Full paper / Mémoire

Exchange coupling in $Cu^{II}Gd^{III}$ dinuclear complexes: A theoretical perspective

Jordi Cirera, Eliseo Ruiz*

Departament de Química Inorgànica and Institut de Recerca de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Abstract

Theoretical calculations using density functional methods combined with relativistic approaches have been employed to study the magnetic properties of heterodinuclear $Cu^{II}Gd^{III}$ complexes. The calculated exchange coupling constants show an excellent agreement with the experimental ferromagnetic data confirming a magnetostructural correlation with the Cu−O−Gd−O torsion angle. Thus, for planar $CuGdO_2$ frameworks the coupling is more ferromagnetic that can be related to an increase of the 3d−4f overlap when the structure becomes non-planar. The analysis of the spin density shows that the spin polarization effects are predominant for the ligand atoms directly coordinated to the Gd^{III} cations. *To cite this article: J. Cirera, E. Ruiz, C. R. Chimie 11 (2008).*
© 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Calculs théoriques utilisant des méthodes basées en la théorie de la fonctionnelle de la densité combinés avec des approximations relativistes ont été employées pour étudier les propriétés magnétiques des complexes hétérodinucleaires $Cu^{II}Gd^{III}$. Les constantes d'échange calculées montrent un excellent accord avec les données ferromagnétiques expérimentales confirmant une corrélation structurale avec l'angle de torsion Cu−O−Gd−O. Ainsi, pour un coeur $CuGdO_2$ plan le couplage est plus ferromagnétique, peut-être lié à une augmentation du recouvrement 3d−4f lorsque la structure devient non-plane. L'analyse de la densité de spin montre que les effets de polarisation de spin sont prédominants pour les atomes liés directement aux cations Gd^{III}. *Pour citer cet article : J. Cirera, E. Ruiz, C. R. Chimie 11 (2008).*
© 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

* Corresponding author.
  E-mail address: eliseo.ruiz@qi.ub.es (E. Ruiz).

1. Introduction

Actually, many research groups working on Molecular Magnetism have regularly employed lanthanides due to the their large magnetic moment and magnetic anisotropy [1,2]. Recently, some mixed d/f compounds have shown single-molecule magnet properties [3], such as Cu_2Tb_2 [4], Mn_6Dy_6 [5], $Mn_{11}Dy_4$ [6], Mn_2Dy_2 [7], Fe_2Dy_2 [8], Fe_2Ho_2 [8] and $Mn_{11}Gd_2$ complexes [9]. Thus, since the seminal paper in 1985 of Bencini et al. [10] devoted to a $Cu^{II}Gd^{III}$ heterodinuclear complex, many groups have dedicated much attention to this kind of systems; it is worth noting among others, those of Costes et al. [11,12] and Kahn et al. [13,14]. The Gd^{III} complexes are probably the most studied complexes in this field due to the presence of the largest possible magnetic moment $S = 7/2$ and the lack of an important orbital contribution that facilitates the analysis of the magnetic properties. Also, the d/f Gd^{III} complexes show another appealing feature, practically all of them present ferromagnetic coupling [15].

During the last years we have successfully employed theoretical methods based on density functional theory to calculate exchange coupling constants in dinuclear transition metal complexes [16–18] as well as in large polynuclear complexes [19–21] achieving a surprising accuracy when hybrid exchange correlation functionals, e.g. B3LYP [22], have been used [23]. Despite the large number of d/f complexes reported [15], few theoretical studies have been carried out especially for the difficulty to handle the spin–orbit effects in relatively large complexes. Yan et al. have studied the exchange coupling and the spin distributions in three MGd^{III} complexes ($M = Cu^{II}$, Fe^{III} and Cr^{III}) using density functional methods [24]. A detailed analysis of the ferromagnetic $Gd^{III}Cu^{II}$ coupling was performed by Paulovic et al. using CASSCF and CASPT2 methods combined with spin–orbit terms [25]. However, considering the large number of atoms present in some of the polynuclear complexes mentioned above, only theoretical methods based on density functional theory can handle this kind of system. Thus, our first goal is to check the accuracy of density functional methods to describe this type of exchange interactions in $Cu^{II}Gd^{III}$ complexes, analyzing specifically the role of the relativistic effects even if the f^7 configuration of the Gd^{III} cation has no orbital degeneracy associated with the ground state. A second step will be an analysis of the exchange interactions in the $Cu^{II}Gd^{III}$ complexes and the study of the magnetostructural correlations in this kind of systems.

The obvious choice to treat accurately the relativistic effects is the four-component Dirac equation [26]. Therefore, much effort has been spent to approximate the major relativistic contributions by two-component Hamiltonians, which are conceptually simple, variationally stable, sufficiently accurate and computationally more efficient than the four-component equation. Basically in the two-component equations, e.g. Breit–Pauli Hamiltonian, there are five terms, the relativistic kinetic and potential terms, two contributions usually known as scalar relativistic corrections (also called spin-free relativistic corrections), the mass–velocity and the Darwin corrections and finally, the spin–orbit term. In order to include scalar relativistic effects in this kind of calculation [27]; we have considered a set of possibilities: (*i*) the use of quasi-relativistic pseudopotentials; (*ii*) the Zeroth-Order Regular Approximation (ZORA), a two-component approximation to the Dirac equation [28]; and (*iii*) the Douglas–Kroll–Hess Hamiltonian (DKH) [29,30]. These approaches are limited to introducing only the scalar relativistic effects while we expect that the spin–orbit effects are of minor importance for the correct description of the f^7 configuration of the Gd^{III} cations.

2. Results and discussion

2.1. Validation of the methodology

In order to verify the methodology used to describe the exchange interactions in the $Cu^{II}Gd^{III}$ complexes, we have selected one of them [31] (refcode ZUVTIT) that was also employed by Paulovic et al. in multiconfigurational calculations [25] (see Fig. 1). The calculated J values using the hybrid B3LYP functional are collected in Table 1 (see Section 4).

From the obtained results, we can extract the following conclusions: (*i*) The inclusion of the scalar relativistic effects plays a crucial role to reproduce correctly the sign of the interaction; (*ii*) The results using the ZORA and DKH approximations are very similar as it is usually found [27,32]; (*iii*) The use of quasi-relativistic pseudopotentials seems to be not an alternative to the ZORA and DKH approximations because the sign of the interaction is not well reproduced. We have verified the influence of the acetone molecule in the model and despite the long Cu···O bond distance of 2.607 Å due to Jahn–Teller effect in the $4 + 1$ coordination sphere, the B3LYP-DKH value using the Gaussian basis set is $+1.7$ cm^{-1}. This value is relatively close to that obtained with the whole model,
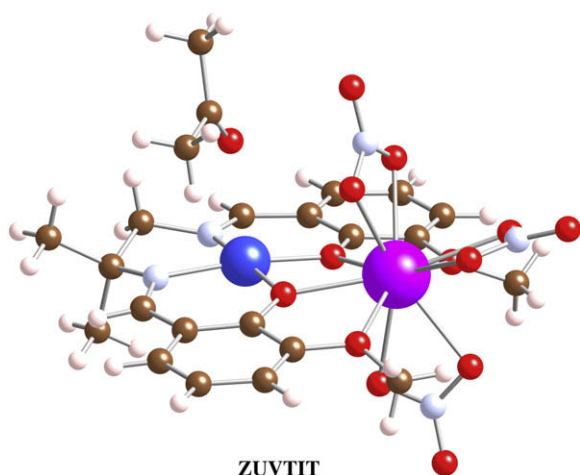
Fig. 1. Molecular structures of [LCuGd(NO₃)₃]·Me₂CO (L = 1,2-bis((3-methoxysalicylidene)amino)-2-methylpropanato) (refcode ZUVTIT). The Cu^{II} and Gd^{III} cations, oxygen, nitrogen, and carbon atoms are represented as blue, pink, red, light blue, and brown spheres, respectively.

however, it is worth noting the influence of the acetone molecule, taking into account that the "magnetic orbital" [33] of the Cu^{II} cation is perpendicular to the Cu···O interaction and the long Cu···O distance.

2.2. Magnetostructural correlations

Our aim is to establish some magnetostructural correlations, thus, we have collected in Table 2 the main structural parameters and the exchange coupling constants for all reported dinuclear Cu^{II}Gd^{III} complexes showing a central Cu^{II}Gd^{III}O₂ framework with only two bridging ligands. The analysis of such results indicates the existence of a fair correlation between the J value and the Cu–O–Gd–O torsion angle [11,15,34] that measures the planarity of the central framework (see Fig. 2) rather than with the Gd···Cu distance [35]. Thus, for the "planar" structures the coupling becomes more ferromagnetic as was previously noticed

Table 1
Calculated and experimental J exchange coupling constants (in cm^{-1}) for the LCuGd(NO₃)₃·Me₂CO complex (see Fig. 1, refcode ZUVTIT) including the scalar relativistic effects using the ZORA (ORCA code) and DKH (Gaussian code) approaches

	J
B3LYP. SDD pseudo Gd (Gaussian)	−4.41
B3LYP. all electron (Gaussian)	−0.66
B3LYP. all electron, DKH (Gaussian)	+2.4
B3LYP. all electron (ORCA)	−0.96
B3LYP. all electron, ZORA (ORCA)	+2.4
exp.	+7.0

by different authors [11,15,34]. However, there are two clear exceptions to such correlations that are the complexes [36,37] with NEBLUB and OBEMAK refcodes (see Fig. 3 and Table 2), in both cases, despite a structure relatively planar, the coupling is rather weak (left lower part in Fig. 2).

In order to study theoretically the exchange coupling in this family of complexes, we have selected three Cu^{II}Gd^{III} complexes [11,31,39] (JOGQAX, ZUVTIT and KEQRED, see Fig. 3) to cover a wide range of Cu–O–Gd–O torsion angle values, together with the two exceptions to the magnetoestructural correlation (NEBLUB and OBEMAK) [36,37] indicated previously (see results in Table 3). From the calculated J values, we can extract the following remarks: (i) The calculated J values for the two complexes (NEBLUB and OBEMAK), where the experimental J values do not follow the magnetoestructural correlation with the Cu–O–Gd–O torsion angle, are larger than the experimental ones, and thus, they are closer to the predictions of the correlation; (ii) For the other three complexes, the calculated exchange coupling constants reproduce correctly the sign and the relative strength of the exchange interaction, only, the value obtained for the ZUVTIT complex is slightly smaller than the experimental one or that expected for its Cu–O–Gd–O torsion angle value.

To check the existence of the magnetostructural correlation, we have performed calculations using the KEQRED complex [11] as reference modifying the Cu–O–Gd–O torsion angle just by doing a vertical displacement in the same direction of the two bridging oxygen atoms. The results are plotted in Fig. 4, showing a nice agreement with the experimental data confirming that planar CuGdO₂ frameworks are more ferromagnetic. As final conclusion, we can mention that the applied methodology gives very good results for the exchange interactions for the Cu^{II}Gd^{III} complexes and corroborates the existence of a correlation between the magnetic properties and the Cu–O–Gd–O torsion angle.

2.3. Analysis of the exchange interactions

The ferromagnetic nature of the Cu^{II}Gd^{III} in this kind of complex has been attributed by Kahn et al. to influence the excited state produced for the electron jump from the 3d Cu^{II} electrons to the 5d Gd^{III} shell. Originally, Gatteschi et al. proposed the participation of the 6s orbital of the Gd^{III} cation through a spin polarization model [52,53], however, recent CASPT2 calculations [25] seem to confirm the mechanism

Table 2
Structural data of the $Cu^{II}Gd^{III}$ complexes, Cu···Gd distances, Cu–O–Gd bond angles and Cu–O–Gd–O torsion angle (in Å and degrees, respectively) and experimental J exchange coupling constants (in cm^{-1})

|	Refcodes	Cu···Gd	Cu–O–Gd	Cu–O–Gd–O	J_{exp}	Ref.
GdCu(OTf)(bdmap)$_2$(H$_2$O)·THF	NEBLUB	3.310	104.7, 105.5	0.49	−0.08	[36]
Gd(hfa)$_3$Cu(salen)	RINQAG	3.230	95.8, 94.3	32.99	0.4	[38]
		3.199	93.6, 93.8	34.56		
Cu(salabza)Gd(hfac)$_3$	JOGQAX	3.248	93.1, 98.5	34.28	0.8	[39]
Cu(salen)Gd(pta)$_3$	OFELAM	3.288	95.2, 99.8	23.72	1.21	[40]
Cu(acacen)Gd(hfa)$_3$	OFELIU	3.288	98.1, 96.6	28.46	1.25	[40]
		3.313	99.8, 96.7	25.59		
LCuGd(NO$_3$)$_3$·Me$_2$CO	OBEMAK	3.444	106.8, 105.1	4.05	1.3	[37]
Gd(hfa)$_3$Cu(salen)(Meim)	RINQIO	3.252	95.0, 98.3	27.72	1.42	[38]
Cu(acacen)Gd(pta)$_3$	OFELEQ	3.274	98.0, 94.6	29.81	1.47	[40]
Cu(ehphi)Gd(hfac)$_3$	MIDHIQ	3.252	99.7, 94.5	30.78	1.91	[41]
CuGd(hmp)$_2$(NO$_3$)$_3$(H$_2$O)$_2$	XAYTIB	3.346	102.8, 102.0	15.32	3.36	[15]
[CuGd(ems)(NO$_3$)·3H$_2$O]Cu(ems)	XOZZUH	3.306	98.9, 100.1	17.77	3.76	[34]
LCuGd(NO$_3$)$_3$·CH$_3$OH	WIXYIL	3.224	97.0, 97.1	23.31	4.33	[42]
LCu(C$_3$H$_6$O)Gd(NO$_3$)$_3$	NEVHIF	3.523	106.5, 109.0	13.52	4.8	[43]
LCuGd(NO$_3$)$_3$	AWUQUE	3.443	103.7, 103.4	14.12	4.98	[44]
LCu(H$_2$O)Gd(NCS)$_3$·Me$_2$CO	BERPAQ	3.454	106.6, 106.3	15.44	5.5	[45]
LCuGd(NO$_3$)$_3$·Me$_2$CO	QEMYAI	3.425	109.0, 109.8	9.60	5.6	[46]
LCu(MeOH)Gd(NO$_3$)$_3$	NEVHEB	3.484	106.5, 109.0	10.00	6.8	[43]
LCuGd(NO$_3$)$_3$·Me$_2$CO	ZUVTIT	3.428	107.4, 105.9	10.15	7.0	[31]
LCuGd(NO$_3$)$_3$·Me$_2$CO	NAMDIP	3.475	106.9, 107.3	10.05	7.3	[47]
LCuGd(NO$_3$)$_3$·Me$_2$CO	EZAPAW	3.473	107.3, 107.6	9.29	7.4	[48]
		3.477	107.8, 107.8	11.06		
LCuGd(NO$_3$)$_3$	GANFIL	3.498	107.4, 108.9	7.45	7.6	[49]
		3.499	106.7, 108.7	10.99		
LCuGd(NO$_3$)$_3$	LOYTOI	3.400	103.7, 106.6	3.36	8.08	[50]
LCuGd(NO$_3$)$_3$·Me$_2$CO	FAKLOT	3.454	106.7, 107.3	8.96	8.63	[12]
[LCuCl$_2$Gd(H$_2$O)$_4$]Cl·2H$_2$O	KEQRED	3.512	108.8, 108.7	1.38	10.1	[11]
LCuGd(NO$_3$)$_3$	LAMBOR	3.449	105.3, 107.8	5.50	10.8	[51]
LCuGd(NO$_3$)$_3$	LAMBUX	3.401	105.8, 104.2	1.61	12.6	[51]
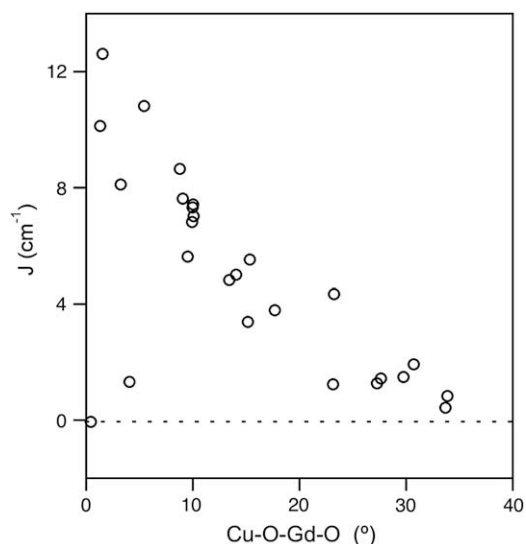
Fig. 2. Representation of the dependence of the J values for Cu^{II} Gd^{III} dinuclear complexes with a central $CuGdO_2$ framework with the Cu–O–Gd–O torsion angle for the complexes indicated in Table 2.

proposed by Kahn et al. [13]. Despite the role of the stabilization of the ferromagnetic ground state due to the interaction with excited states, we want to study the influence of the antiferromagnetic contribution analyzing the overlap between the 3d Cu^{II} and 4f Gd^{III} magnetic orbitals. Hence, we have calculated such overlap values for the previously studied KEQRED complex [11] (see Fig. 3) and the same complex with a distorted Cu–O–Gd–O torsion angle of 40° corresponding to the weakest ferromagnetic case (see Fig. 4). As noticed previously by us and other authors [54,55], the empty ''magnetic orbitals'' of the low spin wavefunction are the best choice in order to avoid problems in the determination of the ''magnetic orbitals'' due to a strong mixing with the ligand orbitals that appear in the occupied orbitals. The analysis of the calculated overlap values using such orbitals shows that for the original KEQRED complex, with an almost planar $CuGdO_2$ framework and relatively strong calculated ferromagnetic coupling ($+8.5$ cm^{-1}), there are only two non-orthogonal 3d–4f interactions (see
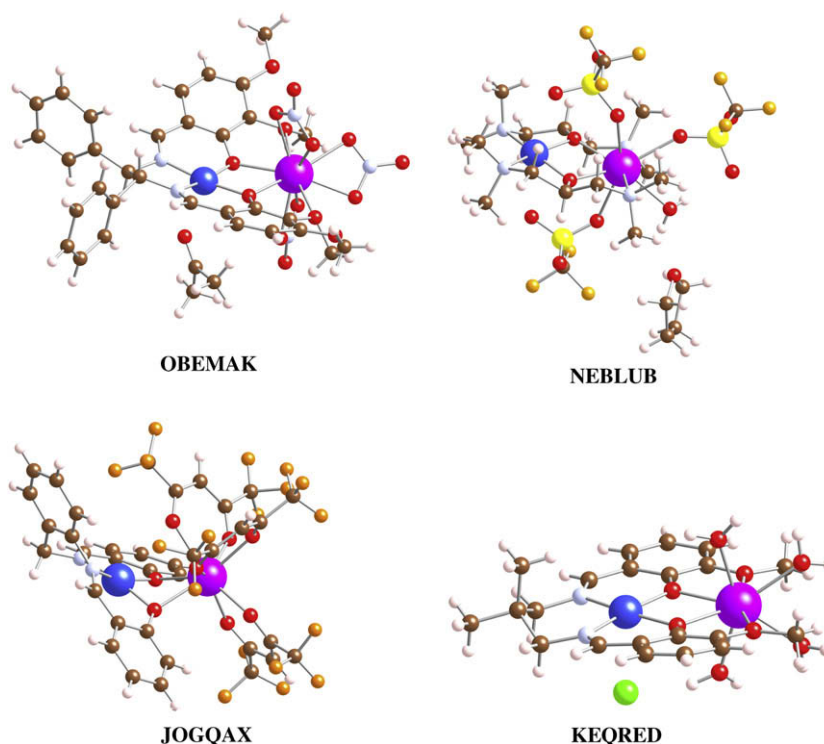
Fig. 3. Molecular structures of the four studied Cu^{II}−Gd^{III} complexes: [LCuGd(NO$_3$)$_3$]·Me$_2$CO (L = N,N′-bis((5,6-dimethoxyphenolato-2-yl)me-thylene)ethylenediamine) (refcode OBEMAK), [LCuGd(CF$_3$SO$_3$)(H$_2$O))$_3$]·THF (L = 1,3-bis (dimethylamino)-2-propanol (refcode NEBLUB), [LCuGd(hfac)$_3$] (L = N,N′-bis(salicylidene)-2-aminobenzylamine; hfac = hexafluoroacetylacetanato) (refcode JOGQAX) and [LCuGd(-H$_2$O)$_3$Cl$_2$]Cl·H$_2$O (L = 1,2-bis((3-methoxysalicylidene)amino)-2,2′-dimethylpropanato) (refcode KEQRED). The Cu^{II} and Gd^{III} cations, oxygen, nitrogen, sulphur, fluorine, chlorine and carbon atoms are represented as blue, pink, red, light blue, yellow, orange, green and brown spheres, respectively.

left column in Fig. 5, taking a threshold overlap value of 0.01), and consequently five ''orthogonal'' ferro-magnetic contributions, while for the distorted com-plex with a $J = +2.5$ cm^{-1}, the opposite situation is found with five non-orthogonal 3d−4f interactions (see right column in Fig. 5). Thus, the sum of the ab-solute value of the seven overlap integrals for the 3d−4f interactions for the original KEQRED complex

is 0.086, considerably lower than the value of 0.115 for the distorted complex, despite the longer Cu−O bond distance in the distorted model. This increase of the overlap matches with the weakening of the ferromag-netic coupling for larger Cu−O−Gd−O torsion angles due to a larger antiferromagnetic contribution as pro-posed in the Kahn−Briat model [56,57].

2.4. Spin density

The spin density corresponding to the ferromagnetic $S = 4$ ground state of the KEQRED complex [11] is plotted in Fig. 6. The two metals show a very different behavior; thus, the unpaired electron of the Cu^{II} cation is located in an antibonding $d_{x^2−y^2}$ orbital that is con-siderably mixed with the ligand orbitals resulting in a spin delocalization over the neighboring atoms [58,59]. However, the spin density of the Gd^{III} cation remains almost integrally in the lanthanide due to the internal character of the 4f orbitals caused by their poor screening of the nuclear charge. The calculated spin density in the Gd^{III} cations ranges from 6.94 to

Table 3
Calculated and experimental J exchange coupling constants (in cm^{-1}) for the four studied complexes (see Fig. 1) including the scalar relativ-istic effects (DKH approach in Gaussian code) using the B3LYP func-tional with an all electron basis set

	Cu−O−Gd−O	J_{calc}	J_{exp}
NEBLUB	0.49	+8.9	−0.08
JOGQAX	34.28	+1.5	+0.8
OBEMAK	4.05	+4.6	+1.3
ZUVTIT	10.15	+2.4	+7.0
KEQRED	1.38	+8.5	+10.1

The experimental Cu−O−Gd−O torsion angles (in degrees) are pro-vided for comparison.
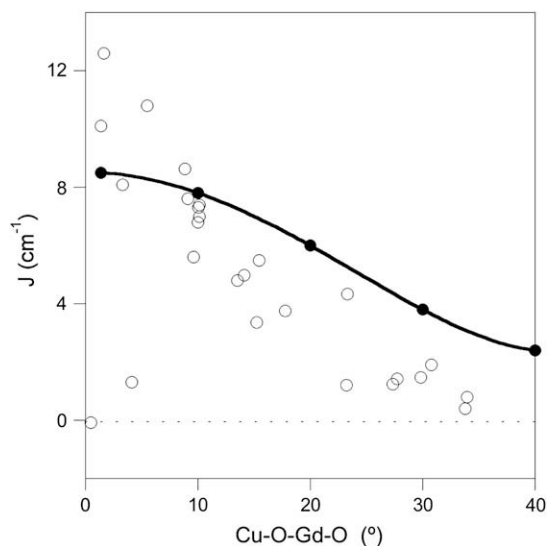
Fig. 4. Representation of the variation of the calculated *J* values (black circles) with the Cu−O−Gd−O torsion angle for a model structure based on KEQRED complex. The experimental data (empty circles) for the complexes of Table 2 are provided for comparison.

$6.97\,e^{-}$ for the five calculated complexes. The more surprising fact is the predominance of the spin polarization mechanism on the terminal atoms directly coordinated to the Gd[III] cation. Despite the presence of a spherical spin density in such cations, the mixture of the 4f orbitals with those of the ligands (see also the highly localized Gd orbitals in Fig. 5) is so weak that the spin delocalization is smaller than the spin polarization. This behavior is completely different than that usually found with transition metal cations if the symmetry of the ligand orbitals allows the mixing with those bearing the unpaired electrons of the metal, the spin delocalization mechanism is the predominant one [58,59].

3. Conclusions

From the methodological point of view for the magnetic properties of the Cu[II]Gd[III] complexes, the inclusion of the relativistic effects using ZORA or DKH approaches is crucial to obtain a good agreement with the experimental exchange coupling constants. The calculations combining such approaches with B3LYP functional and all electron basis set provide an accurate description of the ferromagnetic coupling present in the studied complexes. For the Cu[II]Gd[III] complexes with a central $CuGdO_2$ framework, the exchange coupling constant seems to be directly related with the Cu−O−Gd−O torsion angle. Thus, for planar $CuGdO_2$ frameworks the ferromagnetic coupling
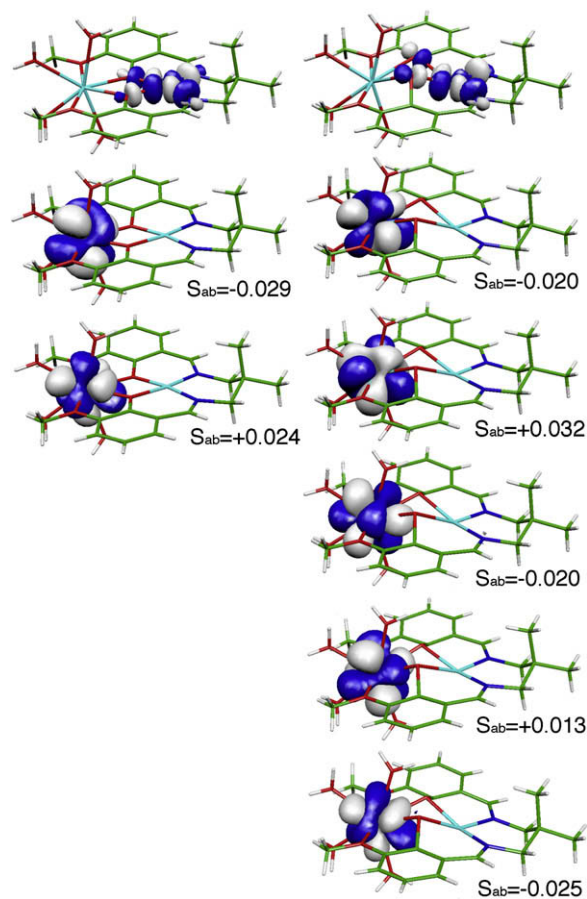

Fig. 5. Representation of the ''non-orthogonal'' magnetic orbitals for the KEQRED complex (left column) and for the distorted model of the same complex with a Cu−O−Gd−O torsion angle of 40°. The S_{ab} value corresponds to the overlap integral with the magnetic orbital centered on the Cu[II] cation represented above on each column.

becomes stronger. The analysis of the overlap integrals for the 3d−4f interactions confirms such magnetostructural correlation due to an increase of the overlap for the non-planar structures, and consequently a larger antiferromagnetic contribution. Finally, it is worth noting that the spin density of the Cu[II]Gd[III] complexes shows surprisingly that the spin polarization effects are predominant over the spin delocalization despite that mixing of the 4f orbitals of the Gd[III] cations is allowed by symmetry with the orbital ligands.

4. Computational details

Since a detailed description of the computational strategy adopted in this work can be found elsewhere [18,23,60,61] we will only briefly sketch its most relevant aspects here. Using a phenomenological Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1\hat{S}_2$ to describe the
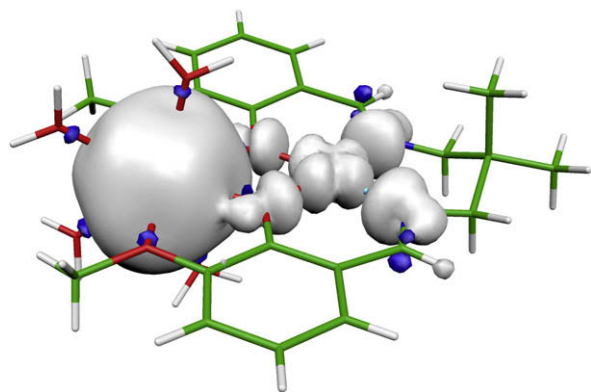
Fig. 6. Representation of the spin density corresponding to the ferromagnetic $S = 4$ ground state of the KEQRED $Cu^{II}Gd^{III}$ complex. The isodensity surface represented corresponds to a value of 0.0015 e$^-$/bohr^3 (white and blue regions indicate positive and negative spin populations, respectively).

exchange coupling in a dinuclear compound, where J is the coupling constant, and S_1 and S_2 the local spins on centers 1 and 2, respectively. It has been found that, when using DFT-based wavefunctions, a reasonable estimate of the exchange coupling constants can be obtained from the energy difference between the low spin wavefunction, E_{LS} (traditionally called broken-symmetry solution for symmetric complexes) and the state with highest spin, E_{HS} through the following equation:

$$J = \frac{E_{LS} - E_{HS}}{2S_1S_2 + S_2} \tag{1}$$

This solution corresponds to the non-projected approach that usually gives good results because the presence of the self-interaction error in the commonly used exchange–correlation functional incorporates some static correlation terms resulting in that the energy corresponding to the single-determinant low spin wavefunction is a good approximation to that of low spin state [23]. Thus, in the case of the $Cu^{II}Gd^{III}$ complexes the J values are calculated as the energy difference between the two single-determinant wavefunctions ($S = 3$ and $S = 4$):

$$J = \frac{E_{S=3} - E_{S=4}}{4} \tag{2}$$

The calculations were performed with the Gaussian [62] and ORCA [63] codes using in all cases the hybrid B3LYP functional [22]. We have employed the triple zeta basis set proposed by Schaefer et al. [64] and for Gd atoms an all electron basis set with a contraction pattern (10 64322111/8442211/6421/411) obtained from an uncontracted basis set proposed by Nakajima et al. [65] while the basis set to use combined with a small

core quasi-relativistic pseudopotential was proposed by Dolg et al. (36 electrons in valence space) with the contraction scheme (5111111111/61111111/61111/5111/411) including also g functions [66].

Acknowledgments

References

[1] C. Benelli, D. Gatteschi, Chem. Rev. 102 (2002) 2369.
[2] J.-P. Sutter, M.L. Kahn, in: J.S. Miller, M. Drillon (Eds.), Magnetism: Molecules to Materials, Wiley-VCH, Weinheim, 2005, p. 161.
[3] D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, Oxford, 2006.
[4] (a) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, J. Am. Chem. Soc. 126 (2004) 420;
(b) G. Novitchi, J.-P. Costes, J.-P. Tuchagues, L. Vendier, W. Wernsdorfer, New J. Chem. 32 (2008) 197.
[5] C. Zaleski, E. Depperman, J. Kampf, M. Kirk, V. Pecoraro, Angew. Chem. Int. Ed. 43 (2004) 3912.
[6] A. Mishra, W. Wernsdorfer, K.A. Abboud, G. Christou, J. Am. Chem. Soc. 126 (2004) 15648.
[7] A. Mishra, W. Wernsdorfer, S. Parsons, G. Christou, E.K. Brechin, Chem. Commun. (2005) 2086.
[8] M. Murugesu, A. Mishra, W. Wernsdorfer, K.A. Abboud, G. Christou, Polyhedron 25 (2006) 613.
[9] V.M. Mereacre, A.M. Ako, R. Clérac, W. Wernsdorfer, G. Filoti, J. Bartolomé, C.E. Anson, A.K. Powell, J. Am. Chem. Soc. 129 (2007) 9248.
[10] A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, J. Am. Chem. Soc. 107 (1985) 8128.
[11] J.-P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 165.
[12] J.-P. Costes, G. Novitchi, S. Shova, F. Dahan, B. Donnadieu, J.-P. Tuchagues, Inorg. Chem. 43 (2004) 7792.
[13] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J.C. Trombe, J. Am. Chem. Soc. 115 (1993) 1822.
[14] O. Kahn, Acc. Chem. Res. 33 (2000) 647.
[15] F. He, M.-L. Tong, X.-M. Chen, Inorg. Chem. 44 (2005) 8285.
[16] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, J. Am. Chem. Soc. 119 (1997) 1297.
[17] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.
[18] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 20 (1999) 1391.
[19] E. Ruiz, Struct. Bonding 113 (2004) 71.
[20] E. Ruiz, J. Cano, S. Alvarez, Chem. Eur. J. 11 (2005) 4767.

[21] E. Ruiz, A. Rodríguez-Fortea, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 24 (2003) 982.

[22] A.D. Becke, J. Chem. Phys. 98 (1993).

[23] E. Ruiz, S. Alvarez, J. Cano, V. Polo, J. Chem. Phys. 123 (2005) 164110.

[24] F. Yan, Z. Chen, J. Phys. Chem. A104 (2000) 6295.

[25] J. Paulovic, F. Cimpoesu, M. Ferbinteanu, K. Hirao, J. Am. Chem. Soc. 126 (2004) 3321.

[26] K.G. Dyall, J.J. Faegri, Introduction to Relativistic Quantum Chemistry, Oxford Univesity Press, Oxford, 2007.

[27] C. van Wüllen, J. Comput. Chem. 20 (1999) 51.

[28] C. Chang, M. Pélissier, P. Durand, Phys. Scr. 34 (1986) 394.

[29] M. Douglas, N.M. Kroll, Ann. Phys. (NY) 82 (1974) 89.

[30] B.A. Hess, Phys. Rev. A32 (1985) 756.

[31] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, Inorg. Chem. 35 (1996) 2400.

[32] J. Autschbach, in: M. Kaupp, M. Bühl, V.G. Malkin (Eds.), Calculation of NMR and EPR Parameters, Wiley-VCH, Weinheim, 2004, p. 227.

[33] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.

[34] A.M. Atria, Y. Moreno, E. Spodine, M.T. Garland, R. Baggio, Inorg. Chim. Acta 335 (2002) 1.

[35] C. Benelli, A.J. Blake, P.E.Y. Milne, J.M. Rawson, R.E.P. Winpenny, Chem. Eur. J. 9 (1995) 414.

[36] S. Gao, O. Borgmeier, H. Lueken, Acta Phys. Polym. A90 (1996) 393.

[37] O. Margeat, P.G. Lacroix, J.P. Costes, B. Donnadieu, C. Lepetit, K. Nakatani, Inorg. Chem. 43 (2004) 4743.

[38] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, Inorg. Chem. 36 (1997) 930.

[39] M. Sasaki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, Y. Sadaoka, M. Ohba, H. Okawa, Chem. Lett. (1998) 911.

[40] M. Ryazanov, V. Nikiforov, F. Lloret, M. Julve, N. Kuzmina, A. Gleizes, Inorg. Chem. 41 (2002) 1816.

[41] C. Brewer, G. Brewer, W.R. Scheidt, M. Shang, E.E. Carpenter, Inorg. Chim. Acta 313 (2001) 65.

[42] M.L. Kahn, T.M. Rajendiran, Y. Jeannin, C. Mathoniere, O. Kahn, C.R. Acad. Sci., Ser. IIc. Chim. 3 (2000) 131.

[43] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, Inorg. Chem. 36 (1997) 3429.

[44] J.-P. Costes, F. Dahan, G. Novitchi, V. Arion, S. Shova, J. Lipkowski, Eur. J. Inorg. Chem. (2004) 1530.

[45] G. Novitchi, J.-P. Costes, B. Donnadieu, Eur. J. Inorg. Chem. (2004) 1808.

[46] H. Kara, Y. Elerman, K. Prout, Z. Naturforsch., B: Chem. Sci. 55 (2000) 1131.

[47] C.T. Zeyrek, A. Elmali, Y. Elerman, J. Mol. Struct. 740 (2005) 47.

[48] A. Elmali, Y. Elerman, Z. Naturforsch., B: Chem. Sci. 59 (2004) 535.

[49] S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, Inorg. Chem. 44 (2005) 3270.

[50] S. Mohanta, H.-H. Lin, C.-J. Lee, H.-H. Wei, Inorg. Chem. Commun. 5 (2002) 585.

[51] R. Koner, G.-H. Lee, Y. Wang, H.-H. Wei, S. Mohanta, Eur. J. Inorg. Chem. (2005) 1500.

[52] C. Benelli, A. Caneschi, A.C. Fabretti, D. Gatteschi, L. Pardi, Inorg. Chem. 29 (1990) 4153.

[53] C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, L. Pardi, Inorg. Chem. 29 (1990) 1750.

[54] C. Blanchet-Boiteux, J.M. Mouesca, Theor. Chem. Acc. 104 (2000) 257.

[55] C. Desplanches, E. Ruiz, A. Rodríguez-Fortea, S. Alvarez, J. Am. Chem. Soc. 124 (2002) 5197.

[56] O. Kahn, B. Briat, J. Chem. Soc. Trans. 72 (1976) 268.

[57] O. Kahn, B. Briat, J. Chem. Soc. Trans. 72 (1976) 1441.

[58] J. Cano, E. Ruiz, S. Alvarez, M. Verdaguer, Comments Inorg. Chem. 20 (1998) 27.

[59] E. Ruiz, J. Cirera, S. Alvarez, Coord. Chem. Rev. 249 (2005) 2649.

[60] E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, in: J.S. Miller, M. Drillon (Eds.), Magnetism: Molecules to Materials, Wiley-VCH, Weinheim, 2001, p. 227.

[61] E. Ruiz, A. Rodríguez-Fortea, J. Tercero, T. Cauchy, C. Massobrio, J. Chem. Phys. 123 (2005) 074102.

[62] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, H. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 (Revision D.1), Gaussian, Inc., Pittsburgh, PA, 2003.

[63] F. Neese, ORCA 2.6, Bonn, 2007.

[64] A. Schaefer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.

[65] T. Nakajima, K. Hirao, J. Chem. Phys. 116 (2002) 8270.

[66] M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 90 (1981) 1730.