A discrete dinuclear Cu(II)–Gd(III) complex derived from a Schiff base ligand, [CuGd(ems)$(NO_3)_3H_2O$]Cu(ems) (ems: *N*,*N*′-ethylene-bis-5-methoxy salicylaldiimine)

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Abstract

A Cu(II)–Gd(III) heteronuclear complex with *N*,*N*′-ethylene-bis-5-methoxy salicylaldiimine (ems) as ligand has been synthesized. The complex crystallizes in the monoclinic system *C*2/*c* space group. The structure consists of two different discrete molecules: a mononuclear unit containing a single Cu(II) center, and a dinuclear one containing both a nine coordinated Gd(III) plus a four coordinated Cu(II) cation [CuGd$(H_2O)(NO_3)$(ems)]. The complex was characterized by magnetic susceptibility and electron paramagnetic resonance. The Cu(II)–Gd(III) complex presents a ferromagnetic interaction ($J = 1.88$ cm^{-1}); its effective magnetic moment was found to increase with decreasing temperature. Both electronic and structural parameters are shown to influence the magnitude of the magnetic interaction.

Keywords: Heterometallic complexes; Crystal structures; Magnetic properties; Gadolinium–copper complexes

1. Introduction

Magnetism of molecular complexes simultaneously comprising d and f transition metal ions has been the subject of investigation in the last few years. In particular the copper(II)–gadolinium(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)–Gd(III) and polynuclear systems with Cu_2Gd, Cu_4Gd, Cu_4Gd_2 or $(CuGd)_n$ cores, bridged by phenoxo or multidentate ligands with hetero donating groups [1–22].

In a previous work [23] we found the oxydiacetate ligand to be quite effective in bridging Ln–Cu couples, in particular Cu(II)–Gd(III) [22], but the resulting structures appeared too complicated for modeling purposes. Looking for simpler systems containing the isolated Cu(II)–Gd(III) pair we tried *N*,*N*′-ethylene-bis-5-methoxy salicylaldiimine (*ems*) as a ligand. As a result we present herein the synthesis, crystal structure and magnetic characterization of the novel discrete dinuclear complex thus obtained, [CuGd$(H_2O)(NO_3)$(*ems*)]. Until recently structural determinations of 3d–4f complexes deriving from salen-type Schiff base ligands pointed out their tri and tetranuclearity [6]. In this work we have been able to obtain a dinuclear species with no subsituents on the diamine arm or extra donor sites on the nucleus [24] by simply increasing the basicity of the phenoxo donor atoms. As most of the complexes presenting an isolated Cu(II)–Gd(III) couple the compound shows a ferromagnetic character, a behavior so generalized that led some authors to propose it to be an intrinsic property of the copper(II)–gadolinium(III) couple [19]. However, there are also a few examples in the recent literature where an antiferromagnetic beha-

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vior has been detected [18,19,23], so no conclusive evidence on the particular 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 amenable of different interpretations. In particular, we have looked at the planarity of the closed dinuclear bridge as a possible relevant feature, and analyzed all the copper(II)–gadolinium(III) nuclei reported so far for a correlation between the degree of distortion and the J value. This phenomenological analysis leads to a discussion herein.

2. Experimental

2.1. Synthesis

The Schiff base (*ems*) was prepared as reported elsewhere [25] and its copper complex was obtained by adding copper acetate to the Schiff base ligand in an equimolar relation, in methanol. The obtained complex was filtered and dried at room temperature (r.t.). For obtaining the heteronuclear complex two solutions containing the metal ions were then prepared: one containing 2.5 mmol of the copper complex dissolved in approximately 200 ml of dichloromethane and a second one with 1 mmol of gadolinium(III) nitrate dissolved in approximately 20 ml of methanol. These solutions were warmed under stirring and then mixed. A precipitate was filtered, washed with methanol and dried. The final compound was satisfactorily analyzed for copper and gadolinium on a mass ICP spectrometer, giving a Cu:Gd 2:1 ratio.

2.2. X-ray structure determination

A summary of crystal parameters and data collection and refinement details is given in Table 1. Data were collected on a Siemens R3m diffractometer equipped with graphite-monochromated Mo Kα ($\lambda = 0.7107$ Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections in the range $15^\circ < 2\theta < 25^\circ$. Intensity data were collected in the range $3^\circ < 2\theta < 50^\circ$ by the ω–2θ scan technique, and corrected by Lorentz polarization and absorption effects (Ψ scan). Two standard reflections were monitored every 98, and showed no significant changes ($< 2\%$). The structure was solved by a combination of direct methods and difference Fourier syntheses. Refinement was performed by full-matrix least-squares in F^2, with anisotropic displacement parameters for non-hydrogen atoms. Hydrogens fully defined by the stereochemistry were positioned at their expected values, and allowed to ride both in coordinates (C–H = 0.96 Å) as well as in displacement factors (1.2 times theirs host's). Those corresponding to the aqua molecule were located in the late difference Fourier, and refined with restrained O–H and H···H distances so as to prevent anomalous drifts.

Table 1
Crystallographic data

Formula	$C_{36}H_{38}Cu_2GdN_7O_{18}$
Formula weight	1141.06
Crystal system	monoclinic
Space group	$C2/c$ (No. 15)
Crystal dimensions (mm)	0.30 × 0.12 × 0.10
Crystal color, shape	redish needles
a (Å)	13.501(3)
b (Å)	19.249(3)
c (Å)	16.549(3)
β (°)	93.39(2)
V (Å^3)	4293(1)
Z	8
D_{calc} (g cm^{-3})	1.76
$F(000)$	2276
μ (mm^{-1})	2.59
Absorption correction	Semiempirical (Ψ scan)
Unique reflection, R_{int}, parameters	7563, 0.058, 600
R_1 [a] $[F^2 > 2\sigma(F^2)]$, all data	0.067, 0.141
wR_2 [b] $[F^2 > 2\sigma(F^2)]$, all data	0.123, 0.167
Max, min $\Delta\rho$ (e Å^{-3})	1.45, −2.43

[a] R_1:$\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] wR_2:$[\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$.

Computer programs used in this study were SHELXL97, SHELXTL/PC [26,26a,26b] and NARDELLI [27].

2.3. Magnetic and EPR measurement

The EPR spectra were recorded at r.t. with a Bruker ECS 106 Spectrometer, at 9.85 GHz, in a rectangular cavity with 50 kHz field modulation. The magnetic susceptibility measurements on powder samples were performed using a Cryogenic variable temperature susceptometer, operating at an applied field strength of 5 kG, in the range between 5 and 300 K. The susceptometer was calibrated with $HgCo(CNS)_4$. Pascal's constants were used to estimate the correction of the diamagnetism of the sample, and the temperature independent paramagnetism contribution for each copper atom was taken as 60 cm^{-3} mol^{-1}.

3. Results and discussion

3.1. Crystal structure

The structure consists of two different discrete molecules: a mononuclear unit containing a single Cu(II) center and a dinuclear one containing both a nine coordinated Gd(III) plus a second Cu(II) cation (Fig. 1a and b). The structure, which comprises a dinuclear (Cu, Gd) complex and a mononuclear Cu entity, is consistent with the microanalytical data. Table

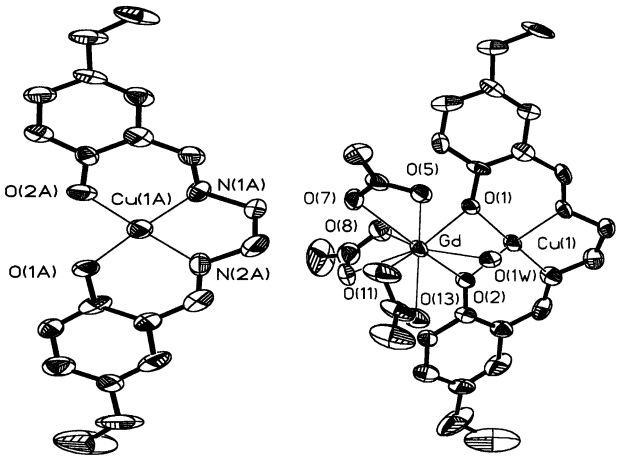


Fig. 1. (a) Partial view of $[CuGd(H_2O)(NO_3)_3(ems)]$ complex. (b) Partial view of $[CuGd(H_2O)(NO_3)_3(ems)]$ complex.

Table 2
Coordination bond lengths (Å) and bond angles (°)

Bond lengths			
Gd–O(1W)	2.362(8)	Gd–O(1)	2.363(6)
Gd–O(2)	2.405(6)	Gd–O(11)	2.461(9)
Gd–O(10)	2.467(8)	Gd–O(5)	2.472(7)
Gd–O(13)	2.493(8)	Gd–O(7)	2.500(7)
Gd–O(8)	2.550(9)	Gd···Cu(1)	3.306(1)
Cu(1)–N(1)	1.917(8)	Cu(1)–N(2)	1.917(9)
Cu(1)–O(2)	1.927(7)	Cu(1)–O(1)	1.931(7)
Cu(1A)–O(1A)	1.910(8)	Cu(1A)–O(2A)	1.911(8)
Cu(1A)–N(2A)	1.944(10)	Cu(1A)–N(1A)	1.946(10)
Bond angles			
O(1)–Cu(1)–O(2)	87.0(3)	O(1)–Gd–O(2)	67.6(2)
Cu(1)–O(1)–Gd	100.2(3)	Cu(1)–O(2)–Gd	98.9(3)

2 contains relevant bond distances and angles. In both entities, the copper ions are chelated by the Schiff base ligand, which binds through a fourfold bite involving two nitrogens and two oxygens to define a square planar coordination.

The two square–planar environments of the copper ions Cu1 and Cu1A are quite similar, the main differences arising from the bridging character of the oxygens in the former which leads to a slight lengthening of the Cu1–O bond (1.927–1.931(7) Å vs. 1.910–1.911(8)) and an increase of the value of O–Cu1–O angle (93.0(3)° vs. 88.8(3)°). Concomitantly, N–Cu1 bonds appear a bit shorter (1.917(7) Å vs. 1.944–1.946(10) Å).

The nine coordinated gadolinium presents a narrow spread in Gd–O bonds distances, the shortest one corresponding to the aqua (Gd–O1W: 2.362(8) Å) and the phenolate bridge (Gd–O1: 2.363(6), Gd–O2: 2.405(6) Å), and the longest, to the nitrato groups (range: 2.461(9)–2.550(9) Å). In the Cu(II)–Gd(III) dinuclear moiety these oxygens coordinate to gadolinium as well, acting as a bridge between the two cations and giving rise to a rather short intermetallic distance of 3.306(2) Å. This short distance can be compared with the Cu(II)–Gd(III) distance of 3.428(1) Å reported for the complexes derived from 3-methoxy salicylaldehyde 3.512(5) Å [2]. In this latter complex the donor methoxy group is bonded to Gd(III) and is apparently responsible for the increase of the intermetallic distance. For the studied Schiff base ligand, the 5-methoxy substituent can not act as an auxiliary donor atom to the metal center and has no parametric influence. Similar environments have already been described as is shown in Table 3. The coordination polyhedron for gadolinium is completed by six oxygen atoms from three different bidentate nitrato groups, thus completing the ninefold coordination sphere. The double bridge of phenolate oxygens holding together the dinuclear moiety defines a closed loop which is far from planar, as visualized by the dihedral angle between the O1–Gd–O2 and O1–Cu1–O2 planes, 24.5°.The only strong intermolecular interaction is the one linking the aqua molecule in the dinuclear unit (acting as a donor) and the phenolate oxygens in the mononuclear one (acting as acceptors): O1W–H1WA: 0.81(8) Å, H1WA···O1A: 1.90(9) Å, O1W–H1WA···O1A: 153(8)°; O1W–H1WB: 0.81(10) Å, H1WB···O2A: 2.02(10) Å, O1W–H1WB···O2A: 135(9)°. This kind of arrangement in which the two fragments are linked via a water molecule has been informed by Costes et al. for a similar Cu(II)–Er(III) complex, which also crystallizes together with a mononuclear Cu(II) complex [6]. The separation between the metal ions belonging to neighboring molecules are again large, as for the Cu(II)–Er(III) complex, [Cu(1)–Cu(1A) = 4.18, Cu(1A)–Gd = 5.704, Gd–Gd = 9.783 Å], thus precluding any significant intermolecular interaction of magnetic data.

The trinuclear units thus formed (Fig. 2) cannot be described as a genuine trinuclear compound, similar to the ones reported by Gatteschi et al. [1,7]. The studied species can be seen as isolated entities interacting with their symmetry equivalents through weak H contacts involving C–H's, and van der Waals interactions.

3.2. Magnetic properties

The magnetic behavior of the title compound was studied in the range 5–300 K. The plot of $1/\chi_M$ versus T follows the Curie–Weiss law. The best fit of the experimental data allows the calculation of $\theta = 2.66$ K, with $C = 9.012$ emu mol^{-1}, thus demonstrating that a very weak ferromagnetic interaction is operative in this complex. The temperature dependence of the magnetic susceptibility of $CuGd(H_2O)(NO_3)(ems)$ is represented in Fig. 3, in the form of the temperature dependence of the χ_M as well as the effective magnetic moment. The temperature plot of $\chi_M T$ shows that the effective magnetic moment gradually increases to reach a max-

Table 3
Comparative table of some Cu–Gd complexes

Formula	J (cm^{-1})	Dihedral angle of eq. 2	O–Cu–X X = O or N	O–Gd–O	Distance Cu–Gd	Coordination scheme
1 GdCu(OTf)(bdmap)$_2$(H_2O)THF [18]	−0.04	0.6[b]	81.6	67.2	3.31	Scheme 1
2 CuGdL $Cl_2(H_2O)_4Cl.2H_2O$ [25]	10.1	1.7[a]	78.19	64.3	3.51	Scheme 1
3 Cu $L^1Gd(NO_3)_3$ [19]	−0.49	6.1[a]	89.7	84.4	3.65	Scheme 2
4 CuGdL^2_2(MeOH) $(NO_3)_3$ [3]	6.8	12.5[a]	79.3	63.3	3.48	Scheme 1
5 CuGdL$(NO_3)_3Me_2CO$ [2]	7.01	12.9[b]	81.8	63.0	3.43	Scheme 1
6 CuGd $L^4(OCMe_2)$ $(NO_3)_3$ [3]	4.8	16.6[a]	78.3	62.1	3.52	Scheme 1
7 CuGd(H_2O)(NO_3)(*ems*) this work	1.88	24.5	87.0	67.6	3.31	Scheme 1
8 CuGdL^2(H_2O)(H2O)$(NO_3)_3$ [19]	3.5	39.1[a]	97.25	84.4	3.62	Scheme 2
9 CuGd$(hfa)_3$(salen)(meim) [4]	1.42	39.6[a]	83.6	66.4	3.25	Scheme 1
10 CuGd(salabza)$(hfac)_3$ [16,17]	0.8	47.4	81.5	62.2	3.25	Scheme 1
11 CuGd$(hfa)_3$(salen) [4]	1.02	48.3[c]	83.8[b]	62.3[c]	3.22[c]	Scheme 1
12 $Cu_3Gd_2(ODA)_6(H_2O)_6\cdot 12H_2O$ [24]	< 0	Not applicable	–	–	4.66	Scheme 3

1 OTf = SO_3 CF_3, bdmapH = 1,3-bis(dimethylamino)2-propanol THF = tetrahydrofurane. **2** L^1H2 = 1,3-bis(3-methoxysalicylidene)amino-2,2′-dimethyl propano. **3** L^1H = 3-methoxysalicylaldehyde with N–CH_2–$C(CH_3)_2$–CH_2–N. **4** L^2 = 3-methoxysalicylaldiimine. **5** L = 1,2′-bis((3-methoxysalicylidene)diamino-2-methylpropano), Me_2Co = acetone. **6** L^4 = (3-methoxysalicylidene)amino(2,2′-dimethylpropano). **8** L^1 = 3-methoxysalicylaldehyde with N–$C(CH_3)_2$–CH_2–N. **9** L^2 = 1-(2,4,4-trimethyl-hexahydro-2-imidazolidinyl)-1-ethanone oxime. **10** hfa = exafluoroacetylacetonato, salen = *N*,*N*′-ethylen-bis(salicylideneamino). Meim = 1-methylimidazole. **11** hfa = hexafluoroacetylacetonato, salen = *N*,*N*′-ethylen-bis(salicylideneamino). **12** salabza = *N*,*N*′-bis(salicylidene)-2-aminobenzylamine, Hhfac = 1,1,1,5,5,5-hexafluoroacetylacetone.

[a] Literature values.

[b] Calculated dihedral angles.

[c] Mean values of geometric parameters corresponding to two independent molecules.

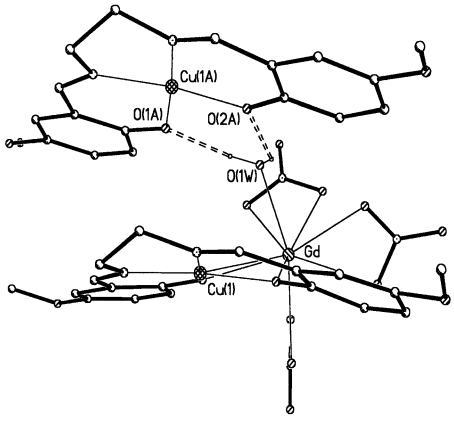


Fig. 2. An illustration of the hydrogen bonding interaction between the mononuclear and binuclear entities of [CuGd(H_2O)$(NO_3)_3$(*ems*)] complex.

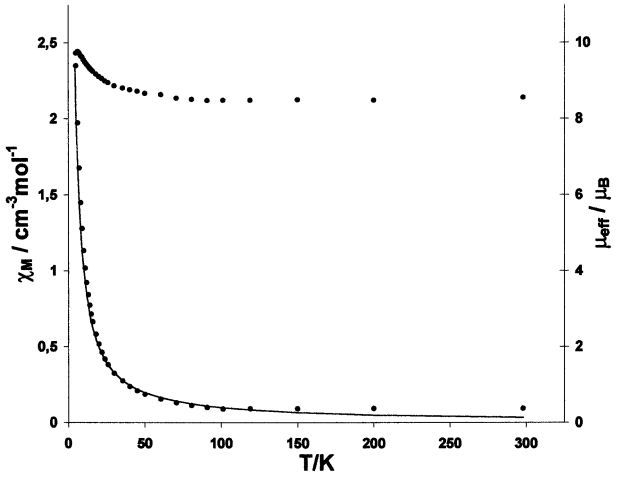


Fig. 3. Temperature dependence of the magnetic susceptibility and effective magnetic moment of [CuGd(H_2O)$(NO_3)_3$(*ems*)].

imum value with the decrease of the temperature. This behavior is consistent with the positive Weiss constant and corroborates the ferromagnetic character of the compound. The observed effective moment at 5 K is $9.79\mu_B$, while at room temperature it is $8.56\mu_B$. This last value is slightly higher than the spin only value $8.31\mu_B$ calculated from the equation $\mu_{eff} = (2\mu^2_{Cu} + \mu^2_{Gd})^{1/2}$ derived by assuming that the spin–spin interaction is absent between Cu(II) ($S = 1/2$) and Gd(III) ($S = 7/2$). The Van Vleck equation was used to analyze the magnetic susceptibility due to the presence of a binuclear Cu(II)–Gd(III) couple in the asymmetric unit; an additional term had to be included in order to describe the contribution of the monomeric copper complex. Considering the two low-lying levels $E(4) = 0$ and $E(3) = 4$ J, the working expression for the molar susceptibility is given in equation

$$\chi_M T = \frac{4Ng_1^2\beta^2}{k}\left[\frac{15 + 7\exp(-8J/kT)}{9 + 7\exp(-8J/kT)}\right] + \frac{Ng_2^2\beta^2}{4k} \qquad (1)$$

The spin-only equation (1) with the spin Hamiltonian $H = -2J_{Cu-Gd}S_{Cu}S_{Gd}$ was used since the contributions of the angular momentum and the anisotropic effect were not taken into account on the basis of the electronic configuration of both metal ions. The least-squares fit of the experimental data gave the following set of parameters: $g_1 = 2.12$, $J = 1.878$ cm^{-1}, $g_2 = 2.28$.

The positive value of J indicates a ferromagnetic coupling between Cu(II) and Gd(III).

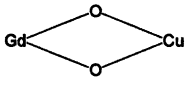
Comparing the dihedral angle between the planes O(I)–Cu–O(2) and O(I)–Gd–O(2) in the complexes which figure in Table 3, it is possible to notice that **4** and **5** have similar dihedral angles, which correlate well with the value of the coupling constant J. However, for the other species a poor correspondence is observed. This is not surprising if the complexity of these systems is taken into account. Apparently the J values depend not only on steric factors, but are also influenced by the nature of the ligand. Thus, if the stabilization of the ferromagnetic spin state ($S = 4$) is attributed to the coupling between the ground state of the Cu(II)–Gd(III) couple and the charge-transfer excited state Cu(III)–Gd(II) as was proposed by Goodenough, the transfer integral $\beta_{5dGd-3dCu}$ is influenced by the basicity of the bridging atoms as well as by the bending parameter [18].

The polycrystalline powder EPR spectra of the complex at room temperature exhibits a broad asymmetric peak with absence of any hyperfine structure, dominated by one g value at 2.06. This spectrum corresponds to the superposition of the signal of the two copper (II) ions in different environments, including the Gd(III) signal.

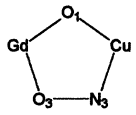
3.3. Final remarks

Goodenough proposed that the ferromagnetic contribution in the copper(II)–gadolinium (III) couple was due to the interaction between the $4f_{Gd}$–$3d_{Cu}$ ground configuration and the $3d_{Cu}/5d_{Gd}$ excited configuration [28]. In the Anderson–Hoffman model [29,30] ferromagnetism arises from the $3d_{Cu}$–$4f_{Gd}$ ground configuration and the charge transfer configuration ($3d_{Cu}$–$4f_{Gd}$). In the Kahn approach the antiferromagnetic interaction between the metal ions arises solely from the overlap between the localized magnetic orbitals of the ground state configuration [31].

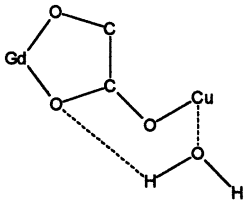
In an attempt to find some structural characteristic, which could correlate with the magnetic behavior in this type of compounds, we analyzed all the copper(II)–gadolinium(III) complexes reported in the literature. In Table 3 we present the J value of a series of heteronuclear complexes as well as the dihedral angle subtended by the O–Gd–O and O–Cu–O planes in the loop (Scheme 1). Some of these (b) were calculated using data from the Cambridge Data File. In Scheme 2 the dihedral angles correspond to the angles between the O1–Cu–N2 and O1–Gd–O3 planes but in Scheme 3 we



Scheme 1.



Scheme 2.



Scheme 3.

cannot compare because the geometry is rather different.

The expression $|J| = A\exp(Bc)$ (2)

with $A = 11.5$ and $B = -0.063$ informed by Costes et al. [24] was used to correlate the planarity of the double bridge connecting the metallic centers (c) with the exchange interaction J. However, a poor fit of the available data was obtained with the above mentioned equation; ($\chi^2 = 17.7$). A different approach was considered by Winpenny et al. [19], who correlated the J value of a group of ferromagnetic Cu(II)–Gd(III) complexes with the distance between the two metal centers. This latter correlation is again not valid for the data given in Table 3.

The only two known cases where a negative J has been reported [18,19] present a rather small distortion from planarity. The third known antiferromagnetic complex [23] is not amenable of this kind of treatment, due to the complexity of the linking bridge. The reported antiferromagnetic behavior of the two mentioned copper(II)–gadolinium(III) complexes suggests that the overlap density in these complexes has a finite value and plays an important role in the observed magnetic behavior of these species. However, dependence of J with the dihedral angle is not that which could be expected from the Kahn theory, since the most planar compound does not show the greatest antiferromagnetic coupling. In fact, the complex CuGd(salen)(Meim)$(hfa)_3$ reported by Costes et al. [24] has a very small dihedral angle and shows the greatest positive J value of all the exchange constants which have been measured for Cu(II)–Gd(III) complexes. As the nature of the bridging unit is not the same for the reported complexes, the need of further studies in this area is evident. Thus a generalization on the ferromagnetism of the Cu(II)–Gd(II) couple is questionable, since most of the reported complexes have very similar bridging atoms. The existing data indicate that the nature of the bridging ligands is an important factor controlling the magnitude of the spin–spin coupling, to be con-

sidered together with the distance between the metal ions and the angle of the bridging atoms.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 182300. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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