

Macrocyclic and Open-Chain Cu^{II}-4f (4f = Gd^{III}, Ce^{III}) Complexes with Planar Diamino Chains: Structures and Magnetic Properties

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Until now, the known structures of heterodinuclear Cu–Ln complexes involve compartmental Schiff-base ligands with saturated diamino chains. We report here two Cu–Ln complexes (Ln = Gd or Ce) which are the first structurally characterized Cu–Ln entities involving *S*-methylisothiosemicarbazide as the diamino bridge, with open chain and macrocyclic ligands. The macrocyclic Cu–Gd entity is a well isolated dinuclear complex whereas two hydrogen bonds join together a pair of binuclear Cu–Ce complexes to give tetra-

nuclear {Cu–Ce...Ce–Cu} entities. The Cu–Gd complexes [$H = -J(S_{Cu}S_{Gd})$] exhibit ferromagnetic interactions between 5 and 5.5 cm^{−1}. Since the Cu–Ce complexes do not follow the Curie law due to the presence of orbital degeneracy, an analysis based on a simple spin-only Hamiltonian is not possible. Nevertheless, the EPR spectra of the Cu–Ce complexes do confirm the existence of magnetic interactions.

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1. Introduction

Heteronuclear lanthanide (4f) and 3d metal coordination complexes are mainly studied for their interesting magnetic properties.^[1–9] These bimetallic complexes are important for studying the nature of the magnetic exchange interactions between lanthanide and transition metal atoms, and they can potentially be used as magnetic materials^[1–4] and high temperature superconductors.^[10] Studies aimed at understanding the coupling mechanism in paramagnetic rare earth metal complexes with other spin carriers are mainly restricted to gadolinium(III) ($S = 7/2$) derivatives and $S = 1/2$ species such as copper(II)^[5,6,11–24] or vanadyl(II)^[25] metal centers. Consistently, in the great majority of Cu–Gd, VO–Gd, or radical–Gd species studied so far, the intramolecular interaction between the gadolinium ion and the 1/2 spin has been found to be ferromagnetic, but a few examples of complexes showing antiferromagnetic behavior do exist.^[6,24–27] The most frequently used ligands

are polydentate Schiff bases involving saturated diamino chains. In order to extend the number of known examples, we have considered simple Cu–Ln heterodinuclear complexes involving Schiff-base ligands with *S*-methylisothiosemicarbazide as the diamino chain. Indeed, the use of an unsaturated diamino chain introduces planarity into the five-membered metallacycle that can induce geometric modifications in the Cu–Ln bridge and, consequently, change the magnitude and/or the nature of the magnetic interaction. Keeping this in mind, we have also synthesized a macrocyclic Cu–Gd complex which should be more constrained. It should be stressed that these examples are the first structurally characterized Cu–Ln entities involving *S*-methylisothiosemicarbazide as the diamino bridge.

2. Results and Discussion

2.1 Synthesis of the Complexes

The reaction of 3-methoxysalicylaldehyde or 3-ethoxysalicylaldehyde with *S*-methylisothiosemicarbazide hydroiodide in a 2:1 molar ratio in methanol, followed by treatment with AgNO₃, removal of AgI and addition of CuOAc₂·H₂O afforded red crystals of the CuL_A·(H₂O) and CuL_B·(H₂O) complexes, respectively (Scheme 1). The corresponding H₂L_A and H₂L_B ligands are represented in Scheme 2. CuL_C·2H₂O was obtained from L_CCuBa(CF₃SO₃)₂ by reaction with guanidinium sulfate in CHCl₃/H₂O (1:1).^[28]

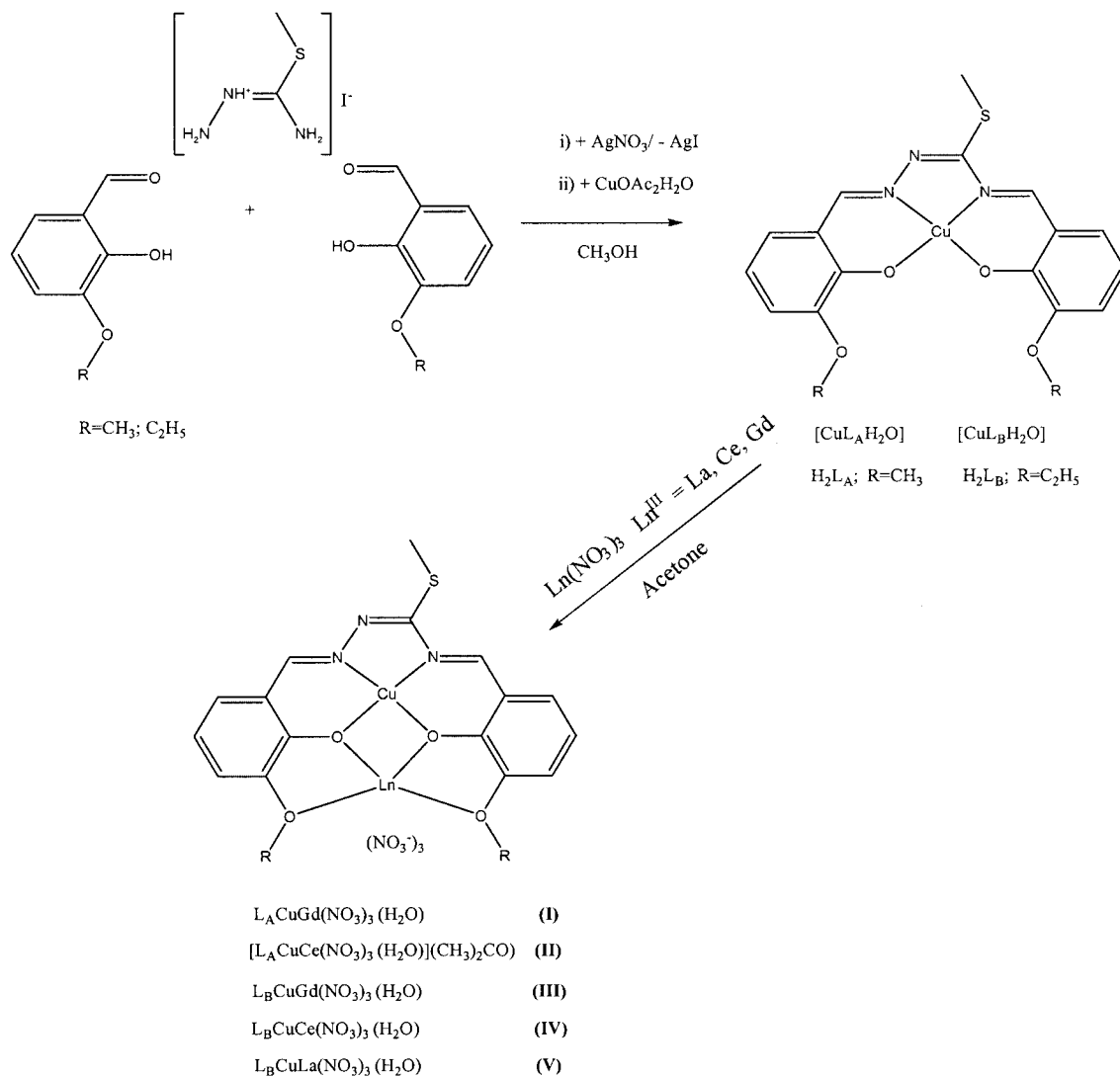
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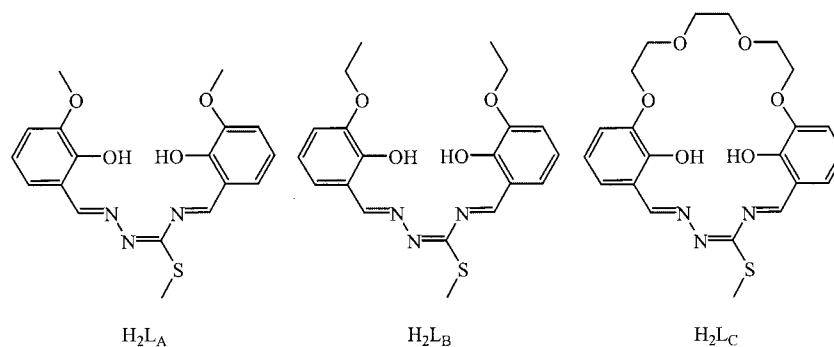
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Scheme 1



Scheme 2

The heterometallic complexes **I–V** were synthesized by reaction of the related copper complexes with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, or $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in acetone, while **VI** was obtained by utilizing the same reaction in a mixture of dichloromethane and methanol.

2.2 Structures of the Complexes

2.2.1 $[\text{L}_\text{A}\text{CuCe}(\text{NO}_3)_3 (\text{H}_2\text{O})](\text{CH}_3)_2\text{CO}$ (II)

An X-ray crystallographic study of **II** shows that the unit cell contains two neutral dinuclear $[\text{L}_\text{A}\text{CuCe}(\text{NO}_3)_3 (\text{H}_2\text{O})]$

species and two acetone molecules which are not coordinated to the copper or cerium ions but involved in hydrogen bonding with the cerium-coordinated water molecule. A perspective drawing of the asymmetric unit appears in Figure 1. The molecular structure of **II** is very similar to those of analogous 3d–4f Schiff-base complexes studied earlier.^[12–14] The Ce^{III} and Cu^{II} ions are connected by two bridging phenoxo oxygen atoms, with a Cu...Ce distance of

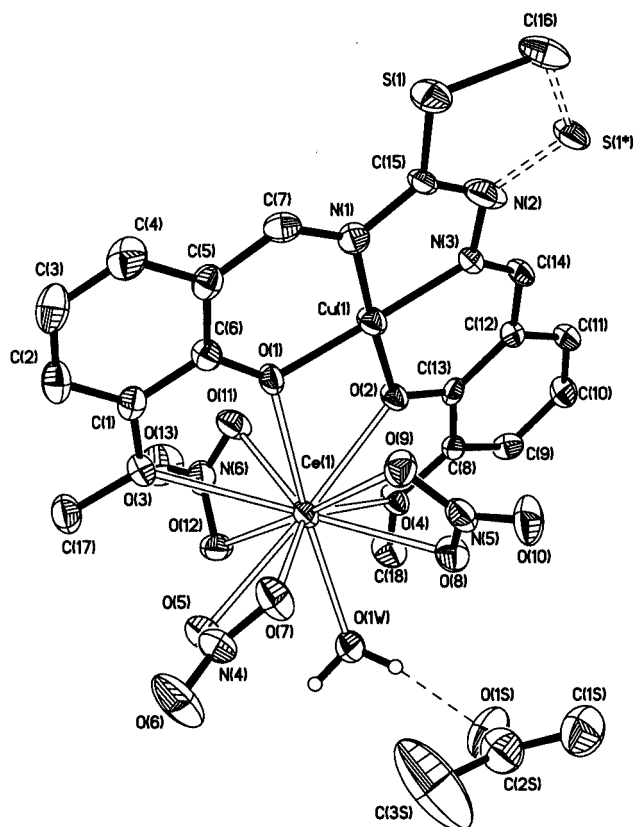


Figure 1. View of $[\text{L}_A\text{CuCe}(\text{NO}_3)_3(\text{H}_2\text{O})](\text{CH}_3)_2\text{CO}$ (**II**); the thermal ellipsoids are drawn at the 50% probability level

3.457(1) Å. The Ce^{III} ion is eleven-coordinate, bound to oxygen atoms from the two bridging phenoxo groups, two methoxy groups, three nitrate anions acting as η^2 chelating ligands and one aqua ligand. The Ce–O bond lengths range from 2.503(4) to 2.900(4) Å. As usual, the shortest bonds involve the bridging O(1) and O(2) oxygen atoms, the longest ones corresponding to the methoxy groups, are 2.900(4) and 2.787(4) Å. This can be easily explained because the cerium ion is displaced from the mean O_4 ligand coordination plane by 0.962(5) Å. The Ce–O nitrate bond lengths are within 2.540(4)–2.604(4) Å, except for Ce–O(9) which is longer [2.756(4) Å]. The short intramolecular O(9)···Cu(1) contact [2.706(4) Å] is probably responsible for this lengthening. The Cu^{II} ion is located in the inner N_2O_2 cavity of the Schiff-base ligand and has a square-pyramidal (4+1) geometry, with the nitrogen and oxygen atoms of the ligand in the basal plane and the nitrate oxygen atom in the apical position. The *S*-methylisothiosemicarbazide fragment was found to be disordered over two positions with occupancy factors of 0.57 and 0.43 for the S(1) and S(1*) atoms respectively (Figure 1). This feature is characteristic of the *S*-methylisothiosemicarbazone moiety and has already been observed in a large number of complexes.^[29,30] The five-membered ring formed by the *S*-methylisothiosemicarbazone moiety coordinated to the copper ion is perfectly planar and induces planarity in the whole ligand, which implies a better electronic delocalization. As a consequence, the Cu–N and Cu–O bond lengths are practically equal [1.890(3)–1.909(4) Å range] and slightly shorter than in the previous structurally characterized Cu–Ce complex.^[31]

A significant intermolecular interaction $\text{O}(1w) \cdots \text{H} \cdots \text{O}(12)^i$ ($i: 1-x, -y, -z$) between the coordinated water molecule O(1w) and the nitrate oxygen O(12) of the neighboring molecule with $\text{O}(1w) \cdots \text{H}$: 0.86(1) Å, $\text{O}(1w) \cdots \text{H} \cdots \text{O}(12)$: 1.99(2) Å, $\text{O}(1w) \cdots \text{O}(12)^i$: 2.831(6) Å and $\angle \text{O}(1w) \cdots \text{H} \cdots \text{O}(12)^i$: 167(8)° should be mentioned. Two of the above mentioned H-bonds join together a pair

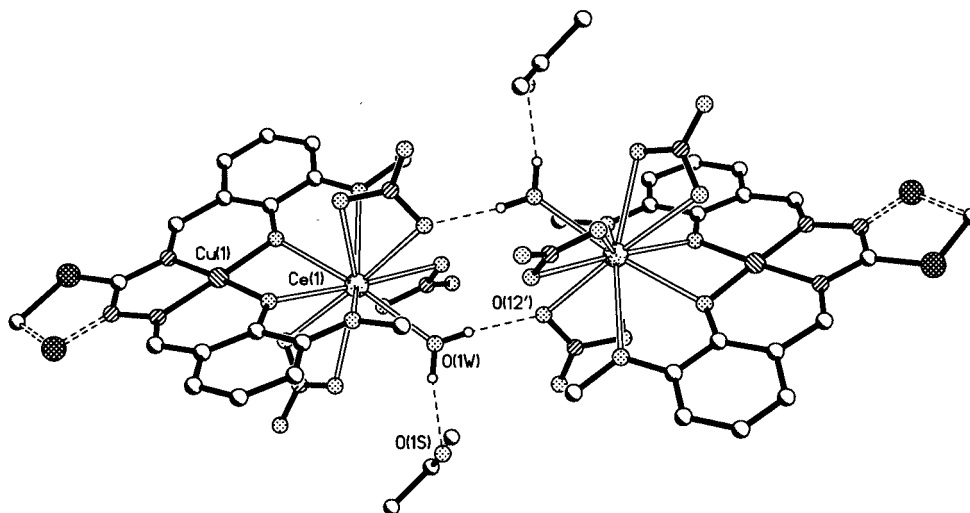


Figure 2. Structure of the tetranuclear entity $\{[\text{L}_A\text{CuCe}(\text{NO}_3)_3(\text{H}_2\text{O})](\text{CH}_3)_2\text{CO}\}_2$

of binuclear complexes **II** to give tetranuclear Cu–Ce...Ce–Cu units. The coordinated water molecules are also hydrogen-bonded to the oxygen atom of an acetone molecule [O(1w)–H: 0.87(1) Å, O(1w)–H...O(1S): 1.90(1) Å, O(1w)...O(1S): 2.757(6) Å and ∠O(1w)–H...O(1S): 173(6)°]. The resultant tetranuclear entity, formulated as $\{[L_A CuCe(NO_3)_3(H_2O)](CH_3)_2CO\}_2$, is depicted in Figure 2. Furthermore, the centrosymmetrically related tetranuclear $\{[L_A CuCe(NO_3)_3(H_2O)](CH_3)_2CO\}_2$ species are linked through π – π interactions, giving two-dimensional layers oriented parallel to the *ac* plane of the crystal. The distances between the mean planes of neighboring overlapping aromatic rings vary from 3.45 to 3.52 Å.

2.2.2 L_CCuGd(NO₃)₃ (VI)

The asymmetric unit of the macrocyclic complex **VI** is shown in Figure 3. In contrast to **II**, the copper ion in **VI** has a square-planar geometry and only two nitrate ions act as η^2 chelating ligands, the third one being mono-coordinated to the gadolinium ion. The bridging network Cu(O,O)Ln is not planar. The dihedral angle between the planes O(1)–Cu–O(2) and O(1)–Ln–O(2) is larger in **II** [24.3(2)°] than in **VI** [18.9(1)°].

Interestingly, the gadolinium ion is eleven-coordinate, bound to five oxygen atoms from nitrate ions and six oxygen atoms from the macrocyclic ligand. As in **II**, the distances of the gadolinium ion to the oxygen atoms of the alkoxy groups are the longest. The shortest Gd–O bond [2.330(4) Å] involves the mono-coordinated nitrate ion. The bonds involving the bridging phenoxo oxygen atoms [2.465(3) and 2.477(3) Å] are larger than in other Cu–Gd complexes.^[5,6,13,14] The *S*-methylisothiosemicarbazide fragment was again found to be disordered over two positions.

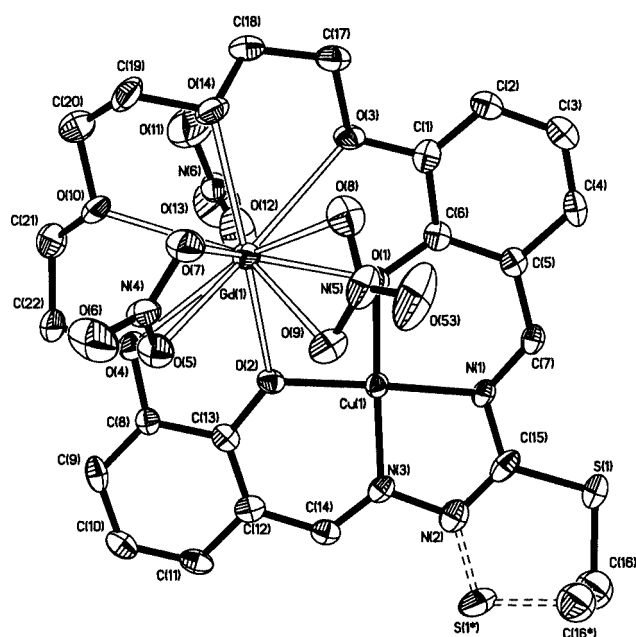


Figure 3. Molecular structure of L_CCuGd(NO₃)₃ (**VI**)

2.3. Magnetic Properties

Almost identical magnetic behavior is observed for compounds **I**, **III**, and **VI**. As an example, the data for **I** are quoted in Figure 4 in the form of the thermal variation of the $\chi_M T$ product, χ_M being the molar susceptibility corrected for diamagnetism. At 300 K, $\chi_M T$ for **I** is equal to 8.20 cm³mol^{−1}K, which corresponds to the value expected for two uncoupled metal ions. Lowering the temperature causes $\chi_M T$ to increase to 9.89 cm³mol^{−1}K at 7 K. This value compares well with that (10.0 cm³mol^{−1}K) expected for an *S* = 4 spin state resulting from ferromagnetic coupling between Cu^{II} (*S* = 1/2) and Gd^{III} (*S* = 7/2) and assuming $g_{Cu} = g_{Gd} = 2$. A quantitative analysis has been performed on the basis of an expression derived from the spin-only Hamiltonian $H = -J_{Cu-Gd}S_{Cu}S_{Gd}$. Taking into consideration the *g* values associated with the low lying levels $E(4) = 0$ [$g_4 = (7g_{Gd} + g_{Cu})/8$] and $E(3) = 4J$ [$g_3 = (9g_{Gd} - g_{Cu})/8$],^[32] the following expression can be obtained [Equation (1)].

$$\chi T = N\alpha + \frac{4N\beta^2 T}{\kappa(T - \theta)} \cdot \frac{15g_4^2 + 7g_3^2 \cdot \exp(-\frac{4J}{kT})}{9 + 7 \cdot \exp(-\frac{4J}{kT})} \quad (1)$$

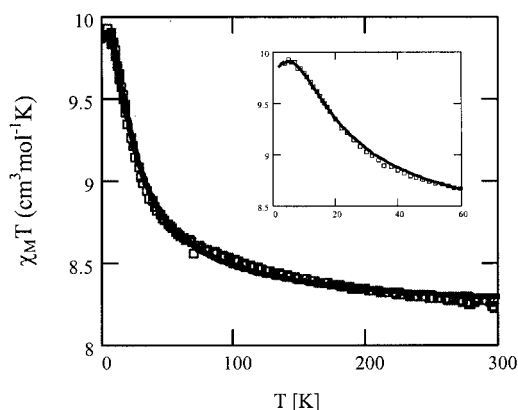


Figure 4. Thermal dependence of $\chi_M T$ for **I** at 0.1 T; the full line corresponds to the best data fit

Least-squares fitting of the experimental data led to the following set of parameters: $g_{Gd} = 1.99$, $g_{Cu} = 2.02$, $\theta = -0.02$ K, $J = 5.2$ cm^{−1} for **I**. The other two complexes give the following values: $g_{Gd} = 1.99$, $g_{Cu} = 2.01$, $\theta = -0.09$ K, $J = 5.5$ cm^{−1} for **III** and $g_{Gd} = 1.98$, $g_{Cu} = 2.02$, $\theta = -0.06$ K, $J = 4.98$ cm^{−1} for **VI**. The agreement factors $\Sigma(\chi T_{calc} - \chi T_{obs})^2 / \Sigma(\chi T_{obs})^2$ are then respectively equal to $1 \cdot 10^{-5}$, $4 \cdot 10^{-5}$, and $2 \cdot 10^{-5}$. The small θ values suggest that second-order effects, such as intermolecular interactions or partial saturation at low temperature are, at best, very weak. The positive *J* value indicates a ferromagnetic coupling between Cu^{II} and Gd^{III}. This is further supported by the experimental values of the magnetization for **I** measured at 2.0 K which are correctly fitted by the Brillouin function

for an $S = 4$ spin state, which confirms the ferromagnetic nature of the Cu–Gd interaction. The magnitude of the Cu–Gd interaction does not differ widely from one compound to the others.

It has been reported that the J_{CuGd} values and Cu...Gd distances could be correlated using an exponential function.^[33] More recently, from the magnetic properties of several Cu–Gd complexes, we have found a satisfying correlation between the absolute value of the ferromagnetic coupling constant J_{CuGd} and the dihedral angle α defined by the two OCuO and OGdO planes of the bridging network.^[5] The value obtained for **VI** is in good agreement with our previously published values. This relation implies that the dihedral angle must be lower than $18.9(1)^\circ$ in **I** and **III** for the J values associated with them are larger. Unfortunately, the structural parameters for these complexes are not available. However we know the dihedral angle $[24.2(2)^\circ]$ for the Cu–Ce complex **II**. Since there is a decrease in the ionic radius on going from Ce^{III} to Gd^{III} , a decrease of α from $24.2(2)^\circ$ to a value slightly lower than $18.9(1)^\circ$ may be reasonably expected.

The magnetic behavior of the Cu–Ce compound **II** is more complex since the cerium ion does possess an orbital contribution, so that the observed $\chi_{\text{M}}T$ decrease in Figure 5 may be due to two concomitant factors namely depopulation of the Stark levels as T decreases and a possible Cu–Ce antiferromagnetic interaction.^[18,33,34] A semi-qualitative analysis would necessitate the synthesis of the equivalent Ni–Ce complex with the nickel ion in a low spin state in order to evaluate the contribution of the Stark effect.^[33] Unfortunately we did not succeed in preparing this complex. To complete our study we have considered the EPR spectra of complexes **IV** and **V**. For **IV** we observed a strong feature at $g = 2.04$ and a four component hyperfine structure centered at $g = 2.19$, these features being attributable to isolated copper ions (Figure 6, a). The spectrum of **V** consists of a single signal at $g = 2.07$ (Figure 6, b). It is tempting to attribute the difference to the presence of a (Cu–Ce) exchange interaction in **IV** which has no counterpart in **V** due to the diamagnetism of the lanthanum ions. To support this hypothesis we refer to the early work of Bleaney^[35] devoted to the systems made up from two ions with very different relaxation rates. A recent review focuses on this question and gives the relaxation times for monomeric systems involving copper (10^{-8} , 10^{-9} s) and cerium

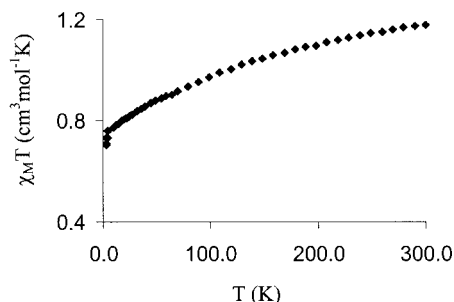


Figure 5. Thermal dependence of $\chi_{\text{M}}T$ for $[\text{L}_\text{A}\text{CuCe}(\text{NO}_3)_3\text{-(H}_2\text{O)}](\text{CH}_3)_2\text{CO}$ (**II**)

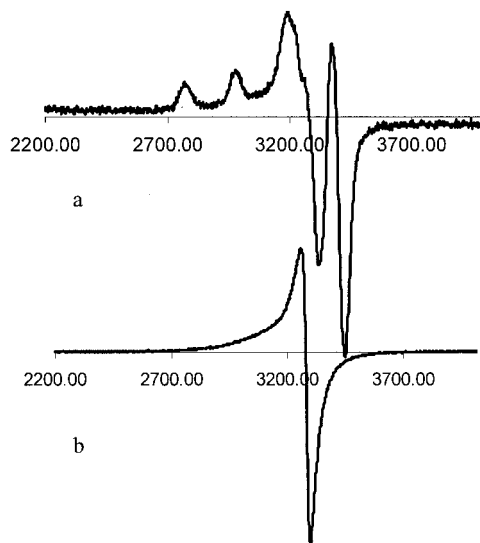


Figure 6. The solid state EPR spectra of (a) $\text{L}_\text{B}\text{CuCe}(\text{NO}_3)_3(\text{H}_2\text{O})$ (**IV**) and (b) $\text{L}_\text{B}\text{CuLa}(\text{NO}_3)_3(\text{H}_2\text{O})$ (**V**) at 90 K

ions (10^{-13} s).^[36] In the case of complex **IV** the cerium resonance was not observed because the signals are strongly enlarged due to an abnormally low value of the spin lattice relaxation time. Contrary to the cerium ions, the copper ions have normal relaxation times that lead to an observable and even well-resolved spectrum. The absence or at least the lowering of the signal broadening would be due to a supplementary relaxation mechanism of the copper ions through the (Cu–Ce) exchange interaction. Due to the complexity of the relaxation mechanisms,^[36] a more complete description of that behavior would necessitate further experimental data. Eventually this experimental evidence for a (Cu–Ce) exchange interaction gave no information concerning the sign of the interaction and we have to keep in mind that these interactions are very weak. Nevertheless, from the variation of the χT product at very low temperature for **II** (Figure 5) and from previous examples in literature,^[31,34] it seems more likely that the Cu–Ce interaction is antiferromagnetic. Such an interaction is also present in **II**, but the π – π stacking present in this complex is responsible for the lower intensity of the parallel part of the spectrum.

3. Conclusion

The complexes considered in this work exhibit ferromagnetic $J_{\text{Cu-Gd}}$ interactions, as in the majority of previously published Cu–Gd complexes. Although the variation of the $J_{\text{Cu-Gd}}$ interactions is relatively limited, from 1.0 to 10.1 cm^{-1} , it appears that the decrease of the interaction parameter J can be related to an increase in the dihedral angle α defined by the two OCuO and OGdO planes of the bridging network.^[5] The compounds described in this work fit in with the previous results. The best J values have been obtained with the most planar Cu–(O)₂–Gd cores corresponding to α angles near 0° . From a synthetic point of view, these complexes with *S*-methylisothiosemicarbazide as

diamino chains are the first examples of structurally characterized Cu–Ln heterodinuclear complexes with planar and unsaturated diamino chains. Thus, it was tempting to investigate if the use of more planar ligands could increase this *J* value. Unfortunately, other constraints coming from the macrocyclic structure or a greater rigidity of the ligand did not allow us to obtain higher *J* values. Furthermore, the EPR spectra of the Cu–Ce complexes have given a satisfying confirmation for the existence of magnetic interactions in these complexes that do not follow the Curie law due to the presence of orbital degeneracy.

4. Experimental Section

All starting materials and solvents were purchased from Aldrich and were used without further purification. *S*-methylisothiosemicarbazide hydriodide was obtained by the reaction of thiosemicarbazide with methyl iodide in dry ethanol.^[37] Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse. Magnetic susceptibility data were collected on powdered samples of a SQUID-based sample magnetometer on Quantum Design model MPMS instrument. All data were corrected for the diamagnetism of the ligands estimated from Pascal's constants.^[38] The *N*_a parameter, which is very weak, was omitted in our calculations.

CuL_A·H₂O: To a methanolic solution (50 mL) of 3-methoxysalicylaldehyde (0.3 g 2.0 mmol) was added dropwise a solution of *S*-methylisothiosemicarbazide hydriodide (0.23 g, 1.0 mmol) in CH₃OH (15 mL). The obtained mixture was carefully stirred at 50 °C for 2 h. The resultant pale-yellow solution was heated to reflux for a further 20 min. After cooling to room temperature, a solution of AgNO₃ (0.26 g, 1.0 mmol) in CH₃OH/H₂O (1:2, 15 mL) was added. The AgI was removed by filtration and a solution of Cu(CH₃COO)₂·H₂O (0.2 g, 1.0 mmol) in CH₃OH (15 mL) was added in one portion to the filtrate. The red product which crystallized overnight was filtered and washed with a small amount of cold methanol. Yield 0.32 g (70%). C₁₈H₁₉CuN₃O₅S: calcd. C 47.73, H 4.23, N 9.28; found C 48.65, H 4.53, N 9.32%.

The complex **CuL_B·H₂O** was prepared using an analogous experimental procedure. Yield 0.25 g (55%). C₂₀H₂₃CuN₃O₅S: calcd. C 49.94, H 4.82, N 8.74; found C 50.03, H 4.83, N 8.90%.

CuL_C·2H₂O was prepared as described elsewhere.^[30]

L_ACuGd(NO₃)₃·H₂O (I): CuL_A·H₂O (0.22 g 0.5 mmol) dissolved in acetone (50 mL) was slowly added to an acetone solution (20 mL) of Gd(NO₃)₃·5H₂O (0.23 g 0.5 mmol) with vigorous stirring. After partial evaporation of the solvent bright brown crystals were formed, separated by filtration, washed with cold acetone and air dried. Yield 0.28 g (70%). C₁₈H₁₉CuGdN₆O₁₄S: calcd. C 27.15, H 2.41, N 10.55; found C 27.44, H 2.46, N 10.52%.

[L_ACuCe(NO₃)₃(H₂O)](CH₃)₂CO (II), L_BCuGd(NO₃)₃(H₂O) (III), and L_BCuCe(NO₃)₃(H₂O) (IV) were prepared similarly. Single crystals of **II** suitable for X-ray diffraction study were obtained by slow evaporation of an acetone solution of **CuL_A·H₂O** and Ce(NO₃)₃·6H₂O.

[L_ACuCe(NO₃)₃(H₂O)](CH₃)₂CO (II): Yield 0.20 g (50%). C₂₁H₂₅CeCuN₆O₁₅S: calcd. C 30.13, H 3.01, N 10.04; found C 30.70, H 3.25, N 9.98%.

L_BCuGd(NO₃)₃(H₂O) (III): Yield 0.25 g (45%). C₂₀H₂₃CuGdN₆O₁₄S: calcd. C 29.14, H 2.81, N 10.20; found C 28.92, H 2.83, N 9.94%.

L_BCuCe(NO₃)₃(H₂O) (IV): 0.32 g (75%). C₂₀H₂₃CeCuN₆O₁₄S: calcd. C 29.76, H 2.87, N 10.41; found C 30.42, H 2.93, N 10.35%.

L_BCuLa(NO₃)₃(H₂O) (V): 0.35 g (80%). C₂₀H₂₃CuLaN₆O₁₄S: calcd. C 29.80, H 2.88, N 10.43; found C 29.42, H 2.81, N 10.25%.

L_CCuGd(NO₃)₃ (VI): To CuL_C·2H₂O (0.27 g, 0.5 mmol) in a dichloromethane/methanol mixture (3:2 ratio) (50 mL) was added to Gd(NO₃)₃·6H₂O (0.29 g, 0.6 mmol) in methanol (20 mL). The solution was heated to reflux for 15 min until the crystallization of the product had begun. The solvent was evaporated to 15 mL and methanol (20 mL) was added. The dark-red product was filtered, washed with methanol and dichloromethane and dried in vacuo. Yield 0.34 g (40%). C₂₂H₂₃CuGdN₆O₁₅S: calcd. C 30.57, H 2.68, N 9.72; found C 30.46, H 2.85, N 9.57%.

X-ray Crystallographic Studies of [L_ACuCe(NO₃)₃(H₂O)](CH₃)₂CO (II): Crystallographic measurements for **II** were carried out on a Nonius Kappa CCD diffractometer equipped with a graphite-monochromated Mo-*K*_α radiation source. Intensity data were collected at 150 K using θ rotations with 2degree scan and a detector-to-crystal distance of 35 mm. The unit cell determination and data integration were carried out using the program DENZO-SMN.^[39] Data sets were corrected for Lorentz and polarization effects. The absorption correction was introduced by a semi-empirical method from symmetry equivalent reflections.^[40] The structure was solved by direct methods with the program SHELXS-97.^[41] Refinement was performed using full-matrix least-squares on *F*², with anisotropic displacement parameters for the non-hydrogen atoms using the program SHELXL-97.^[42] The hydrogen atoms of the polydentate ligand and solvent molecule (acetone) were placed in calculated positions and given isotropic displacement parameters equal to 1.2×*U*_{eq} of the relevant carbon atom. Positional parameters of the H atoms of water molecules were obtained from difference Fourier syntheses and were verified by the geometric parameters of corresponding hydrogen bonds.

X-ray Crystallographic Studies of L_CCuGd(NO₃)₃ (VI): The selected crystal of **VI** (orange-red plate) was mounted on a Stoe Imaging Plate Diffractometer System (IPDS) equipped with an Oxford Cryosystems cooler device at 160 K using a graphite monochromator ($\lambda = 0.71073$ Å). The crystal-to-detector distance was 80 mm. Data were collected^[43] with a ϕ rotation movement ($\phi = 0.0$ – 249.6° , $\Delta\phi = 1.3^\circ$). Numerical absorption^[44] corrections were applied. Maximum and minimum transmission factors were respectively 0.7576 and 0.3294. The structure was solved by direct methods using SHELXS-97^[41] and refined by full-matrix least-squares on *F*_o² with SHELXL-97^[42] with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced by calculations using the riding model with isotropic thermal parameters 1.1 times higher than those of the riding atom. Scattering factors were taken from ref.^[45] The molecular plot was obtained using the ZORTEP program.^[46]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. Copies of the data (CCDC-215450 for **II** and CCDC-215647 for **VI**) can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Summary of crystal data for **II** and **VI**

Compound	II	VI
Empirical formula	C ₂₁ H ₂₅ CeCuN ₆ O ₁₅ S	C ₂₂ H ₂₃ CuGdN ₆ O ₁₅ S
<i>M</i>	837.19	846.31
Temperature [K]	150	160
Wavelength [Å]	0.71073	0.71073
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.8460(4)	9.103(1)
<i>b</i> [Å]	12.4470(5)	11.395(1)
<i>c</i> [Å]	13.8610(6)	26.997(3)
α [deg]	84.937(2)	90
β [deg]	71.745(2)	99.32(1)
γ [deg]	67.371(1)	90
<i>V</i> [Å ³]	1488.0(1)	2763.5(5)
<i>Z</i>	2	4
$\rho_{\text{calcd.}}$ [Mg·m ⁻³]	1.869	2.077
μ_{Mo} [mm ⁻¹]	2.376	3.312
<i>F</i> (000)	832	1704
Crystal size [mm]	0.2 × 0.1 × 0.1	0.3 × 0.1 × 0.03
θ range [deg]	2.35 to 26.00	1.94 to 24.10
Index ranges	−12 ≤ <i>h</i> ≤ 12, −15 ≤ <i>k</i> ≤ 15, −17 ≤ <i>l</i> ≤ 17	−10 ≤ <i>h</i> ≤ 10, −13 ≤ <i>k</i> ≤ 13, −30 ≤ <i>l</i> ≤ 30
Number of reflections:		
Measured	10884	20916
Unique	5821 [<i>R</i> _(int) = 0.0831]	4235 [<i>R</i> _(int) = 0.0692]
Number of refined parameters	418	424
Max. and min. transmission	0.7971 and 0.6480	0.7576 and 0.3294
GOOF for <i>F</i> ²	1.107	0.903
^[a] <i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0693	0.0284
^[b] <i>wR</i>	0.0842	0.0499
Δρ _{max} and Δρ _{min} [e·Å ⁻³]	1.605 and −0.921	1.164 and −0.706

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

Table 2. Selected bond lengths [Å] and angles [deg.] for **II** and **VI**

Bond	II ^[a]	Compound VI ^[b]	Bond	II ^[a]	Compound VI ^[b]
Ln(1)–O(2)	2.503(4)	2.465(3)	Ln(1)–O(1w)	2.512(3)	–
Ln(1)–O(3)	2.900(4)	2.774(3)	Ln(1)–O(7)	2.540(4)	2.590(3)
Ln(1)–O(1)	2.525(3)	2.477(3)	Ln(1)–O(5)	2.591(4)	2.481(3)
Ln(1)–O(12)	2.565(4)	2.330(4)	Ln(1)–O(11)	2.604(4)	–
Ln(1)–O(8)	2.592(4)	2.564(3)	Ln(1)–O(4)	2.787(4)	2.893(3)
Ln(1)–O(9)	2.756(4)	2.475(3)	Ln(1)–O(14)	–	2.594(3)
Ln(1)–O(15)	–	2.677(3)	Cu(1)–O(2)	1.890(3)	1.890(3)
Cu(1)–O(1)	1.891(4)	1.885(3)	Cu(1)–N(3)	1.909(4)	1.900(4)
Cu(1)–N(1)	1.900(4)	1.913(4)			
O(1)–Cu(1)–O(2)	86.7(2)	86.1(1)	O(1)–Cu(1)–N(1)	96.0(2)	95.5(2)
O(2)–Cu(1)–N(1)	177.0(2)	176.4(1)	O(1)–Cu(1)–N(3)	178.5(2)	178.2(2)
O(2)–Cu(1)–N(3)	94.7(2)	95.7(2)	N(1)–Cu(1)–N(3)	82.6(2)	82.7(2)
Cu(1)–O(2)–Ln(1)	102.7(2)	103.7(1)	Cu(1)–O(1)–Ln(1)	101.9(1)	103.4(1)

^[a] Ln = Ce. ^[b] Ln = Gd.

The crystallographic data together with the refinement details for **II** and **VI** are summarized in Table 1, selected bonds lengths and angles are listed in Table 2.

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