# Nature of the Magnetic Interaction in the ($Cu^{2+}$, $Ln^{3+}$) Pairs: An Empirical Approach Based on the Comparison Between Homologous ($Cu^{2+}$, $Ln^{3+}$) and ($Ni^{2+}_{LS}$, $Ln^{3+}$) Complexes**

**Jean-Pierre Costes,* Françoise Dahan, Arnaud Dupuis, and Jean-Pierre Laurent**

**Abstract:** The reaction of {2,2′-[1-methyl-1,2-propanediyl bis(nitrilomethylidyne]-di(6-methoxyphenolato)}copper(II) (LCu) or nickel(II) (LNi) with $Ln(NO_3)_3$ in acetone led to strictly heterodinuclear $[LCu(Me_2CO)Ln(NO_3)_3]$ and $[LNi(Me_2CO)Ln(NO_3)_3]$ complexes (with Ln = all the lanthanides except prometheum; Ni in the low-spin state). Three complexes [($Cu^{2+}$, $Ce^{3+}$), ($Cu^{2+}$, $Yb^{3+}$) and ($Ni^{2+}$, $Dy^{3+}$)] have been structurally characterized. They crystallize in the same monoclinic space groups $P2_1/c$ (no. 14) and are isomorphous. This relationship in conjunction with the diamagnetism of the $Ni^{2+}$ ion allow an empirical evaluation of the effect of the crystal field on the magnetic properties as well as an approach towards the nature of the coupling between the copper(II) and the lanthanide(III) ions in the $[LCu(Me_2CO)Ln(NO_3)_3]$ complexes. The Cu–Ln interaction is antiferromagnetic for Ln = Ce, Nd, Sm, Tm, and Yb, and ferromagnetic for Ln = Gd, Tb, Dy, Ho, and Er; however, the Cu–Pr and the Cu–Eu pairs are devoid of any significant interaction along with the Cu–La and Cu–Lu pairs, in accordance with the nonmagnetic nature of the ground state for these lanthanide ions.

**Keywords:** copper · heterodinuclear complexes · lanthanides · magnetic properties · nickel

## Introduction

We have previously described[1, 2] the synthetic possibilities offered by Schiff base ligands derived from 2-hydroxy-3-methoxybenzaldehyde to produce strictly dinuclear ($Cu^{2+}$, $Ln^{3+}$) complexes (Ln = Pr, Eu, Gd, Yb). However, we did not succeed in determining the nature (ferro- or antiferromagnetic) of the exchange interaction, except for the ($Cu^{2+}$, $Gd^{3+}$) pair. The discrete dinuclear ($Cu^{2+}$, $Gd^{3+}$) complexes, devoid of any intermolecular interaction, have given unambiguous support to the conclusions extracted from the investigations of polynuclear complexes.[3–10] The observed ferromagnetic behavior is an intrinsic property of the ($Cu^{2+}$, $Gd^{3+}$) pair. More recently we have shown that this conclusion may be extended to the nickel(II, high-spin)-gadolinium(III) pair.[11] The major difficulties in analyzing the magnetic properties of the ($Cu^{2+}$, $Ln^{3+}$) couples arise from the fact that the ground state of the $Ln^{3+}$ ion (Ln ≠ La, Eu, Gd, Lu) has a first-order angular momentum which prevents the use of a spin-only Hamiltonian for isotropic exchange.[12, 13] The joint effects of the crystal field and orbital contribution can result in an important anisotropy of the magnetic susceptibility and exchange interaction. The crystal field splitting is usually of the order of $kT$ at room temperature, so that the thermal dependence of the populations of the Stark levels has to be implicitly taken into account. To date, the studies addressing these problems in the case of (3d, 4f) molecular complexes are very scarce.[5, 10, 14, 15]

This situation prompted us to investigate the possibilities of a more empirical approach based on a comparison of the magnetic properties of homologous ($Cu^{2+}$, $Ln^{3+}$) and ($Ni^{2+}_{LS}$, $Ln^{3+}$) complexes. Just after the completion of our study, we were made aware of a very similar analysis which leads to the conclusion that a ferromagnetic exchange interaction is operative in the ($Cu^{2+}$, $Dy^{3+}$) pair.[16]

The present work focuses on the study of the magnetic susceptibility of 22 complexes belonging to the homologous families $[LNi_{LS}(Me_2CO)Ln(NO_3)_3]$ and $[LCu(Me_2CO)Ln(NO_3)_3]$, where L represents the dideprotonated form of {2,2′-[1-methyl-1,2-propanediyl bis(nitrilomethylidyne]-di(6-methoxyphenol)}, and Ln represents all the lanthanides except prometheum. Structural characterizations of the ($Cu^{2+}$, $Ce^{3+}$), ($Cu^{2+}$, $Yb^{3+}$), and ($Ni^{2+}$, $Dy^{3+}$) complexes are reported.

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[**] $Ln^{3+}$ = all the lanthanides except prometheum.

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## Results and Discussion

**Preparation and characterization**: The synthetic strategies that we have previously used to obtain several examples of dinuclear ($Cu^{2+}$, $Ln^{3+}$) complexes have been recently extended to the preparation of ($Ni^{2+}_{HS}$, $Ln^{3+}$) and ($VO^{2+}$, $Gd^{3+}$) complexes.[11, 17] A slight modification of these processes affords convenient routes to ($Ni^{2+}_{LS}$, $Ln^{3+}$) complexes. Indeed, the spin state of the $Ni^{2+}$ ion depends on the nature of the diimino chain present in the Schiff base ligand. Shortening the chain from N-C-$CMe_2$-C-N to N-C-$CMe_2$-N prevents the axial coordination of solvent molecules and stabilizes the low-spin state of $Ni^{2+}$. For the investigations reported here, we have prepared two series of dinuclear ($Cu^{2+}$, $Ln^{3+}$) and ($Ni^{2+}_{LS}$, $Ln^{3+}$) complexes, where Ln represents any ion of the 4 f family, except prometheum which is radioactive.

The IR spectra of all of these compounds are superimposable. Owing to the large electronic delocalization occurring in these complexes, any absorption cannot be considered in isolation and attributed with certainty. However, two bands at 1464(±2) and 1368(±1) $cm^{-1}$ are attributable to the bidentate nitrato ions. The complexes display very similar mass spectra ($FAB^+$). In every case, the predominant signal is attributable to the $[LMLn(NO_3)_2]^+$ ion (M = Cu or Ni).

Table 1. Crystallographic data of **1**–**3**.

| | **1** | **2** | **3** |
|---|---|---|---|
| chemical formula | $C_{23}H_{28}CeCuN_5O_{14}$ | $C_{23}H_{28}CuN_5O_{14}Yb$ | $C_{23}H_{28}DyN_5NiO_{14}$ |
| $M_r$ | 802.17 | 835.09 | 819.71 |
| $T$ [K] | 293(2) | 293(2) | 293(2) |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$ [Å] | 9.7853(13) | 9.8357(13) | 10.0653(10) |
| $b$ [Å] | 19.069(2) | 18.858(2) | 18.724(2) |
| $c$ [Å] | 16.136(2) | 15.957(2) | 15.757(2) |
| $\beta$ [°] | 96.60(2) | 96.42(2) | 96.827(10) |
| $V$ [$Å^3$] | 2990.9(6) | 2941.1(7) | 2948.6(6) |
| $Z$ | 4 | 4 | 4 |
| $F(000)$ | 1600 | 1648 | 1628 |
| $\rho_{calcd}$ [$Mg\,m^{-3}$] | 1.781 | 1.886 | 1.847 |
| $\mu(Mo_{K\alpha})$ [$mm^{-1}$] | 2.289 | 3.944 | 3.229 |
| crystal size [mm] | 0.40 × 0.35 × 0.20 | 0.50 × 0.20 × 0.15 | 0.50 × 0.40 × 0.25 |
| $T_{min}-T_{max}$ | 0.8248–0.9992 | 0.7361–0.9990 | 0.5928–0.9997 |
| $2\theta$ range [°] | 3–54 | 3–54 | 3–54 |
| no. of data collected | 6894 | 6762 | 6758 |
| no. of unique data | 6524 | 6401 | 6406 |
| Rav. (on $I$) | 0.0149 | 0.0175 | 0.0135 |
| observed data [$I > 2\sigma(I)$] | 4069 | 4708 | 4973 |
| variable parameters | 327 | 327 | 327 |
| $S$ | 1.077 | 1.078 | 1.209 |
| $(\Delta/\sigma)_{max}$ | 0.010 | 0.002 | 0.009 |
| $R$[a] | 0.0362 | 0.0284 | 0.0314 |
| $wR$[b] | 0.0989 | 0.0717 | 0.0793 |
| $(\Delta/\rho)_{min}$ [$e\,Å^{-3}$] | −0.581 | −0.665 | −0.558 |
| $(\Delta/\rho)_{max}$ [$e\,Å^{-3}$] | 0.694 | 0.724 | 0.667 |

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ (obsd reflections).
[b] $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w |F_o^2|^2]^{1/2}$ (all reflections).

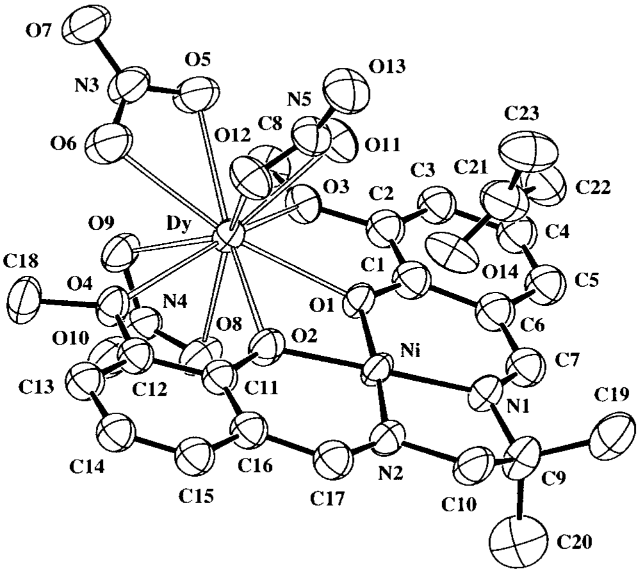

Figure 1. Molecular plot for $[LNi(Me_2CO)_2Dy(NO_3)_3]$ (**3**) (ellipsoids drawn at the 40% probability level).

The structures of three complexes $[LCuCe(NO_3)_3]$ (**1**), $[LCuYb(NO_3)_3]$ (**2**), and $[LNiDy(NO_3)_3]$ (**3**) were determined by X-ray crystallography. In all three cases, the crystal system is monoclinic with space group $P2_1/c$ (no. 14), and the unit cell contains four discrete $[LMLn(NO_3)_3]$ entities with intervening acetone molecules (Table 1). A view of **3** is represented in Figure 1. Significant bond lengths and angles are given in Table 2 for the three complexes along with those of the previously reported complex $[LCuGd(NO_3)_3]$ (**4**).[1] The following features were observed for **1**, **2**, and **3**:

1) The central region of the structure is occupied by the $M^{2+}$ and $Ln^{3+}$ ions which are bridged one to the other by two phenolato oxygen atoms from the ligand.
2) The four atoms of the bridging entity are not exactly coplanar which leads to a roof-shaped $MO_2Ln$ core.

**Abstract in French:** *La réaction des complexes {2,2'-[1-méthyl-1,2-propanedyil bis(nitrilométhylidine]-di(6-méthoxyphénolato)} cuivre(*II*) (LCu) ou nickel(*II*) (LNi) avec $Ln(NO_3)_3$ conduit, dans l'acétone, à des complexes $[LCu(Me_2CO)Ln(NO_3)_3]$ et $[LNi(Me_2CO)Ln(NO_3)_3]$ strictement dinucléaires (avec Ln = tous les lanthanides excepté le prométhéum radioactif et Ni présentant un état bas spin). La détermination structurale de trois complexes (($Cu^{2+}$, $Ce^{3+}$), ($Cu^{2+}$, $Yb^{3+}$), ($Ni^{2+}$, $Dy^{3+}$)) a été réalisée. Ils cristallisent dans le même groupe d'espace $P2_1/c$ (N° 14) et sont isomorphes. Cet isomorphisme, ainsi que le diamagnétisme des centres nickel, permettent une évaluation empirique de l'effet du champ cristallin sur les propriétés magnétiques ainsi qu'une approche de la nature du couplage entre le cuivre(*II*) et les ions lanthanide(*III*) dans les complexes $[LCu(Me_2CO)Ln(NO_3)_3$. Ainsi, l'interacction Cu–Ln est antiferromagnétique pour Ln = Ce, Nd, Sm, Tm, Yb et ferromagnétique pour Ln = Gd, Tm, Dy, Ho, Er. Les complexes Cu–Pr et Cu–Eu sont dépourvus d'interaction significative, tout comme Cu–La et Cu–Lu, en accord avec la nature non magnétique de niveau fondamental de ces ions lanthanide.*

Table 2. Selected bond lengths [Å] and angles [°] for **1**–**4**.[a]

| | 1 | 2 | 3 | 4[a] |
|---|---|---|---|---|
| M–O1 | 1.913(4) | 1.896(3) | 1.827(3) | 1.879(5) |
| M–O2 | 1.933(4) | 1.898(3) | 1.840(3) | 1.904(5) |
| M–N1 | 1.924(5) | 1.903(3) | 1.829(4) | 1.942(6) |
| M–N2 | 1.918(5) | 1.926(3) | 1.849(4) | 1.918(7) |
| Ln–O1 | 2.435(4) | 2.307(3) | 2.372(3) | 2.398(5) |
| Ln–O2 | 2.417(4) | 2.298(3) | 2.356(3) | 2.337(5) |
| Ln–O3Me | 2.684(4) | 2.586(3) | 2.563(3) | 2.626(5) |
| Ln–O4Me | 2.659(4) | 2.586(2) | 2.550(3) | 2.614(5) |
| Ln–O(nitrato) [b] | 2.556(4)–<br>2.580(4) | 2.393(3)–<br>2.486(3) | 2.432(4)–<br>2.500(4) | 2.452(5)–<br>2.529(5) |
| Ln–O1-M | 106.1(2) | 106.2(1) | 107.7(1) | 105.9(2) |
| Ln-O2-M | 106.1(2) | 106.4(1) | 107.9(2) | 107.4(2) |
| O1-M-O2 | 82.4(2) | 80.8(1) | 81.4(1) | 81.8(2) |
| O1-Ln-O2 | 63.0(1) | 64.55(9) | 60.7(1) | 63.0(2) |
| *D*[c] | 14.3(4) | 13.2(3) | 14.0(3) | 12.9(5) |

[a] Cf. ref. [1]. [b] Minimum and maximum values. [c] Dihedral angle between the M-O1-O2 and Ln-O1-O2 planes.

3) The acetone molecule is axial with respect to the $M^{2+}$ ion, but not coordinated to it in the case of the ($Ni^{2+}$, $Dy^{3+}$) complex (Ni–O = 3.139 Å) and, at best, semicoordinated (Cu–O = 2.623(3) and 2.601(5) Å) for the ($Cu^{2+}$, $Ce^{3+}$) and ($Cu^{2+}$, $Yb^{3+}$) complexes.
4) The copper ion adopts a square-based [4+1] coordination mode, the equatorial $N_2O_2$ donors are from L. The copper ion protrudes out of the mean $N_2O_2$ plane by 0.11–0.12 Å.
5) The geometry around the nickel ion is square planar.
6) The Ln ion is ten-coordinate. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms from the OMe side arms of L and six oxygens from the three bidentate nitrato ions.
7) The separations between metal ions belonging to neighboring dinuclear units are much larger than the related intramolecular M···Ln separations and preclude any significant intermolecular interaction.

A preliminary structural study of the ($Cu^{2+}$, $Er^{3+}$) and ($Ni^{2+}$, $Er^{3+}$) complexes show that these complexes are also isomorphous.

**Magnetic study**: Of the 30 possible complexes, or 15 M–Ln pairs (M = $Ni^{2+}$, $Cu^{2+}$), one pair has to be deleted because Pm is radioactive, and two other pairs have no 3d–4f interaction because the Ln centers are diamagnetic (Ln = La, Lu), and a fourth, M–Gd, has already been studied.[1] Informative magnetic susceptibility measurements have been performed for the 22 remaining low-spin nickel and copper complexes in the 2–300 K temperature range. In these 22 complexes, the lanthanide ions possess a first-order angular momentum which prevents the use of a spin-only Hamiltonian for isotropic exchange. This is the reason why we investigated the possibility of a more empirical approach based on a comparison of the magnetic properties of homologous (Cu, Ln) and (Ni, Ln) complexes in which nickel centers are low-spin (diamagnetic). The comparison between isomorphous (Cu,Ln) and (Ni, Ln) complexes is needed in order to eliminate the crystal field contribution of Ln ions in each pair. Thus, the resulting behavior can be attributed to intramolecular magnetic interactions because the dinuclear complexes are well isolated, as confirmed by the structural determinations which showed that intermolecular interactions are impossible. These results only give information on the type of interaction (ferro- or antiferromagnetic), but they cannot lead to a quantitative determination.

Three types of behaviour are observed; they are illustrated in Figure 2, which reports the thermal dependence of the $\chi_M T$ product for three paired complexes ($Cu^{2+}$, $Ln^{3+}$)/($Ni^{2+}$, $Ln^{3+}$) (Ln = neodymium, europium, and dysprosium). In each case, the third curve represents the variation of the difference $\Delta(T) = (\chi_M T)_{CuLn} - (\chi_M T)_{NiLn}$.

For all the ($Cu^{2+}$, $Ln^{3+}$) complexes, the $\chi_M T$ values at 300 K are practically equal to the sum of the contribution attributable to noninteracting $Cu^{2+}$ and $Ln^{3+}$ ions. In the ($Ni^{2+}$, $Ln^{3+}$) complexes, the experimental $\chi_M T$ values only consist of the contribution of the rare earth ion which, in the free-ion approximation, may be evaluated by the expression given in Equation (1), where $\lambda$ is the spin-orbit coupling parameter and $g_J$ the Zeeman factor [Eq. (2)].

$$\chi = \frac{N g_J^2 \beta^2 J(J+1)}{3kT} + \frac{2\beta^2 (g_J - 1)(g_J - 2)}{3\lambda} \tag{1}$$

$$g_J = \frac{3}{2} + \frac{(S(S+1) - L(L+1)}{2J(J+1)} \tag{2}$$

*S*, *L*, and *J* are the spin, orbital, and total quantum numbers, respectively. On lowering the temperature, $(\chi_M T)_{CuLn}$ and

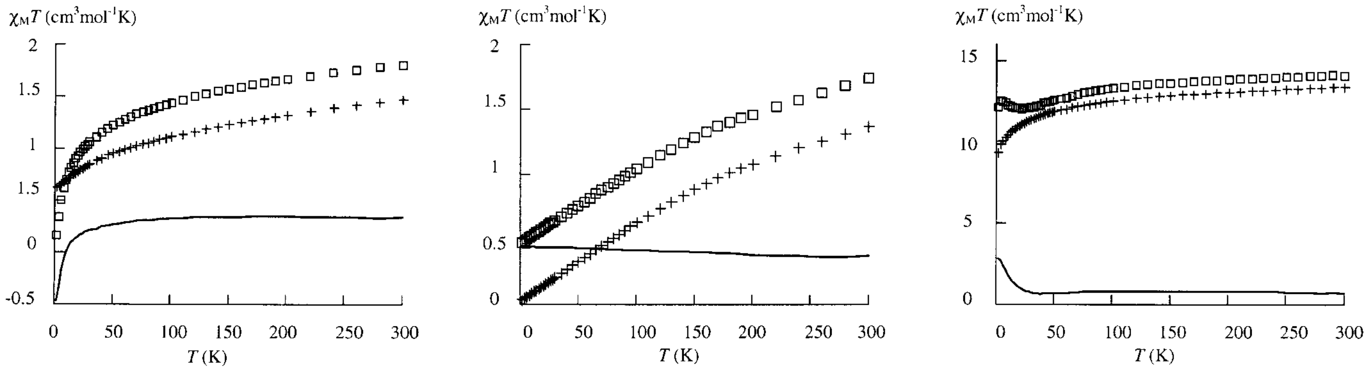

Figure 2. Thermal dependence of $\chi_M T$ for [LCu(Me$_2$CO)Ln(NO$_3$)$_3$] (□) and [LNi(Me$_2$CO)Ln(NO$_3$)$_3$] (+) complexes at 0.1 T. The solid line corresponds to the difference Δ between the two $\chi_M T$. Left: Ln = Nd; center: Ln = Eu; right: Ln = Dy.

$(\chi_M T)_{NiLn}$ decrease. For the ($Ni^{2+}$, $Ln^{3+}$) complexes, the plot of $\chi_M T$ versus $T$ deviates significantly from that predicted from Equation (1). Interestingly, the curves of $(\chi_M T)_{CuLn}$ and $(\chi_M T)_{NiLn}$ versus $T$ are roughly parallel from 300 to 80 K. The difference $\Delta(T)$ is approximately constant and equal to $0.38 \pm 0.05\,cm^3\,mol^{-1}\,K$, which represents the $\chi_M T$ values attributable to an isolated copper(II) ion. These observations indicate that the decrease of $(\chi_M T)_{CuLn}$ and $(\chi_M T)_{NiLn}$ must be considered as an intrisic characteristic of the Ln ion and essentially attributed to the depopulation of the Stark levels. The isomorphism of the various ($Cu^{2+}$, $Ln^{3+}$) and ($Ni^{2+}$, $Ln^{3+}$) complexes suppports the view that, for a given rare earth ion, the same crystal field is operative in both complexes, which gives rise to the same distribution of Stark levels. Below ≈ 80 K, the parallelism of the $\chi_M T$ plots is preserved when Ln = Pr and Eu and $\Delta(T)$ is practically constant. On the contrary, lowering the temperature causes $\Delta(T)$ to decrease when Ln = Ce, Nd, Sm, Tm, and Yb, and to increase when Ln = Gd, Dy, Ho, Tb, and Er. This behavior cannot originate in intermolecular interactions since structural data show that the complexes contain discrete dinuclear entities which are well-isolated from each other. They must be attributed to solely intramolecular magnetic interactions. These interactions are expected to be feeble and, therefore, only perceptible at low temperatures.

To sum up the discussion, we can represent the quantity $\Delta(T)$ by Equation (3).

$$\Delta(T) = (\chi_M T)_{CuLn} - (\chi_M T)_{NiLn} = (\chi_M T)_{Cu} + J_{CuLn(T)} \quad (3)$$

The local contribution $(\chi_M T)_{Cu}$ is equal to the Curie constant, which has been determined in the ($Cu^{2+}$, $La^{3+}$) and ($Cu^{2+}$, $Lu^{3+}$) complexes. The variation of $J_{CuLn(T)}$ with temperature is easily extracted from the experimental data, but is presently not amenable to a detailed analysis which would lead to a quantitative determination of the exchange parameters in the ground and excited crystal-field states.[12, 13] However, the direction (increase or decrease) of that variation is directly related to the nature (ferro- or antiferromagnetic) of the overall interaction between the $Cu^{2+}$ and $Ln^{3+}$ ions. A similar comparison made with the M–Gd pair confirms the ferromagnetic interaction previously observed.[1] According to this rationale, the interaction is antiferromagnetic when Ln = Ce, Nd, Sm, Tm, Yb, and ferromagnetic when Ln = Gd, Tb, Dy, Ho, Er. It may be noted that the ($Cu^{2+}$, $Dy^{3+}$) pair has been found to be ferromagnetic,[10, 16] while according to Gatteschi et al. the isotropic component of the exchange is antiferromagnetic, while the anisotropic parts are ferromagnetic.[5]

Two complexes, ($Cu^{2+}$, $Pr^{3+}$) and ($Cu^{2+}$, $Eu^{3+}$) are characterized by a zero value of $J_{CuLn(T)}$ which suggests that they are devoid of any interaction and the $Pr^{3+}$ and $Eu^{3+}$ ions are acting as nonmagnetic materials at low temperature. In fact, the low temperature limit of $(\chi_M T)_{NiLn}$ (Ln = Pr, Eu) is effectively zero. This conclusion is consistent with the fact that the $^4F_0$ ground state of europium is nonmagnetic, while the ground term $^3H_4$ of praseodymium can give rise to a singlet ground Stark level, as $Pr^{3+}$ is a non-Kramer ion.[18, 19]

## Conclusions

In general, our conclusions regarding the nature of the overall Cu–Ln interactions are in line with the predictions of Kahn et al.[8] These authors have stated that for the $4f^1$–$4f^6$ configurations of of $Ln^{3+}$, angular and spin momenta are antiparallel in $^{2S+1}L_J$ free-ion ground state ($J = L - S$). A parallel alignment of the $Cu^{2+}$ and $Ln^{3+}$ spin momenta would lead to an antiparallel alignment of the angular momenta, that is to an overall antiferromagnetic interaction. Conversely, for the $4f^8$–$4f^{13}$ configurations ($J = L + S$), a parallel alignment of the $Cu^{2+}$ and $Ln^{3+}$ spin momenta would result in an overall ferromagnetic interaction.

All the complexes considered in the present study, except ($Cu^{2+}$, $Tm^{3+}$) and ($Cu^{2+}$, $Yb^{3+}$), comply with this rationale which suggests that the spin momenta of $Cu^{2+}$ and $Ln^{3+}$ are parallel to each other. At present, it is still not clear why the two ($Cu^{2+}$, $Tm^{3+}$) and ($Cu^{2+}$, $Yb^{3+}$) pairs do not follow the general trend.

## Experimental Section

**Materials and methods**: All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). $^1H$ NMR spectra were recorded with a Bruker WM250 spectrometer working at 293 K. Magnetic susceptibility data were collected on a powdered sample of the compound with a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand, estimated from Pascal's constants[21] ($-337 \times 10^{-6}$ emu mol$^{-1}$ for $[LCuLn(NO_3)_3]\cdot Me_2CO$ complexes and $-336 \times 10^{-6}$ emu mol$^{-1}$ for $[LNiLn(NO_3)_3]\cdot Me_2CO$). Positive FAB mass spectra were recorded in DMF as a solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer.

**{2,2′-[1-Methyl-1,2-propanediyl-bis(nitrilomethylidyne]-di(6-methoxyphenolato)(2 – )nickel(II)} ($LNi\cdot H_2O$)**: This complex was prepared as previously described.[20] $^1H$ NMR (250 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.36$ (s, 1H; CH); 7.29 (s, 1H; CH); 6.65 (m, 4H; ArCH); 6.4 (m, 2H; ArCH); 3.81 (s, 3H; $OCH_3$); 3.80 (s, 3H; $OCH_3$); 3.24 (s, 2H; $CH_2$); 1.43 (s, 6H; $CH_3$); anal. calcd for $C_{20}H_{22}N_2NiO_4\cdot H_2O$ (431.1): C 55.7, H 5.6, N 6.5; found C 55.7, H 5.4, N 6.6.

**$[LMLn(NO_3)_3]\cdot Me_2CO$**: These complexes with M = $Cu^{II}$, $Ni^{II}$ and Ln = all the lanthanides(III) except $Pm^{3+}$ (radioactive) were prepared by a reported procedure.[1] All the compounds were characterized by elemental analysis (C, H, N), IR, and mass (FAB +) spectrometries. As a typical example: $Tm(NO_3)_3\cdot 5H_2O$ (0.25 g, $5.5 \times 10^{-4}$ mol) was added to $LNi\cdot H_2O$ (0.23 g, $5.5 \times 10^{-4}$ mol) in acetone. The precipitate which formed was filtered off and washed with cold acetone and diethyl ether. Yield: 0.36 g (80 %); MS (FAB, 3-nitrobenzyl alcohol matrix): *m/z* (%): 705 (100), $[C_{20}H_{22}N_4NiO_{10}Tm]^+$; anal. calcd for $C_{20}H_{22}N_5NiO_{13}Tm\cdot Me_2CO$: C 33.4, H 3.4, N 8.5; found C 33.4, H 3.2, N 8.4.

**Crystal structure analysis of 1, 2, and 3**: Crystals suitable for X-ray crystallography were obtained by the deposition of a few milligrams of $LM\cdot H_2O$ (with M = Cu, Ni) and $Ln(NO_3)_3xH_2O$ in a tube, followed by addition of acetone and slow evaporation of the solution at room temperature. Crystal data for all structures are presented in Table 1. Data were measured on an Enraf–Nonius CAD4 diffractometer with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation and $\omega - 2\theta$ scans at 293 K. The reflections were corrected for Lorentz polarization effects with the MolEN package.[22] Semiempirical absorption corrections,[23] based on $\psi$ scans, were applied. The structures were solved by a Patterson procedure with the SHELXS-86 program[24] and refined against all $F_o^2$ (SHELXL-93)[25] with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $3P = (F_o^2 + 2F_c^2)$ and $a$ and $b$ are constants adjusted by the program. All non-hydrogen atoms were refined anisotropically, except C sp$^2$ atoms which were refined isotropically. Hydrogen atoms were included by a riding model with $U$ equal to 1.1 times $U_{eq}$ of atom of attachment. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100940. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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