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Lanthanide(III)-copper(II) molecular compounds with a ladder-like motif: structure and magnetic properties[†]

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Summary — The reaction of Ln(III) ions with the precursor $[\mathrm{Cu(opba)}]^{2-}$ in DMF has afforded a series of structurally isomorphous compounds of formula $\mathrm{Ln_2[Cu(opba)]_3 \cdot }x\mathrm{DMF \cdot }y\mathrm{H_2O}$ ($x \approx 10$, $y \approx 4$); Ln stands for a lanthanide atom, from Tb to Lu, or for Y, opba stands for *ortho*-phenylenebis(oxamato), and DMF stands for dimethylformamide. The crystal structure has been solved for Ln = Tm. The space group is $P2_12_12_1$, with a = 9.864(2) Å, b = 20.855(2) Å, c = 39.101(9) Å, Z = 4. The structure consists of ladder-type motifs, parallel to each other, with infinite Tm[Cu(opba)] sidepieces and [Cu(opba)] rungs joining two Tm atoms. The temperature dependences of the magnetic susceptibility for all compounds have been investigated, and have revealed a striking difference between the compounds with Ln = Tb and Dy and those with Ln = Ho, Er, Tm, and Yb. For the former compounds, significant Ln(III)–Cu(II) magnetic interactions have been detected, which leads to the divergence of the product $\chi_M T$ of the molar magnetic susceptibility with temperature. At this stage, it has not been possible to specify whether the compounds are one-dimensional ferri- or ferromagnets. In contrast, for the Ln = Ho, Er, Tm and Yb compounds, the Ln(III)–Cu(II) interactions, if any, are hidden by the crystal field effects.

lanthanide / 3*d*–4*f* interaction / molecular magnetism / low dimensionality

Résumé — Composés moléculaires lanthanide(III)-cuivre(II) avec un motif du type échelle: structure et propriétés magnétiques. *La réaction des ions Ln(III) avec le précuseur* $[\mathrm{Cu(opba)}]^{2-}$ *dans le DMF conduit à une famille de composés isomorphes de formule* $\mathrm{Ln_2[Cu(opba)]_3 \cdot xDMF \cdot yH_2O}$ (x ≈ 10, y ≈ 4); *Ln est un élément lanthanide, de Tb à Lu, ou Y, opba représente l'*ortho*-phenylenebis(oxamato), et DMF le diméthylformamide. La structure cristalline a été résolue pour Ln = Tm. Le groupe d'espace est* $P2_12_12_1$ *avec* a = *9.864(2) Å,* b = *20.855(2) Å,* c = *39.101(9) Å,* Z = *4. La structure consiste en motifs du type échelle, parallèles entre eux, avec des montants infinis Tm[Cu(opba)] et des barreaux [Cu(opba)] joignant deux atomes de thulium. La variation thermique de la susceptibilité magnétique a été étudiée pour tous les composés, et a révélé une grande différence entre les composés avec Ln = Tb et Dy d'une part, les composés avec Ln = Ho, Er, Tm, et Yb d'autre part. Pour les premiers composés, une interaction magnétique Ln(III)-Cu(II) a été détectée, conduisant à une divergence du produit* χ_MT *de la susceptibilité magnétique par la température. Il n'est cependant pas possible à ce stade de préciser si les composés doivent être considérés comme des ferri-aimants ou des ferro-aimants monodimensionels. Au contraire, pour les seconds composés, les interactions Ln(III)-Cu(II), si elles existent, sont masquées par les effets de champ cristallin.*

lanthanide / interaction 3*d*–4*f* / magnétisme moléculaire / basse dimensionnalité

Introduction

A few years ago, we initiated a new project of research dealing with the 3*d*–4*f* molecular chemistry. The objective is to design novel molecular compounds incorporating both transition metal ions and rare earths, and to investigate and interpret their physical properties [1-6]. Our main interest concerns 3*d*–4*f* one- two- and three-dimensional molecular materials. First, we focused on the system Ln(III)–$[\mathrm{Cu(pba)}]^{2-}$, where Ln(III) stands for a lanthanide(III) ion and pba for 1,3-propylenebis(oxamato). We found three families of compounds, namely: (i) one-dimensional compounds with ladder-like motifs [3]; (ii) one-dimensional compounds with tube-like motifs [2]; and (iii) two-dimensional compounds with double-sheet layers [1]. All these compounds crystallize with a large number of non-coordinated water molecules, which makes the investigation of their physical properties rather tedious; indeed, most of these water molecules may be easily removed, which may modify the crystal lattice. In an attempt to avoid this difficulty, we decided to work in

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[†] Dedicated to Prof Raymond Weiss.

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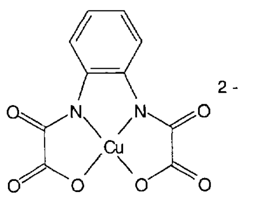
organic solvents rather than in water, and to replace the $[Cu(pba)]^{2-}$ precursor by $[Cu(opba)]^{2-}$, where opba stands for *ortho*-phenylenebis(oxamato). The structure of this precursor anion is schematized below.



Let us recall that in the last few years $[Cu(opba)]^{2-}$ has been successfully utilized to obtain one- two-, and three-dimensional bimetallic materials, some of them behaving as molecular-based magnets [6–11]. Other groups are also working on the $3d$–$4f$ molecular chemistry [12–21].

In this paper, we will describe the synthesis and the crystal structure of isomorphous compounds of formula $Ln_2[Cu(opba)]_3 \cdot x DMF \cdot y H_2O$ ($x \approx 10$, $y \approx 4$), where Ln goes from Tb to Lu along the lanthanide series. Ln may be also Y which, strictly speaking, is not a lanthanide. These compounds will be abbreviated hereafter as Ln_2Cu_3. A preliminary study of the magnetic properties will be also presented.

Experimental section

Synthesis

The copper(II) precursor $Na_2[Cu(opba)] \cdot 3H_2O$ was prepared as previously described [7]. The Ln_2Cu_3 compounds, with Ln = Tb–Yb and Y, were prepared as follows: 1 mmol of Ln(III) nitrate and 1 mmol of $Na_2[Cu(opba)] \cdot 3H_2O$ were ground together in a motar, and intimately mixed. The resulting powder was then dissolved in 5 mL DMF under stirring and warming up to 50 °C. The intense blue solution was then filtered and dropped into a long tube. This tube was kept at 75 °C in a water bath. After a few days, a powder appeared at the bottom of the tube, then some single crystals. The chemical analysis of Tm_2Cu_3 was found to be compatible with the formula $Tm_2[Cu(opba)]_3 \cdot 10DMF \cdot 4H_2O$.

Anal calc: C. 34.71; H, 4.37; N, 10.80; Cu, 9.18; Tm, 16.28.
Found: C. 34.60; H, 4.03; N, 10.65; Cu, 9.44; Tm, 16.06.

Structural determination

The blue, prismatic single crystals of Tm_2Cu_3 are fragile. They are stable only in their mother liquor, and have to be handled with care. The best crystallographic data were obtained after testing several crystals on Weissenberg camera and diffractometer. The crystal used for data collection was sealed in a glass capillary filled with a small amount of the mother liquor, and mounted on an Enraf-Nonius CAD4-F diffractometer. The data were corrected for background, decay, Lorentz-polarization, absorption (empirical procedure), and extinction. The structure was solved by direct methods, and refined (on Fs) by full matrix least-squares calculations. The low number (2530) of significant data ($I \geqslant 3\sigma(I)$) compared with the unique collected data set (8776) led us to refine solely the Tm and Cu atoms with anisotropic temperature factors, the other atoms being kept isotropic. Except for the coordinated water molecules on the rare-earth atoms and one copper atom, it was not possible to model the residual electronic density with disordered coordinated and non-coordinated solvent molecules (water and dimethylformamide). In addition, constraints for one phenyl ring were applied during the refinements. The low diffracting power of the crystal and the associated disorder together with the strategy of refinement are responsible of the relatively high reliability factors. The crystallographic and the atomic positional parameters data are summarized respectively in Table I and II.

Table I. Crystallographic data for Tm_2Cu_3.

Molecular formula	$Tm_2Cu_3C_{30}H_{22}N_6O_{17}$
Formula weight	1267.1
Crystal system	orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
a (Å)	9.864(2)
b (Å)	20.855 (2)
c (Å)	39.101(9)
Z	4
R	0.134
R_w	0.177

Table II. Atomic positional parameters and isotropic displacement parameters for Tm_2Cu_3.

	x/a	y/b	z/c	U
Tm(1)	0.2702(4)	0.2746(3)	0.3929(1)	*0.026(2)
Tm(2)	0.3572(5)	0.2755(3)	0.1083(1)	*0.035(2)
Cu(1)	0.408(2)	0.2765(8)	0.2524(4)	*0.062(6)
Cu(2)	0.493(2)	0.0140(7)	0.0974(3)	*0.040(5)
Cu(3)	0.591(1)	0.5176(6)	0.0809(3)	*0.031(4)
O(1C)	0.627(9)	0.224(5)	0.261(2)	0.08(3)
O(1T)	0.16(1)	0.285(5)	0.458(2)	0.09(3)
O(2T)	0.311(9)	0.266(5)	0.045(2)	0.08(3)
O(111)	0.42(1)	0.307(5)	0.356(2)	0.08(3)
O(112)	0.240(8)	0.224(4)	0.344(2)	0.04(2)
C(111)	0.31(1)	0.238(6)	0.318(3)	0.04(3)
C(112)	0.398(9)	0.302(4)	0.319(2)	0.02(2)
N(101)	0.293(8)	0.222(5)	0.282(2)	0.03(2)
O(101)	0.458(8)	0.333(4)	0.295(2)	0.05(2)
N(102)	0.313(9)	0.222(6)	0.220(2)	0.04(2)
O(102)	0.463(9)	0.323(4)	0.210(2)	0.07(3)
C(211)	0.35(1)	0.241(5)	0.190(3)	0.03(3)
C(212)	0.42(1)	0.304(5)	0.181(3)	0.03(3)
O(211)	0.306(6)	0.216(4)	0.156(2)	0.03(2)
O(212)	0.444(8)	0.325(4)	0.156(2)	0.05(2)
C(101)	0.22(1)	0.177(4)	0.267(2)	0.05(3)
C(102)	0.13(2)	0.130(6)	0.282(2)	0.11(6)
C(103)	0.08(1)	0.079(5)	0.262(3)	0.09(5)
C(104)	0.10(1)	0.081(4)	0.227(2)	0.07(4)
C(105)	0.18(1)	0.128(4)	0.212(2)	0.04(3)
C(106)	0.23(1)	0.178(4)	0.232(2)	0.04(3)
O(121)	0.227(8)	0.382(3)	0.395(2)	0.03(2)
O(122)	0.439(6)	0.337(3)	0.421(1)	0.02(1)
C(121)	0.50(2)	0.401(8)	0.405(4)	0.07(5)
C(122)	0.336(8)	0.417(4)	0.404(2)	0.02(2)
N(201)	0.662(6)	−0.014(3)	0.101(1)	0.02(1)
O(201)	0.344(6)	0.067(3)	0.086(1)	0.02(1)
N(202)	0.587(8)	0.095(4)	0.106(2)	0.03(2)
O(202)	0.441(8)	−0.063(4)	0.084(2)	0.04(2)
C(221)	0.50(1)	0.133(5)	0.105(3)	0.04(3)
C(222)	0.344(9)	0.125(4)	0.099(2)	0.02(2)
O(221)	0.547(7)	0.200(3)	0.110(2)	0.04(2)
O(222)	0.283(6)	0.177(3)	0.093(1)	0.02(1)
C(201)	0.220(9)	0.525(3)	0.389(4)	0.08(5)
C(202)	0.085(9)	0.514(3)	0.378(3)	0.07(4)
C(203)	0.004(7)	0.566(4)	0.369(3)	0.04(3)
C(204)	0.052(7)	0.628(3)	0.375(3)	0.04(3)
C(205)	0.191(7)	0.638(3)	0.378(2)	0.03(3)

C(206)	0.275(6)	0.587(3)	0.388(2)	0.02(2)
O(131)	0.438(4)	0.213(2)	0.396(1)	0.02(1)
O(132)	0.212(8)	0.169(4)	0.409(2)	0.04(2)
C(131)	0.424(8)	0.155(4)	0.407(2)	0.02(2)
C(132)	0.28(2)	0.093(9)	0.408(5)	0.10(7)
N(301)	0.57(1)	−0.008(6)	0.416(3)	0.09(4)
O(301)	0.351(9)	−0.078(4)	0.419(2)	0.05(2)
N(302)	0.503(8)	0.600(3)	0.092(2)	0.02(2)
O(302)	0.78(1)	0.567(5)	0.084(2)	0.07(3)
C(231)	0.529(9)	0.394(4)	0.090(2)	0.02(2)
C(232)	0.395(8)	0.421(4)	0.092(2)	0.02(2)
O(231)	0.311(7)	0.387(3)	0.103(2)	0.04(2)
O(232)	0.548(6)	0.324(3)	0.089(1)	0.02(1)
C(301)	0.687(5)	0.022(2)	0.405(2)	0.02(2)
C(302)	−0.175(6)	0.011(2)	0.403(2)	0.02(2)
C(303)	0.916(6)	0.061(3)	0.406(4)	0.12(7)
C(304)	0.869(6)	0.124(3)	0.402(2)	0.03(3)
C(305)	−0.270(6)	0.136(2)	0.405(2)	0.02(2)
C(306)	0.640(5)	0.085(3)	0.409(2)	0.02(2)

Magnetic measurements

Magnetic measurements were carried out with a Quantum Design MPMS-5S Squid magnetometer in the dc mode. The samples were prepared in a way to prevent the orientation of the microcrystallites within the applied magnetic field.

Description of the structure of Tm_2Cu_3

The asymmetric unit along with the atomic numbering scheme is depicted in figure 1. The structure is based on a discrete, infinite ladder-like motif, as shown in figure 2. The sidepieces of the ladder consist of TmCu(opba) units developing along the [010] direction with an alternance of Ln and Cu atoms. These sidepieces are linked together by rungs made of Cu(opba) groups and located between two Tm atoms. The opba ligands of the rungs have all the same orientation within one ladder, while they alternate along the sidepieces. The ladder motif within the structure is very similar to that identified previously for $Ln_2[Cu(pba)]_3 \cdot 23H_2O$ with again Ln going from Tb to Yb, except for the arrangement of the ladders with respect to each other [3]. In the $Ln_2[Cu(pba)]_3 \cdot 23H_2O$ compounds the ladders are in staggered rows when viewed along a direction perpendicular to the ladder, which is approximately the [101] direction, and eclipsed when viewed along the rungs. In Tm_2Cu_3 the ladders form eclipsed rows when viewed perpendicularily, along the [100] direction (see fig 3a), and in staggered rows along the [001] direction (see fig 3b). The Tm–Cu distances across an oxamato bridge are in the range 5.52 to 5.66 Å, while the distances between two Ln atoms across a Cu(opba) unit vary from 11.08 to 11.16 Å. The shortest distance between two Ln atoms (9.80 Å) involves non-connected Tm atoms belonging to two sidepieces of neighboring ladders.

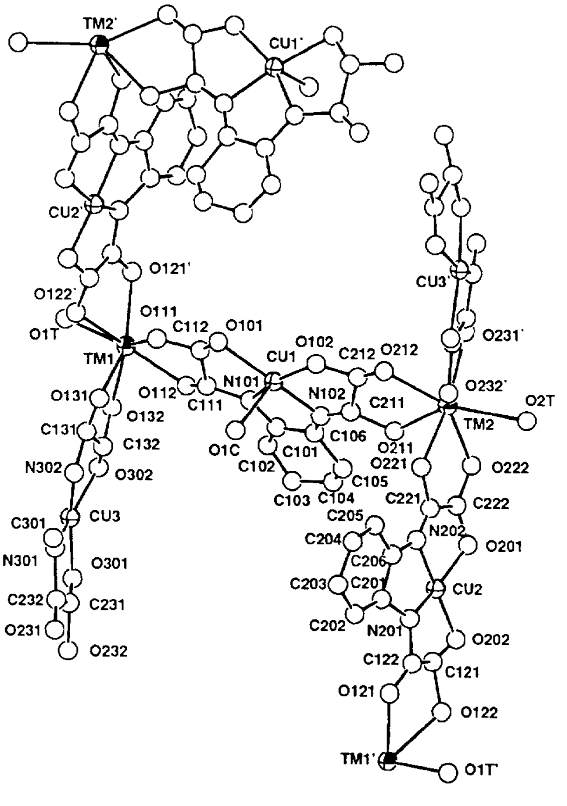


Fig 1. Asymmetric unit along with the atom labeling for Tm_2Cu_3.

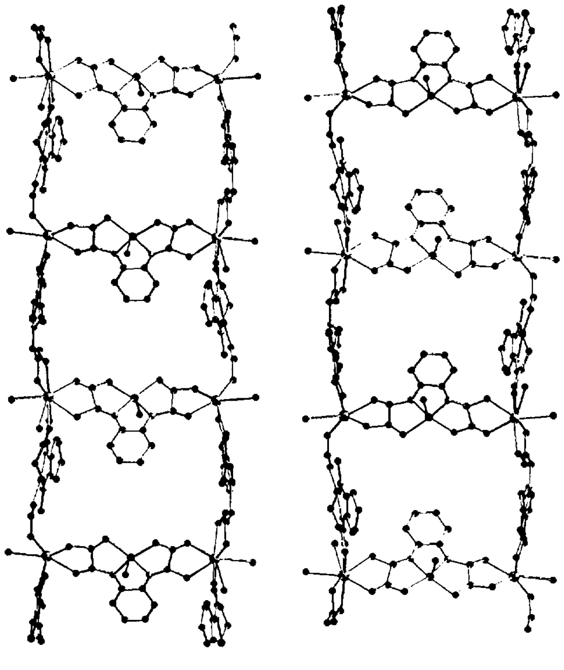


Fig 2. Two nearest neighbor ladder-like motifs in Tm_2Cu_3.

Each Tm atom is surrounded by seven oxygen atoms, six of which belong to three opba ligands and one to a water molecule. The Tm(III) coordination polyhedron shown in figure 4 may be described as a capped trigonal antiprism for Tm2, while the polyhedron around Tm1 is more strongly distorted. We can note that seven-coordination is rather unusual for Ln(III) ions. The Cu(II) ions present a square planar environment along the sidepieces, with two oxygen and two nitrogen atoms of the opba ligand in the basal plane. The Cu(II) ions of

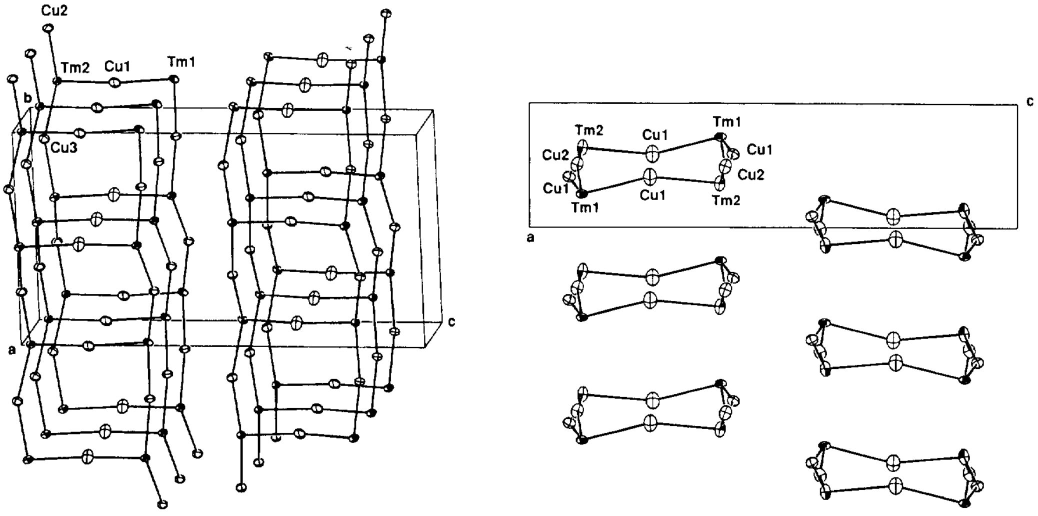


Fig 3. Relative dispositions of the ladders in Tm_2Cu_3: a) viewed along the [100] direction; b) viewed along the [001] direction.

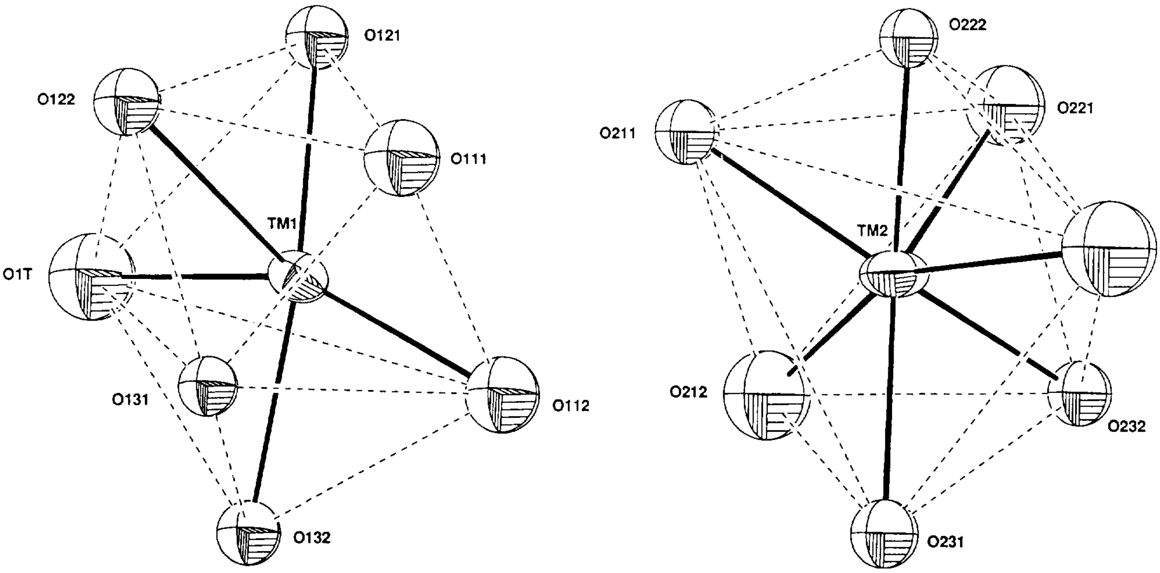


Fig 4. Coordination polyhedra for the two Tm(III) sites of Tm_2Cu_3.

the rungs present a square pyramidal environment with a water molecule occupying the apical position. The non-coordinated DMF and water molecules are probably strongly disordered, and have not been located.

Magnetic properties

For each compound Ln_2Cu_3, with Ln = Tb–Lu, and Y, the temperature dependence of the magnetic susceptibility was measured, and the results represented in the form of the $\chi_M T$ versus T curve, χ_M being the molar magnetic susceptibility (per Ln_2Cu_3 unit) and T the temperature. The profile of these $\chi_M T$ versus T curves may be classified into three categories.

First, for Ln = Lu and Y, $\chi_M T$ is essentially constant in the whole temperature range, and equal to 1.20 cm^3 K mol^{-1}. Both the Lu(III) and Y(III) ions are diamagnetic, and the Cu(II) ions are too far from each other to interact significantly. Therefore, the magnetic susceptibility follows the Curie law expected for three isolated Cu(II) ions.

Second, for Ln = Ho, Er, Tm, and Yb, $\chi_M T$ continuously decreases as T is lowered. A typical curve, that for Er_2Cu_3, is shown in figure 5. Such curves suggest that the Ln(III)–Cu(II) interactions are very weak. In fact, any significant Ln(III)–Cu(II) interaction should lead to a rapid increase of $\chi_M T$ as T tends to the absolute zero, whatever the nature of this interaction may be. Indeed, if this interaction was antiferromagnetic, the compound would behave as a one-dimensional ferrimagnet, with the Ln(III) moments aligning along the field direction, and the Cu(II) moments aligning along the opposite direction. The correlation length for such a system with antiparallel and noncompensating Ln(III) and Cu(II) moments increases as T drops, while $\chi_M T$ increases [22]. A noticeable exception would occur in the case of an accidental quasi-compensation between Ln(III) and Cu(II) moments, as reported recently for a Nd_2Cu_3 species [5]. The large values of the Ln(III) (Ln going from Ho to Yb) magnetic moments allow us to rule out such a situation. The decrease of $\chi_M T$ as T is lowered may be attributed to the thermal depopulation of the excited local states arising from the Ln(III) single-ion ground state ($^4I_{15/2}$ for Er(III)).

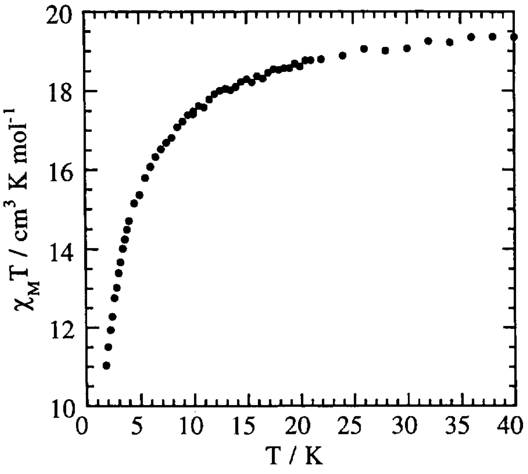


Fig 5. $\chi_M T$ versus T plot for Er_2Cu_3.

Third, for Ln = Tb and Dy, $\chi_M T$ first decreases as T is lowered from room temperature, reaches a minimum at a temperature T_{min}, and then increases very rapidly as T is lowered further. A typical example, that of Dy_2Cu_3, is given in figure 6. T_{min} is then found as 10 K. For Tb_2Cu_3, T_{min} is equal to 20 K. We explained above that the rapid increase of $\chi_M T$ as T tends to the absolute zero reveals significant Ln(III)–Cu(II) interactions, but does not allow us to specify the nature of these interactions. The decrease of $\chi_M T$ between room temperature and T_{min} may again be due to the thermal depopulation of the local low-lying states of the Ln(III) ion.

Discussion and conclusion

The reaction of Ln(III) with the $[Cu(opba)]^{2-}$ precursor in DMF affords one-dimensional compounds with a ladder-type structure when Ln is an atom belonging to the right of the lanthanide series, from Tb to Lu. The same structure is obtained with Ln = Y. With lighter Ln atoms, from La to Gd, no compound with a similar structure has been obtained yet. The infinite ladders are very similar to those found in $Ln_2[Cu(pba)]_3 \cdot 23H_2O$, where Ln goes from Tb to Yb, but they are not disposed in the same manner within the lattice.

The study of the magnetic properties of these novel $3d$-$4f$ compounds has revealed quite a striking feature. For Ln = Tb ($4f^8$, $^7F_6$) and Dy ($4f^9$, $^6H_{15/2}$), a significant Ln(III)–Cu(II) interaction is observed, which leads to a divergence of $\chi_M T$ as T tends to the absolute zero. At this stage, it is not possible to specify the nature of the interaction. If the interaction is antiferromagnetic, the compound behaves as a one-dimensional ferrimagnet; if the interaction is ferromagnetic, it behaves as a one-dimensional ferromagnet. In both cases, $\chi_M T$ is expected to diverge as T is lowered. For compounds containing two different $3d$ metal ions, the fingerprint of ferrimagnetic behavior is the minimum in the $\chi_M T$ versus T plot [22]. For instance, this minimum is observed in all the Mn(II)Cu(II) low-dimensional ferrimagnets described so far [6–11]. When one of the interacting magnetic centers carries a first-order orbital momentum, the situation may be more complicated. It is the case for both Tb(III) and Dy(III). The magnetic susceptibility of an isolated Tb(III) or Dy(III) ion does not follow a Curie law; $\chi_M T$ decreases as T diminishes, owing to the thermal depopulation of the excited states arising from the action of the crystal field on the free-ion ground state. Therefore, the minimum in the $\chi_M T$ versus T plot can no longer be considered as the signature of a ferrimagnetic behavior. In a subsequent paper, we hope to be able to determine unambiguously the nature of the Tb(III)–Cu(II) and Dy(III)–Cu(II) interactions.

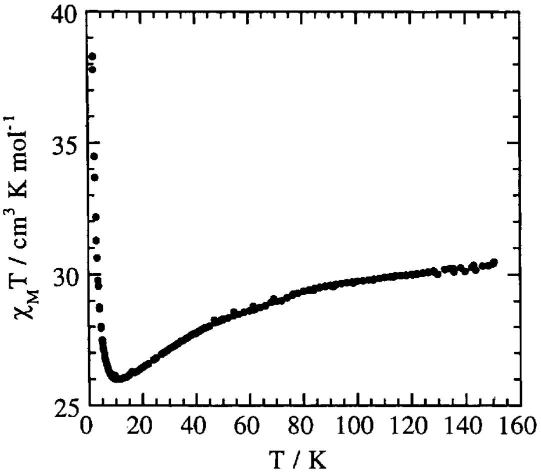


Fig 6. $\chi_M T$ versus T plot for Dy_2Cu_3.

In contrast, for Ln = Ho, Er, Tm, and Yb, the Ln(III)–Cu(II) interactions, if any, are small, and are hidden by the crystal field effects. The reasons why there is such a striking difference between the two groups of Ln(III) ions are not yet clear. We also hope to be able to bring new insights on this problem in a near future.

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