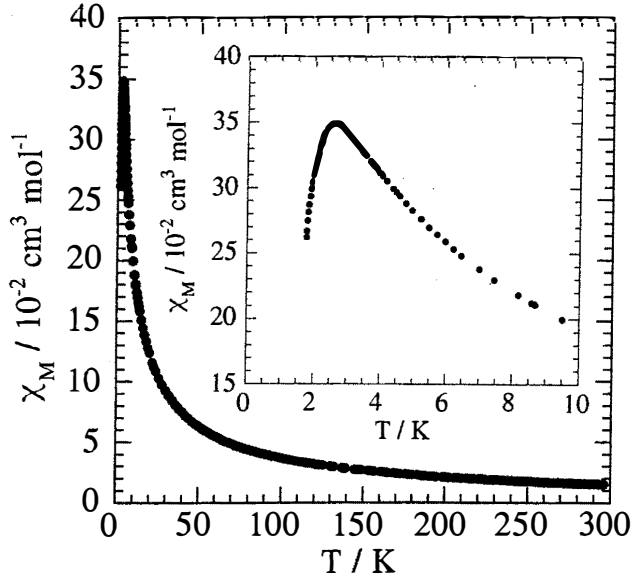


Figure 4. –  $\chi_M T$  versus  $T$  curve for  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23 \text{H}_2\text{O}$ .

a cancellation of the local magnetic moments in the ground state could not be anticipated. A nonmagnetic ground state is usually observed in antiferromagnetically coupled homometallic spin clusters of even nuclearity (binuclear, tetranuclear, etc.), or homometallic lattices (chains, layers, 3D lattices). The spin compensation may also occur in some heteropolymetallic species. This is for instance the case for a Cu(II)Ni(II)Cu(II) trinuclear species with  $S_{\text{Cu}}=1/2$  and  $S_{\text{Ni}}=1$  local spins and antiferromagnetic Cu(II)-Ni(II) interactions. The reason why such a magnetic compensation occurs in  $\text{Nd}_2[\text{Cu}(\text{pba})]_3(\text{H}_2\text{O})_9$  is far from obvious.



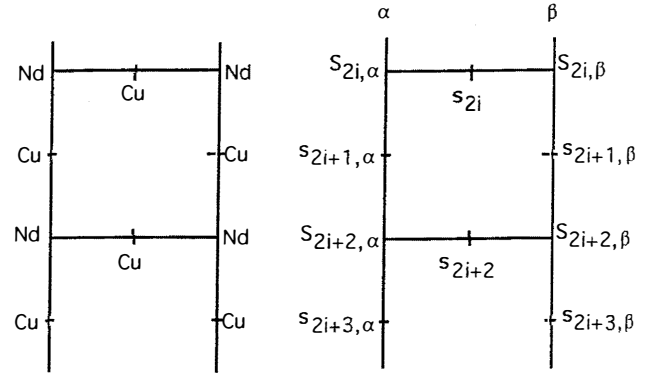
**Figure 5.**  $-\chi_M$  versus  $T$  plot for  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23 \text{H}_2\text{O}$ . The insert emphasizes the rounded maximum of  $\chi_M$  around 2.5K.

When examining the problem in a more thorough fashion, however, an explanation may be found. The free-ion ground state of Nd(III) is  $^4I_{9/2}$ . In a low site symmetry this state is split into five Kramer's doublets, and when the temperature is low enough, only the lowest Kramer's doublet is thermally populated. It is possible to attribute an effective spin,  $S'_{\text{Nd}} = 1/2$ , to this ground Kramer's doublet along with an effective Zeeman tensor,  $g'_{\text{Nd}}$ . Let  $g'_{\text{Nd}}$  and  $g_{\text{Cu}}$  stand for the average Zeeman factors associated with the  $S'_{\text{Nd}}$  and  $S_{\text{Cu}}$  local spins, respectively. Assuming that the coupling between adjacent  $S'_{\text{Nd}}$  and  $S_{\text{Cu}}$  local spins is antiferromagnetic, a spin compensation may be obtained for a critical value  $\rho_C$  of the ratio  $\rho = g'_{\text{Nd}}/g_{\text{Cu}}$ ;  $\rho_C$  is obviously larger than 1. A rather similar situation was theoretically investigated by one of us some years ago, that of an AB antiferromagnetically

coupled bimetallic chain with  $S_A=1/2$  and  $S_B=1$ . When the ratio  $g_A/g_B$  of the local Zeeman factors is equal to 2.66, there is an exact compensation of the local magnetic moments, so that the ground state becomes nonmagnetic<sup>11</sup>. The temperature dependence of the magnetic susceptibility for such a system is expected to display a maximum.

## A theoretical approach

This idea of exact compensation between antiferromagnetically coupled  $S'_{\text{Nd}}$  and  $S_{\text{Cu}}$  local spins has been tested, not on the tube-motif itself, which would be too complicated, but on the simpler ladder motif shown below:



For this, we used  $1/2$  local spins and  $g'_{\text{Nd}}$  and  $g_{\text{Cu}}$  local Zeeman factors. We looked for the critical value  $\rho_C$  of the ratio  $g'_{\text{Nd}}/g_{\text{Cu}}$  for which an exact compensation of the local magnetic moments is obtained. The zero-field spin Hamiltonian associated with such a ladder may be written as:

$$\mathcal{H} = -J \left\{ \begin{aligned} &\sum_i [\mathbf{S}_{2i, \alpha} \cdot (\mathbf{s}_{2i+1, \alpha} + \mathbf{s}_{2i-1, \alpha}) \\ &\quad + \mathbf{S}_{2i, \beta} \cdot (\mathbf{s}_{2i+1, \beta} + \mathbf{s}_{2i-1, \beta})] \\ &+ \sum_i \mathbf{s}_{2i} \cdot (\mathbf{S}_{2i, \alpha} + \mathbf{S}_{2i, \beta}) \end{aligned} \right\} \quad (1)$$

and the Zeeman perturbation when applying an external magnetic field  $H$  as:

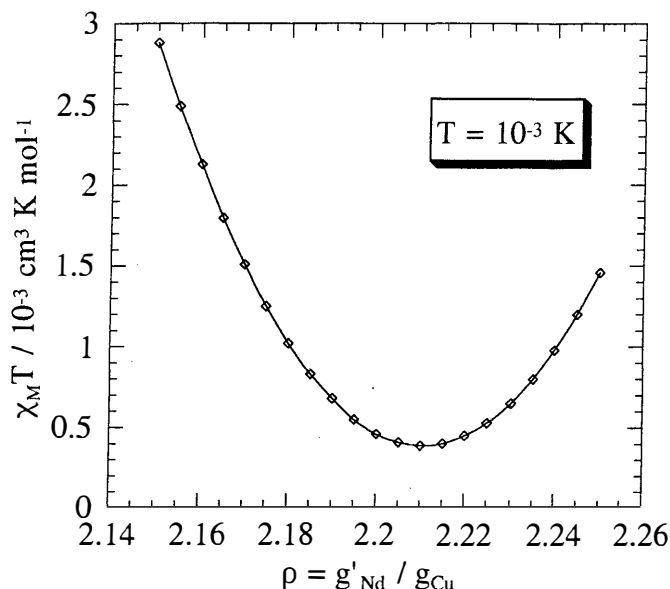
$$\mathcal{H}_{\text{ZE}} = \beta \sum_i [g'_{\text{Nd}} (\mathbf{S}_{2i, \alpha} + \mathbf{S}_{2i, \beta}) + g_{\text{Cu}} (\mathbf{s}_{2i} + \mathbf{s}_{2i+1, \alpha} + \mathbf{s}_{2i+1, \beta})] \cdot \mathbf{H} \quad (2)$$

Unlike the case for the Ising double chain<sup>12</sup>, exact solutions are not available for such a ladder except for

finite fragments which can be solved computationally. As demonstrated a long time ago by Bonner and Fisher for a  $S=1/2$  quantum uniform chain<sup>13</sup>, the general method consists of considering ring chains of increasing size, and then extrapolating for the infinite chain. A significant reduction of the computational work is obtained by taking spin space symmetry into account. The calculation, however, remains very demanding in terms of storage capacities, and so far we have only studied the  $(\text{Nd}_2\text{Cu}_3)_n$  systems with  $n=1$  (five spins), 2 (10 spins), and 3 (15 spins).  $\rho_C$  was determined as the  $\rho$  value corresponding to a minimum for the product  $\chi_M T$  at a very low but finite temperature. The calculation was actually carried out for  $J=-10\text{ cm}^{-1}$  and  $T=10^{-3}\text{ K}$ .  $\rho_C$  was found as 2.7 for  $n=1$ , 2.21 for  $n=2$ , and 2.05 for  $n=3$ . The  $\chi_M T$  versus  $\rho$  curve for  $n=2$  is shown in Figure 6. The extrapolation of the  $\rho_C=f(1/n)$  plot for  $1/n=0$  gives  $\rho_C=1.73$  for the infinite ladder. It would be quite interesting to determine the magnetic properties of a compound with the same structure, where the only spin carriers would be Nd(III) ions. Assuming that the interaction between Nd(III) ions separated by more than  $11\text{ \AA}$  is negligibly small, the low-temperature limit of  $\chi_M T$  would allow us to determine  $g'_{\text{Nd}}$ . Such a compound, however, does not exist. To our knowledge, there is only one report of magnetic data of an isolated Nd(III) mononuclear compound, namely  $[\text{NdL}_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$  with  $\text{L}=2\text{-formyl-4-methyl-6-(N-(2-pyridylethyl)formimidoyl)phenol}$ <sup>14</sup>. The low-temperature limit of  $\chi_M T$  is  $0.80\text{ cm}^3\text{ K mol}^{-1}$ , which corresponds to  $g'_{\text{Nd}} = 2.92$  for the lowest Kramer's doublet.

## Discussion and conclusion

The existence of a nonmagnetic ground state for  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{ H}_2\text{O}$  is quite unexpected. This situation is analyzed as resulting from a compensation between the two Nd(III) and the three Cu(II) local magnetic moments at low temperature. A preliminary calculation indicates that such a compensation may occur if the ratio  $\rho = g'_{\text{Nd}}/g_{\text{Cu}}$  is equal to a critical value  $\rho_C$  close to 1.73;  $g'_{\text{Nd}}$  and  $g_{\text{Cu}}$  refer to the local Kramer's doublets of Nd(III) and Cu(II), respectively. Three points deserve to be emphasized. First the minimum of the  $\chi_M T$  versus  $\rho$  curve for the 10 spin system (see Fig. 6) is very rounded. Therefore, if  $\rho$  is not exactly equal to  $\rho_C$ , but is close to this critical value,  $\chi_M T$  at the absolute zero will not be exactly zero, but will remain extremely weak, and the maximum of the  $\chi_M$  versus  $T$  curve will be retained. In other words, there is a range of  $\rho$  values for



**Figure 6.** –  $\chi_M T$  versus  $\rho = g'_{\text{Nd}}/g_{\text{Cu}}$  curve for  $J=10\text{ cm}^{-1}$  and  $T=10^{-3}\text{ K}$  for a 10-spin 'ring ladder'. The minimum of this curve is obtained for a critical value  $\rho_C$  corresponding to the exact compensation of the local magnetic moments (see text).

which the magnetic susceptibility will present a maximum at a finite temperature. In such cases where  $\rho$  is not exactly equal to  $\rho_C$ , the ground state may be defined as being *quasi-nonmagnetic*. The compensation of the local magnetic moments is almost, but not completely achieved. Secondly the behavior described in this paper and concerning  $\text{Nd}_2[\text{Cu}(\text{pba})]_3 \cdot 23\text{ H}_2\text{O}$  is observed for other related compounds with the  $\text{Nd}_2\text{Cu}_3$  stoichiometry, even if the maximum of  $\chi_M$  does not occur at exactly the same temperature. This situation agrees with the fact that there is a range of  $\rho$  values around  $\rho_C$  for which the ground state remains quasi-nonmagnetic. Finally in both our qualitative interpretation and our theoretical approach the magnetic anisotropy of the Nd(III) ground Kramer's doublet was ignored. For instance, in Eq. (1) the Nd(III)-Cu(II) interaction is assumed to be strictly isotropic. This assumption is obviously questionable. However, the possibility of spin compensation is retained if the Nd(III) ion is anisotropic. For instance, for the two extreme cases of magnetic anisotropy, the Ising and XY cases, the ground state arising from an antiferromagnetic interaction between two local doublets is nonmagnetic to the first order (in the Ising case the nonmagnetic ground state is twofold degenerate).

The results reported in this paper confirm that the molecular materials involving both lanthanide and transition-metal ions may exhibit some totally novel magnetic properties. This obviously incites us to pursue our endeavours along these lines.

## References

- <sup>1</sup> Guillou O., Bergerat P., Kahn O., Bakalbassis E., Boubekeur K., Batail P., Guillot M., *Inorg. Chem.*, 1991, **31**, 110.
- <sup>2</sup> Guillou O., Oushoorn R. L., Kahn O., Boubekeur K., Batail P., *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 626.
- <sup>3</sup> Guillou O., Kahn O., Oushoorn R. L., Boubekeur K., Batail P., *Inorg. Chim. Acta.*, 1992, **198-200**, 119.
- <sup>4</sup> Kahn O., Guillou O., In *Research Frontiers in Magnetochemistry*, O'Connor C. J. Ed., World Scientific, Singapore 1993.
- <sup>5</sup> Bartolomé F., Bartolomé J., Oushoorn R. L., Guillou O., Kahn O., *J. Magn. Magn. Mater.*, in press.
- <sup>6</sup> Andruh M., Ramade L., Codjovi E., Guillou O., Kahn O., Trombe J. C., *J. Am. Chem. Soc.*, 1993, **115**, 1822.
- <sup>7</sup> Georges R., Kahn O., Guillou O., *Phys. Rev. B*, 1994, **49**, 3235.
- <sup>8</sup> Casey A. P., in *Theory and Applications of Molecular Paramagnetism*, Boudreaux E. A., Mulay L. N. Eds., Wiley, New York, 1976, p. 27; Casey A. T., Mitra S., *Ibid.*, p. 135.
- <sup>9</sup> Kahn O., *Molecular Magnetism*, VCH, New York, 1993.
- <sup>10</sup> Kahn O., *Structure Bonding (Berlin)*, 1987, **68**, 89.
- <sup>11</sup> Drillon M., Coronado E., Georges R., Gianguzzo J. C., Curely J., *Phys. Rev., B*, 1989, **40**, 10992.
- <sup>12</sup> Van Koningsbruggen P., Kahn O., Nakatani K., Pei Y., Renard J. P., Drillon M., Legoll P., *Inorg. Chem.*, 1990, **29**, 3325.
- <sup>13</sup> Bonner J. C., Fisher M., *Phys. Rev., A*, 1964, **135**, 640.
- <sup>14</sup> Andruh M., Bakalbassis E., Kahn O., Trombe J. C., Porcher P., *Inorg. Chem.*, 1993, **32**, 1616.