Magnetic Properties and Crystal Structure of a $Cu^{II}Gd^{III}$ Heterodinuclear Schiff Base Complex

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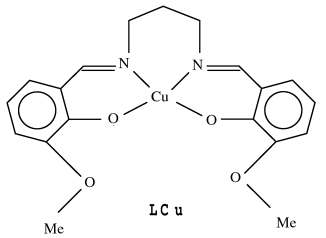
The crystal structure and the magnetic properties of a heterodinuclear complex, $[LCu(Me_2CO)Gd(NO_3)_3]_2$ (L=N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) are reported: $[(C_{19}H_{20}N_2O_4)Cu(C_3H_6O)Gd(NO_3)_3]_2$, triclinic, space group $P1$, with $a = 12.118.3(9)$, $b = 13.562(3)$, $c = 9.391(3)$ Å, $\alpha = 93.03(3)$, $\beta = 107.65(2)$, $\gamma = 73.07(2)^\circ$, $V = 1406.0(7)$ Å^3, $Z = 1$. The crystal structure consists of two independent binuclear $Cu^{II}Gd^{III}$ complexes and two non-coordinating acetone molecules in the asymmetric unit. The central region of the complexs is occupied by Cu^{II} and Gd^{III} ions which are bridged by two phenolato oxygen atoms of the ligand. The Cu^{II} ion is in a square-planar geometry and coordinated by four donor atoms of the ligand (N_2O_2). The Gd^{III} ion is deca-coordinated. In addition to the two phenolate oxygen atoms, its coordination sphere contains two oxygen atoms of the OMe side arms of L and six oxygen atoms from the three bidentate nitrate ions. The average Cu···Gd separation is 3.375(2) Å. The χT versus T plots, χ being the molar magnetic susceptibility per $Cu^{II}Gd^{III}$ unit and T the temperature, has been measured in the 4 – 347 K range. The values of the intrachain interaction parameters have been deduced from the magnetic data: $J = 7.4$ cm^{-1}, $g_{Cu} = 2.12$, $g_{Gd} = 2.06$. This indicates a weak ferromagnetic spin exchange interaction between Cu^{II} and Gd^{III} ions. The nature of the magnetic super-exchange interaction of the title compound is compared with similar $Cu^{II}Gd^{III}$ heterodinuclear complexes.

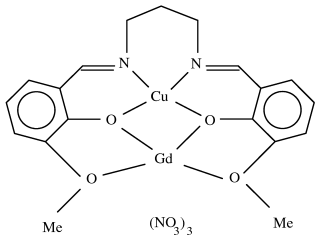
Key words: Heterodinuclear Complex, Copper, Gadolinium, Crystal Structure, Magnetic Properties

Introduction

Crystal structures and magnetic properties of heteropolymetallic complexes simultaneously comprising *d* and *f* transition metal ions have been the subject of several investigations in the last few years. The studies of these compounds have often been performed either in relation to the modeling of some metalloenzymes containing various kinds of metal ions, or with the perspective to design novel molecular materials, in particular molecule-based magnets, with tailored the magnetic properties [1]. In particular the $Cu^{II}Gd^{III}$ couple has been extensively studied both from a structural as well as from a magnetic point of view, in a number of binuclear Cu^{II}-Ln^{III} ploynuclear systems, bridged by phenoxo or multidentate ligands with donating hetero atoms [2 – 12]. As most of the complexes presenting an isolated $Cu^{II}Gd^{III}$ couple show a ferromagnetic coupling, a behavior so general led some authors to propose it to be an intrinsic property of the copper(II)-gadolinium(III) couple [12]. However, there are also few examples in the recent literature where an antiferromagnetic coupling has been detected [12 – 14], so no conclusive evidence on the particulars is available so far. The issue of an eventual link between magnetic behavior and structural properties in the copper(II)-gadolinium(III) system is thus still an open question.

Very recently, we studied the crystal structure and magnetic properties of heterodinuclear Cu^{II}-Ln^{III} complexes; $Cu^{II}Ce^{III}$, $LCu(Me_2CO)Ce(NO_3)_3$ (L=N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) [15] and $Cu^{II}Nd^{III}$, $L^2Cu(Me_2CO)Nd(NO_3)_3$ (L^2=N,N'-bis(2-hydroxyl-3 methoxybenzylidene) ethylenediamine) [16]. In this study, we have synthesized a new heterodinuclear $Cu^{II}Gd^{III}$ compound, $[LCu(Me_2CO)Gd(NO_3)_3]_2$ (L=N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) and determined its crystal structure by X-ray diffraction.





$[LCuGd(NO_3)_3(Me_2CO)]_2$

We have also measured magnetic susceptibilities in the temperature range 4 – 347 K using a SQUID magnetometer in an attempt to gain more information on the magnetic properties of Ln^{III} polynuclear complexes.

Experimental Section

Preparation

The hetero-dinuclear $Cu^{II}Gd^{III}$ complex $[LCu(Me_2CO)Gd(NO_3)_3]_2$ (L=N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) was prepared in two steps. In the first step, the Schiff base ligand was synthesized by reaction of 1,3-diaminopropane and 2-hydroxy-3-methoxybenzaldehyde in a 1:2 molar ratio at r. t. The Schiff base ligand (L) was obtained in the form of yellow crystals. For the preparation of the monomeric copper(II) complex, LCu, to a hot methanol solution (50 ml) of the ligand (1 mmol) a hot methanol solution (40 ml) of copper(II) acetate monohydrate (1 mmol) was added dropwise. The mixture was stirred and then cooled to r. t. give a green precipitate which was collected by suction filtration and washed with cold methanol and finally dried in air.

In the second step, for the preparation of the $Cu^{II}Gd^{III}$ complex, an acetone solution (10 ml) of $Gd(NO_3)_3 \cdot 6H_2O$ (1 mmol) was added to a suspension of the copper(II) complex, LCu (1 mmol), in acetone (40 ml). Soon, the suspension became clear and light green crystals began to precipitate, which were collected by suction filtration and washed with cold acetone and finally dried in air. $C_{44}H_{52}N_{10}O_{28}Cu_2Gd_2$ (1611.1): calcd. C 32.8, H 3.3, N 8.7, Cu 7.9, Gd 19.5; found C 33.5, H 3.6, N 9.2, Cu 8.0, Gd 20.1.

Table 1. Summary of crystallographic data.

Sum formula	$[(C_{19}H_{20}N_2O_4)Cu(C_3H_6O)Gd(NO_3)_3]_2$
f_w (g·mol^{-1})	1611.1
Space group	$P1$
$a = 12.118(3)$ Å	$\alpha = 93.03(3)^\circ$
$b = 13.562(3)$ Å	$\beta = 107.65(2)^\circ$
$c = 9.391(3)$ Å	$\gamma = 73.07(2)^\circ$
Vol [Å^3]	1406.0(7)
Z	1
D_{calc} (g·cm^{-3})	1.903
μ [cm^{-1}]	0.854
$F(000)$	796
Index ranges	$-17 \le h \le 16$, $-19 \le k \le 19$, $0 \le l \le 13$
Reflections collected	8232
Independent reflections	8191
Data / restraints / parameters	8191 / 3 / 776
Goodness-of-fit on F^2	1.182
Final R indices $[I > 2\sigma(I)]$	$R = 0.0405$, $wR = 0.1101$
Flack parameter (Flack, 1983 [31])	0.018(9)
Largest diff. peak and hole	0.0686 and -0.917 e·Å^{-3}

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [14] using a single crystal with dimension $0.05 \times 0.15 \times 0.20$ mm^3 with a graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ($2.16^\circ \le \theta \le 10.53^\circ$) carefully centered on the diffractometer. The standard reflections were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [14]. The structure was solved by SHELXS-97 [15] and refined with SHELXL-97 [16]. All nonhydrogen atoms were treated anisotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Selected bond lengths and angles are summarized in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-228975 [17].

Susceptibility measurements

Magnetic susceptibility data were collected on a powdered sample of the compound with use of a SQUID-

Table 2. Selected bond lengths [Å] and angles [°].

Cu1–O2	1.955(5)	Gd1–O3	2.347(4)
Cu1–O3	1.948(5)	Gd1–O2	2.349(4)
Cu1–N2	1.958(8)	Gd1–O1	2.400(5)
Cu1–N1	1.970(5)	Gd1–O11	2.451(6)
Cu2–O14	1.925(5)	Gd1–O4	2.455(5)
Cu2–O15	1.936(5)	Gd1–N5	2.853(6)
Cu2–N7	1.985(5)	Cu2–N6	1.959(7)
Gd2–O15	2.360(6)	Gd2–O14	2.369(6)
Gd2–O17	2.570(4)	Gd2–O16	2.571(5)
Gd2–N9	2.879(4)		
Cu1–O2–Gd1	107.3(2)	Cu1–O3–Gd1	107.6(2)
Cu2–O14–Gd2	107.7(2)	Cu2–O15–Gd2	107.7(2)
O3–Cu1–O2	79.4(2)	O3–Cu1–N2	89.9(3)
O2–Cu1–N2	168.0(3)	O3–Cu1–N1	169.9(2)
O2–Cu1–N1	90.5(2)	N2–Cu1–N1	100.1(3)
O14–Cu2–O15	79.5(2)	O14–Cu2–N6	91.6(2)
O15–Cu2–N6	171.1(2)	O14–Cu2–N7	171.1(3)
O15–Cu2–N7	91.8(3)	N6–Cu2–N7	97.1(3)
O3–Gd1–O2	64.2(2)	O3–Gd1–O1	126.1(2)
O2–Gd1–O1	64.9(2)	O3–Gd1–O4	65.27(2)
O2–Gd1–O4	125.9(2)	O1–Gd1–O4	143.6(2)
O3–Gd1–N5	95.4(2)	O2–Gd1–N5	94.4(2)
O1–Gd1–N5	72.1(2)	O4–Gd1–N5	2.5(2)
O15–Gd2–O16	63.9(2)	O14–Gd2–O16	122.3(2)
O17–Gd2–O16	142.5(2)	O15–Gd2–N9	125.8(2)

based sample magnetometer on a QUANTUM Design Model PPMS (Physical Properties Measurement System) instrument in the temperature range 4 – 347 K. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [18]. The applied field was 10 KOe.

Results and Discussion

X-ray crystal structure

The complex consists of dinuclear molecules in which Cu^{II} and Gd^{III} ions are bridged by two phenolato oxygen atoms of the ligand. The ORTEP view [19] of the molecular structure is shown in Fig. 1. The distances Cu1···Gd1 and Cu2···Gd2 are 3.473(2) and 3.477(2) Å, respectively.

The Cu^{II} ion is coordinated by two imine N atoms and two phenolate O atoms from the imine-phenolate ligand in a slightly distorted square-planar coordination geometry. The atoms with the greatest deviation from the coordination planes Cu1, N1, N2, O2, O3 and Cu2, N6, N7, O14, O15 are O2 at 0.06(1) Å and O14 at $-0.02(1)$ Å. The average distance Cu–N 1.964(6) Å in the first molecule is slightly smaller than the comparable distance of 1.972(6) Å (average Cu–N) in the other molecule. The average Cu–O distance in the former is 1.952(5) Å while in the other molecule, the average Cu–O distance is 1.931(5) Å, respectively. These distances are in the range of those of conventional Schiff-base Cu^{II} complexes of square-planar coordination [20 – 24].

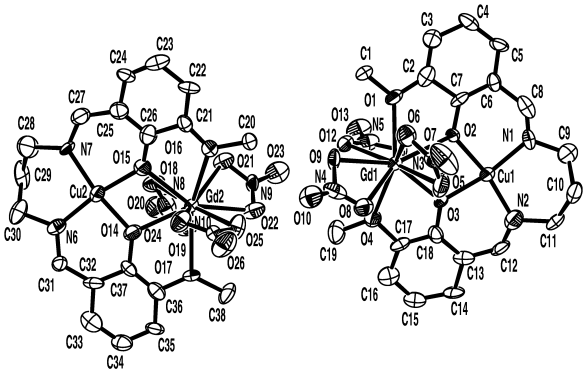


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii. The two Me_2CO solvent molecules and the H atoms are omitted for clarity.

The Gd^{III} ion is deca-coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of L and six oxygen atoms of three bidentate nitrato ions. The average distance between the Gd^{III} ion and the O atoms of the nitrate ions is 2.507(6) Å. The range of the Gd–O bond lengths is rather large (from 2.451(6) to 2.607(7) Å) with significant differences between the phenolic, methoxy, and nitrato oxygen atom. The shortest Gd–O bond (2.369(6) Å) is related to the phenolic oxygen atoms while the largest bond (2.607(7) Å) involves the oxygen atom of a nitrate ion. The Gd1–O2–Cu1 and Gd1–O3–Cu1 bridging angles in the first molecule are 107.3(2) and 107.6(2)°, respectively. In the other molecule, the Gd2–O14–Cu2 and Gd2–O15–Cu2 bridging angles are both 107.7(2)°. The maximum deviation from the bridging planes defined by atoms Cu1, O2, O3 and Gd1 is 0.10(1) Å for the Cu1 atom and for Cu2, O13, O14 and Gd2 it is 0.26(1) Å for the Gd2 atom. The dihedral angle between the Gd1O(2)Cu1 and Gd1O(3)Cu1 planes is 13.9(1)°. In the second molecule, the dihedral angle between the Gd2O(13)Cu2 and Gd2O(14)Cu2 planes is 10.9(1)°. The average dihedral angle between the two halves (OCuO and OGdO) of the bridging cores is 11.6(2)° [O(2)Cu1O(3) and O(2)Gd1O(3) planes: 11.5(2)°, O(14)Cu1O(15) and O(14)Gd1O(15) planes: 11.6(2)°]. The torsion angles N1–Cu1–O2–

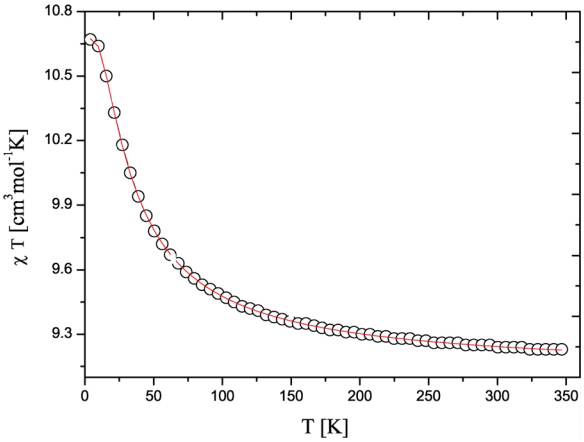


Fig. 2. Plot of χT *versus* temperature.

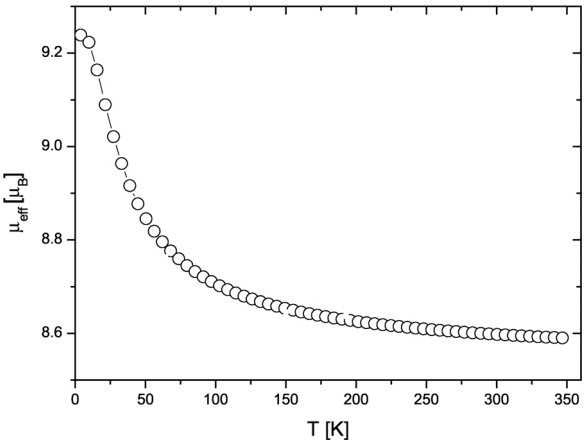


Fig. 3. Plot of the effective magnetic moment, per molecule μ_{eff}, *versus* temperature.

Gd1, N2–Cu1–O3–Gd1, N6–Cu2–O14–Gd2 and N7–Cu2–O15–Gd2, are $-169.8(2)$, 164.3(2), 168.0(2), and 166.2(2)°, respectively.

Magnetic properties

The temperature dependence of the magnetic susceptibility in the range 4 – 347 K is shown in Fig. 2 in the χT *vs* T form, the applied magnetic field being equal to 10 KOe. At 347 K, χT is equal to 9.23 $\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ which roughly corresponds to the value expected for the two uncoupled metal ions. When the temperature is lowered, χT increases and reaches a maximum of 10.67 $\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ at 4 K.

The effective magnetic moment at 347 K is 8.59 μ_{B} (Fig. 3.) This value is close to the spin-only value (8.12 μ_{B}) calculated from the equation $\mu_{\mathrm{eff}} = (\mu_{\mathrm{Cu}}^2 + \mu_{\mathrm{Gd}}^2)^{1/2}$ in the absence of magnetic interactions for the present spin-system ($S_{\mathrm{Cu}} = 1/2$, $S_{\mathrm{Gd}} = 7/2$). As already noted, the ground state of Gd^{III} is ${}^8S_{7/2}$ and the next excited state is well separated in energy, so that μ_{eff} of Gd^{III} can be approximated by the spin-only equation, $\mu_{\mathrm{eff}} = [4S(S+1)]^{1/2}$. As the temperature is lowered the magnetic moment increases gradually and reaches the maximum value 9.24 μ_{B} at 4 K. Such an increase indicates the onset of ferromagnetic spin-coupling between Cu^{II} and Gd^{III}, because the spin-only value for the spin state $S = 4$ resulting from the ferromagnetic interaction between Cu^{II} and Gd^{III} is 8.94 μ_{B}.

The profile of the curve indicates that the Cu^{II}–Gd^{III} interaction is ferromagnetic, with an $S = 4$ ground state and an $S = 3$ excited state. In order to understand quantitatively the magnitude of the spin-exchange interaction between Cu^{II} and Gd^{III} ions, an analysis was performed with the susceptibility equation based on the Heisenberg spin-exchange operator:

$$H = -JS_{\mathrm{Cu}} \cdot S_{\mathrm{Gd}} \tag{1}$$

where J is the magnetic exchange integral between Cu^{II} and Gd^{III} ions. The Hamiltonian results in a septet-nonet energy gap of $4J$. The ratio between the χT values at 4 and 347 K is equal to 1.16, which closely corresponds to the ratio $(\chi T)_{\mathrm{LT}}/(\chi T)_{\mathrm{HT}}$ between low-temperature and high temperature limits of χT for such a ferromagnetically coupled $Cu^{II}Gd^{III}$ pair [$(\chi T)_{\mathrm{LT}}/(\chi T)_{\mathrm{HT}} = 40/33$ if the local Zeeman factors g_{Gd} an g_{Cu} are assumed to be equal]. The theoretical expression of the magnetic susceptibility is easily derived from operator (1):

$$\chi T = \frac{4N\beta^2}{k}\,\frac{7g_3^2 + 15g_4^2\exp(4J/kT)}{7 + 9\exp(4J/kT)} \tag{2}$$

where g_3 and g_4 are the Zeeman factors associated with $S = 3$ and $S = 4$ low-lying states, respectively; g_3 and g_4 are related to the local Zeeman factors through [25]

$$g_3 = (9g_{\mathrm{Gd}} - g_{\mathrm{Cu}})/8 \tag{3}$$

$$g_4 = (7g_{\mathrm{Gd}} + g_{\mathrm{Cu}})/8 \tag{4}$$

χ denotes the molecular susceptibility per binuclear complex, and the other symbols have their usual meanings. Least-squares fitting of the experimental data leads to $J = 7.4\ \mathrm{cm}^{-1}$, $g_{\mathrm{Cu}} = 2.12$, $g_{\mathrm{Gd}} = 2.06$ with

Table 3. Structural and magnetic data for a series of related compounds.

Compound	Cu···Gd [Å]	Cu-O-Gd	J (cm^{-1})	g_{Cu}	g_{Gd}	ϕ^e
a	3.428	106.7	7.01	2.11	2.01	12.9
b	3.484	107.8	6.8	1.99	2.0	12.5
c	3.523	108.1	4.8	1.96	2.0	16.6
d	3.306	99.1	1.88	2.12	2.28	24.5
This work	3.375	107.6	7.4	2.12	2.06	11

[a] $[CuLGd(NO_3)_3]\cdot Me_2CO$ (Costes *et al.* [3]); [b] $[L^2Cu(MeOH)Gd(NO_3)_3]$ (Costes *et al.* [4]); [c] $[L^4Cu(OCMe_2)Gd(NO_3)_3]$ (Costes *et al.* [4]); [d] $[CuGd(H_2O)(NO_3)(ems)]$ (Atria *et al.* [26]); [e] Dihedral angle between coordination planes (OCuO and OGdO).

the agreement factor defined as $R(\chi) = [\Sigma(\chi_{obsd} - \chi_{calcd})^2]/[\Sigma(\chi_{obsd})^2]$ is $9{\cdot}10^{-5}$ which indicates an excellent agreement between observed and calculated values.

Interestingly the variation of J still parallels that of the dihedral angle ϕ between the two halves (OCuO and OGdO) of the bridging core. In the present work, it appears that the highest exchange parameter ($J = 7.4$ cm^{-1}) correspond to ϕ angles of 11.5(2) and 11.6(2)°. Increasing the angle ϕ to 16.6° [4] and 24.5° [26] causes a decrease of J to 4.8 and 1.88 cm^{-1}, respectively (Table 3). Also, when we compare these data with those previously reported for CuGd clusters with similar ligands (Table 3), we see that the present coupling constant is similar to most of them, *i.e* the coupling between Cu^{II} and Gd^{III} ions is ferromagnetic. This is surprising because the Gd^{III} ion has unpaired electrons in all seven f orbitals and at least one of them or one linear combination can give a non-zero overlap with the corresponding orbitals of Cu^{II} to give an antiferromagnetic coupling [27].

The fact that the coupling between Cu^{II} and Gd^{III} in many CuGd clusters is ferromagnetic may be due to the spin polarization [27, 28] that occurs when the single $3d$-type magnetic orbital on Cu^{II} overlaps with the empty $6s$ orbital of Gd^{III}. The fraction of unpaired electrons that is thus transferred from Cu^{II} to Gd^{III} keeps the f electrons parallel as required by Hund's rule, determining a ferromagnetic coupling between the two metal ions [28]. The facts that the $4f$ orbital is shielded by the outer filled $5s$ and $5p$ orbitals, and lanthanide ions generally form complexes using $6s$, $6p$ and/or $5d$ orbitals, support the spin-polarization mechanism [29].

The mechanism of the interaction between Cu^{II} and Gd^{III} ions by coupling between the $4f - 3d$ ground configuration and the excited configuration arising from the $3d_{Cu} \rightarrow 5d_{Gd}$ electron transfer and leading to ferromagnetic character has been suggested first by Goodenough [30]. In such a mechanism, J is given by

$$J = \sum_{i=1}^{5} \left[\beta^2_{5d-3d}\Delta/(4U^2 - \Delta^2)\right]_i \qquad (5)$$

where β_{5d-3d} is a transfer integral involving the singly-occupied copper orbital and a $5d$ gadolinium orbital, Δ is the energy gap between $S = 3$ and $S = 4$ excited states arising from the $4f^7 5d^1$ electron transfer configuration, and U is the energy cost of such a transfer. The summation applies to the five $5d$ gadolinium orbitals. The largest β_{5d-3d} integrals (in absolute values) probably involve the gadolinium $5d$ orbitals oriented along the Gd – O bridging directions. If this is so, one easily understands why bending the bridging network results in a decrease of those $|\beta_{5d-3d}|$ integrals and therefore in a decrease of the Cu^{II} – Gd^{III} interaction. Indeed, ferromagnetic coupling between Cu^{II} and Gd^{III} is possible only through a super-exchange interaction mediated by bridging oxygen ligands. In other words, the orbitals centered on Cu^{II} to Gd^{III} must have a fairly large overlap density on the oxygen atoms, which can be obtained only through a fairly substantial covalency of the Gd-O bond [2].

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