



Theoretical studies on {3d-Gd} and {3d-Gd-3d} complexes: Effect of metal substitution on the effective exchange interaction

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ABSTRACT

Series of DFT calculations on [L^INi(H₂O)₂Gd(NO₃)₃] (**1**) and their transition metal substituted models {Cr^{III}Gd^{III}}, {Fe^{II}Gd^{III}}, {Mn^{II}Gd^{III}} and {Cu^{II}Gd^{III}} have been performed to probe the electronic effects of the metal substitution on the sign and strength of magnetic coupling. Our results unfold an interesting observation that the strength of the exchange is related to the d-orbital occupancy with occupancy on the e_g orbitals resulting in stronger ferromagnetic exchange while progressively filling the t_{2g} orbitals leads to a reduction in the computed *J* values. Further, we extend our studies to the trinuclear {3d-Ln-3d} [L²M₂Ln][ClO₄] (LH₃ = (S)P[N(Me)N = CH-C₆H₃-2-OH-3-OMe]₃) (here M = Cu²⁺, Ni²⁺ and Mn²⁺ and Ln = Gd^{III} and La^{III}) complexes possessing phosphorus, salicylideneaminoxy and Schiff base supported ligands to corroborate our findings in dinuclear models. By computing the nearest neighbor and next-nearest neighbor interactions in all three complexes, our studies reveal that the observation of strong exchange with e_g occupancy is preserved also in the trinuclear complexes. This will have implications in the area of molecular coolants where Cu^{II} and Gd^{III} are the preferred choice as they inherit no/negligible anisotropy, but our finding suggests that Cu^{II} invariably also offers strong exchange interaction – a parameter unsuitable for ideal molecular coolants. Metals ions such as Mn^{II} and Cr^{III} are perhaps better choice for molecular refrigeration as they possess large spin values, negligible anisotropy and mediate relatively a weak magnetic exchange interaction.

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1. Introduction

Molecule based magnets are gaining attention in recent years as potential applications ranging from high-density information storage devices [1], solid state Q-bits in the quantum computing [2] to magnetic refrigerants are proposed for this type of molecules [3]. Molecules which show slow relaxation of magnetization in the absence of magnetic field are called as single molecule magnets (SMMs). Enhancing the energy barrier in SMMs which is related to the ground state *S* and anisotropy *D* (zero-field splitting) is a challenging task and many synthetic strategies have been proposed over the years to achieve this target. One of the attractive strategies is to synthesise heterometallic {3d-4f} complexes as they offer large *S* as well as anisotropy. The interest in the heterometallic {3d-4f} complexes is due to the work of Gatteschi and co-workers [4] where the {CuGd} complexes have been synthesized and the magnetic properties investigated. Subsequent synthesis of similar {CuGd} complexes and the observation that all those

complexes exhibit ferromagnetic coupling has led to the suggestion of an intrinsic ferromagnetic coupling for the {3d-4f} pair with a consequent increase in the *S* value. Costes et al. on the other hand over the years reported numerous {3d-4f} dinuclear and polynuclear complexes and have made significant contribution to the synthesis and characterization of {3d-4f} complexes [5].

Since anisotropy is a prerequisite for SMMs, anisotropic ions such as Dy^{III}, Er^{III} and Tb^{III} are ideal candidates while Gd^{III} is generally isotropic [6] and it finds its applications in magnetic refrigeration. Despite Gd^{III} being isotropic, there are some instances where Gd^{III} complexes have been found to be superior SMMs over their anisotropic counter parts [7]. The {3d-Gd^{III}} complexes are particularly attractive in the area of molecular coolants as these molecules yield very large *S* value and possess negligible anisotropy – a necessary prerequisite for molecular coolants. Besides these two parameters, weak magnetic exchange between the metal ions and a large metal:non-metal ratio are required to achieve new generation refrigeration molecules [7,8]. These prerequisites ideally suit Gd^{III} complexes and its heterometallic {3d-Gd^{III}} analogues. The molecular refrigeration demands a large Magnetic Calorie Effect (MCE) which in turn is related to the magnetic entropy change (ΔS_m) [8]. The magnetic exchange interaction plays a pivotal role in

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the determination of ΔS_m values and understanding the mechanism of magnetic coupling is essential for future success. Theoretical methods, DFT for {3d-Gd} and CASSCF for anisotropic lanthanide ions have made significant advancement in this regard [9]. Our group in recent years has developed interest in computing magnetic exchange interaction in {3d-Gd} pairs and has established the mechanism of coupling and also has developed magneto-structural correlations for {CuGd}, {NiGd}, {VGd} and {radical-Gd} pairs [10a–d].

Recently Brechin and co-workers reported a family of isostructural {Gd₄M₈} clusters (where M = Zn, Ni and Cu) and have demonstrated that the metal substitution indeed affects the MCE properties as the magnetic exchange interactions J varies as Cu^{II} and Ni^{II} ions are substituted in the place of diamagnetic Zn^{II} ions [11]. Although the mechanism of coupling for the {3d-Gd} pair has been established, the reasons for the variation of magnetic coupling vis-à-vis the nature of the 3d metal ion ranging from Cr^{III} to Cu^{II} is not clearly established. Additionally, in polynuclear complexes, apart from near-neighbor {3d–4f} exchange, the next-nearest-neighbor {3d–3d} or {4f–4f} interactions are also present [12]. These interactions, in some instances, determine the ground state and in other cases compete with near-neighbor interactions. Determining the sign as well as the of strength of the next-nearest-neighbor interaction is a challenging task experimentally as this might lead to over parameterization and for this reason this interaction is generally ignored. Consequently, theoretical estimations of these interactions are important. Accordingly, we have performed density functional calculations on a set of dinuclear {3d-Gd} and trinuclear {3d-Gd-3d} complexes (3d = Cr^{III}, Fe^{II}, Mn^{II}, Ni^{II} and Cu^{II}) to estimate the near neighbor as well the next-nearest-neighbor magnetic exchange interactions in order to understand (i) the role of metal substitution on magnetic exchange and (ii) how the sign and strength of the 1,3 interaction varies with different transition metal ions. These results are discussed herein.

2. Computational details

The broken symmetry (BS) method has a proven record of yielding a good numerical estimate of J constants for a variety of complexes [13]. A detailed technical discussion on computational details on the evaluation of J values using broken symmetry approach on dinuclear as well as trinuclear complexes can be found elsewhere [13e,14]. Here, we have performed our calculations using GAUSSIAN 09 suite of programs [15]. We have employed a hybrid B3LYP functional [16] along with a double-zeta quality basis set employing Cundari-Stevens (CS) relativistic effective core potential on the Gd atom [17] and LanL2DZ ECP basis set on Ni [18] with an all electron 6-31G basis set [19] for the rest of the atoms. A comprehensive method assessment performed earlier on {Cu-Gd} complexes by us, reveal that this combination yields a good estimate of the J constants [10a].

For the trinuclear complexes the following exchange Hamiltonian has been used,

$$\hat{H} = -J_1 \cdot S_{3d_1} \cdot S_{Gd} - J_2 \cdot S_{3d_2} \cdot S_{Gd} - J_3 \cdot S_{3d_1} \cdot S_{3d_2}$$

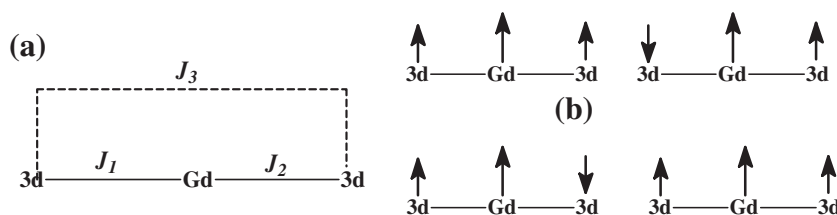
The magnetic exchange interaction in the trinuclear complexes were extracted using pair-wise interaction model [12] where four spin configurations were computed to extract three different exchange interactions J_1 – J_3 (see Scheme 1a). The computed configurations are shown in Scheme 1b. The energy differences between the spin configurations were equated to the corresponding exchange interactions from which all three J values were extracted.

3. Results and discussion

3.1. Studies on dinuclear {3d-Gd} complexes

There are numerous {3d-Gd} dimers reported in the literature with 3d metal ion being Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Cr^{III} and V^{IV} [5a,20]. In these cases as the molecular structure of each complex is distinctly different from each other owing to the presence of varying bridging ligands and consequently different structural parameters, computing the various J s involved on such a structurally diverse family is unlikely to reveal the effect of metal ion substitution. For this reason, we have calculated the exchange coupling [10b] on the full structure of [L¹Ni(H₂O)₂Gd(NO₃)₃] (**1**) (L¹ = [2,2'-(2,2-dimethyl-1,3-propanediylbis (nitriolomethylidyne))bis(6-methoxyphenolato)(2-)] nickel(II)) (see Fig. 1). Besides, a detailed analysis and the mechanism of coupling for **1** has been established earlier by us [10b] and therefore Ni²⁺ ion in the above dimer has been replaced to create models with a series of 3d metal ions [Cr^{III}(**1a**), Mn^{II}(**1b**), Fe^{II}(**1c**), Cu^{II} (**1d**)]. Analyzing the magnitude of computed J s in these model complexes are straight forward. Although the coordination environments are slightly disturbed while modeling, the main structural features which affect the J values are preserved throughout. The structures of the studied models are shown in Fig. SF1 of ESI. The complex **1** possesses two μ -alkoxo bridges with the M–O–M angles of 106.5° and 107.9° while the M–O–Gd–M dihedral angle is determined to be 2.8°. The computed magnetic exchange for **1** is +2.2 cm^{−1} and this is consistent with the experimental estimate of +3.6 cm^{−1}. Table 1 lists the computed J values upon metal substitution along with the spin density value at the metal and the bridging oxygen atoms.

In all cases, the computed J values are positive indicating that for this {M(μ -OR)₂Gd} (where R = alkyl or aromatic groups) structural topology the magnetic exchange is likely to be ferromagnetic. This correlates well with the ferromagnetic J reported for the first row transition metal complexes [5a,20]. The magneto-structural correlations obtained from our study, however, reveal that when there is a large deviation in the structural parameters such as M–O–Gd angles or M–O–Gd–O dihedral angles, the sign can be switched to negative. The strongest exchange was obtained in the case of {CuGd} and this is consistent with the fact that this pair still holds the strongest exchange observed for any {3d-Gd} pair in the literature [21]. In {CuGd} pair, the unpaired electron resides in $d_{x^2-y^2}$ orbital and as we progressively populate other d-orbitals with unpaired spins, the net exchange decreases. The {NiGd} and {CuGd} pairs, possessing unpaired electrons only in e_g -like orbitals,



Scheme 1. (a) Different coupling constants between metal ions (b) high-spin and broken symmetry configurations.

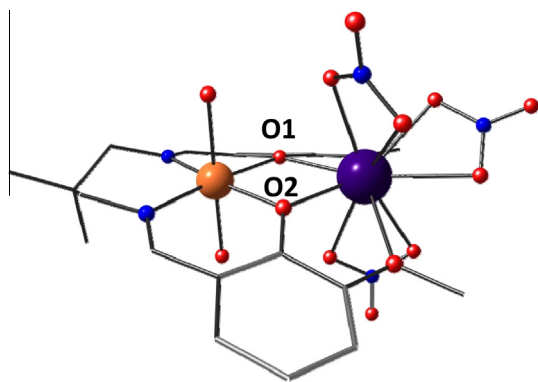


Fig. 1. Crystal structure of complex **1**. Gd^{III}-violet, Ni^{II}-orange, O-red and N-blue. (Color online.)

Table 1

Computed spin densities of 3d metal ions and the Gd^{III} ions with bridging oxygen atoms. (see Fig. 1 for labeling).

Model complexes	<i>J</i> values (cm ⁻¹)		Spin densities			
	<i>J</i> _{DFT}	<i>J</i> [#] _{Exp}	Gd	M	O1	O2
{Cr–Gd} 1a	0.12	–0.36 ^A	7.032	3.061	–0.004	–0.011
{Mn–Gd} 1b	1.2	–1.7 ^B	7.034	4.718	0.023	0.017
{Fe–Gd} 1c	1.4	0.2–0.5 ^C	7.031	3.804	0.049	0.043
{Ni–Gd} 1	2.2	–0.2–3.6 ^D	7.029	1.709	0.045	0.041
{Cu–Gd} 1d	5.8	–0.49–7 ^E	7.029	0.689	0.063	0.059

(#) Experimentally reported *J* values for a similar structures are given for comparison Refs.: (A) – [20a]; (B) – [20c]; (C) – [5c,e]; (D) – [5f,20c,21]; (E) – [5a,g,h].

possess the strongest exchange among the series while the presence of unpaired electrons on the *t*_{2g}-like orbitals effectively reduces the magnitude of the interaction. This is also supported by the experimental *J*s reported for {3d–Gd} pairs possessing a similar structural core to the one computed here [5,20].

For the {3d–Gd} pair, there are essentially three contributions to the net exchange. The ferromagnetic contributions arise (i) from

Table 2

B3LYP computed *J*_s along with experimental values for complexes **2–6**. All the values are given in cm⁻¹.

Complexes	<i>J</i> _{DFT}			<i>J</i> _{exp}		
	<i>J</i> ₁	<i>J</i> ₂	<i>J</i> ₃	<i>J</i> ₁	<i>J</i> ₂	<i>J</i> ₃
{Ni–Gd–Ni} (2)	0.68	0.68	–0.12	0.750	0.750	–
{Ni–La–Ni} (3)	–	–	–0.15	–	–	–0.34
{Mn–Gd–Mn} (4)	0.16	0.16	–0.02	0.08*	0.08*	–
{Mn–La–Mn} (5)	–	–	–0.02	–	–	–
{Cu–Gd–Cu} (6)	1.06	1.90	0.72	5.00	5.00	0.0
{Fe–Gd–Fe} (7)	1.27	1.27	–	1.38	1.38	–

Values are given for different Mn–Gd–Mn complex possessing similar structural motif see Ref. [5d] for details.

the interaction of the 3d magnetic orbitals with the empty 5d orbitals of Gd^{III} orbitals (ii) from the orbital orthogonality between 3d and 4f magnetic orbitals; the antiferromagnetic contributions solely arise due to the (iii) overlap between a pair of {3d–4f} magnetic orbitals. The presence of unpaired electrons in e_g-like orbitals is likely to have a larger contributions from point (i) mentioned above while increasing the number of unpaired electrons in the systems is likely to increase due to point (iii) mentioned above. Thus for Cr^{III} possessing unpaired electrons only in *t*_{2g}-like orbital, ferromagnetic and antiferromagnetic contributions are of similar in strength and this lead to an extremely weak ferromagnetic exchange for this pair.

As evident from Table 1 and Fig. 2, spin density of Gd^{III} ions in all the model dimers is found to be nearly 7.02 revealing intricate information that there is no significant alteration in the occupation of 4f orbitals i.e. the 4f orbitals are inert and are not influenced by the metal substitution. While for transition metal ions, except for Cr^{III}, all the other metal ions have less than what is expected from the number of unpaired electrons. This is due to the fact that Cr^{III} promotes polarization while the other metal ions possessing unpaired spins in e_g-like orbitals promote spin delocalization. This is very well reflected in the computed spin densities on the bridging oxygen. The oxygen atoms of the {CuGd} complex possess the largest spin density and this diminishes as we go up in the Table 2. This is also correlated with the computed *J* values.

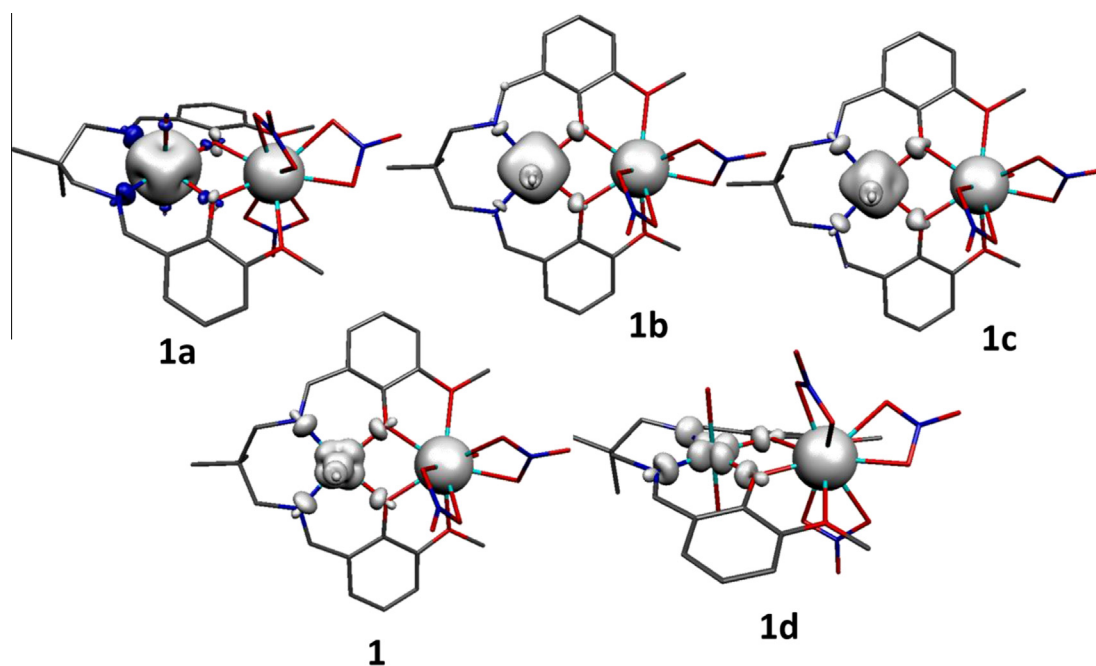


Fig. 2. DFT computed spin density plots for complexes **1** to **1d**.

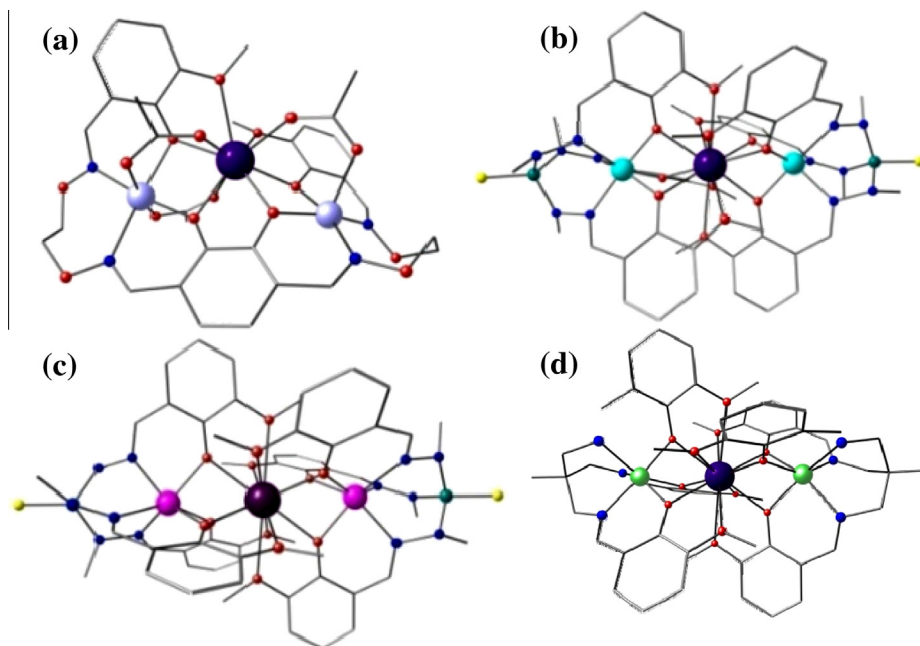


Fig. 3. Structures of the trinuclear M–Gd–M complexes [M = (a)–Cu, (b)–Ni, (c)–Mn, (d)–Fe].

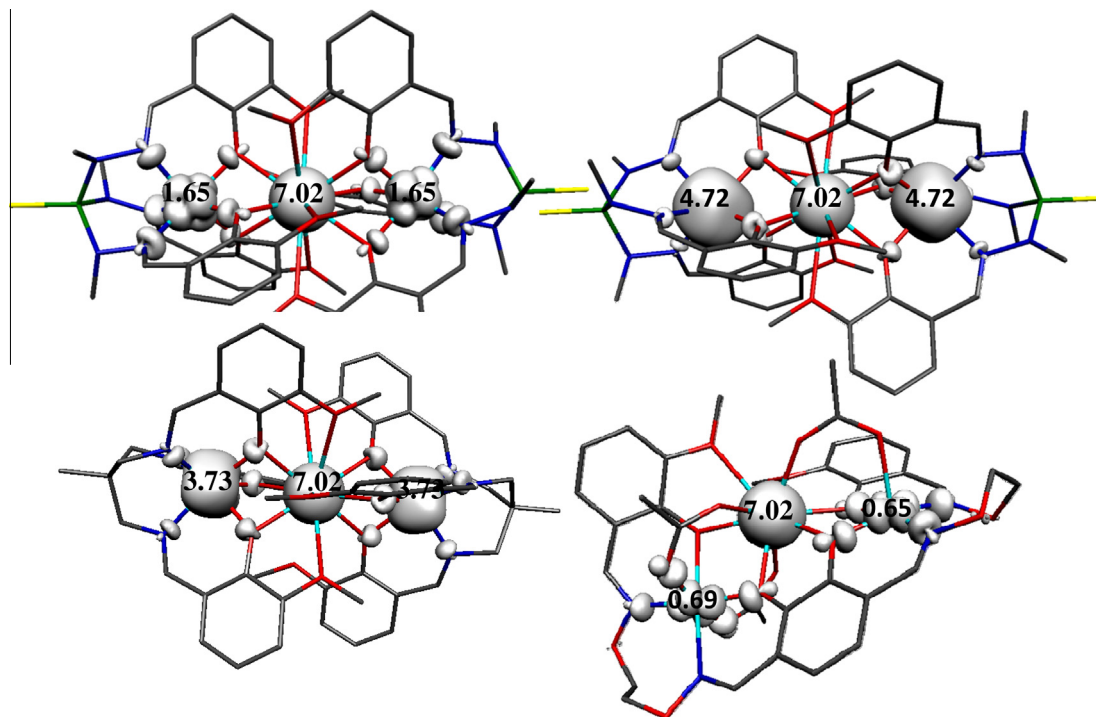


Fig. 4. DFT computed spin density plot of **2**, **4**, **6**, and **7**. The isodensity surface represented corresponds to a value of $0.007 e^-/\text{bohr}^3$. The white and blue region indicates positive and negative densities. (Color online.)

3.2. Studies on trinuclear {3d–Gd–3d} complexes (3d = Mn²⁺, Co²⁺, Ni²⁺, Fe²⁺, Cu²⁺)

To probe the trends obtained in 3d/4f dinuclear systems further and to analyze the role of 1,3 interactions calculations have been performed on a series of trinuclear {3d–Gd–3d} complexes [L²Ni₂Gd][ClO₄] (**2**) (LH₃ = (S)P[N(Me)N = CH–C₆H₃–2–OH–3–OMe]₃), [L²Ni₂La][ClO₄] (**3**), [L²Mn₂Gd]⁺ (**4**), [L₂Mn₂La]⁺ (**5**), [L³Cu₂Gd(OAc)₃] (**6**) (H₄L³ = dimeric units of H₂salamo where Salamo = 1,2-bis(sali-

cylideneaminoxy)ethane), [L⁴FeGdFeL⁴][ClO₄] (H₃L⁴ = N,N',N''-tris-(2-hydroxy-3-methoxybenzilidene)-2-(aminomethyl)-2-methyl-1,3-propanediamine) (see Fig. 3) [5d,22]. Except complex **6**, all other complexes are nearly isostructural. Important structural features of complexes **2**, **4**, **6** and **7** are summarized in the Table ST1 of ESI.

The computed *J* values for all the complexes are summarized in Table 2. In general, there is a good agreement between the experimental and the DFT calculated values. For all the complexes *J*₁ and

J_2 (where applicable) interactions are found to be ferromagnetic while the J_3 interaction is found to be antiferromagnetic except in the case of complex **6**. The strength of J_1 and J_2 interactions are also almost same in all the complexes except in complex **6**. In case of complex **6**, the two {CuGd} and {GdCu} units are non-equivalent as additional μ_2 -acetate has been found on one of the moiety and this is nicely reflected in the computed J values. Although the J_1 and J_2 strengths (assumed to be $J_1 = J_2$ in fitting) deviate from experiments, our set of J values yield a reasonable fit to the experimental curve (see Fig. SF2 of ESI). These explicit calculations on the trimeric models support the predicted trend on the dimeric structure although there are some slight deviation due to the difference in the structural parameter within the set of structures studied (Table ST1 of ESI). This suggests that our trend is likely to be generic and can be easily extended to polynuclear complexes.

The J_3 interaction is experimentally hard to determine in the Gd^{III} analogues and therefore diamagnetic La^{III} substituted complexes (complex **3**) has been used to extract the 1,3 next-nearest neighbor J_3 interactions. Our test set calculations on trinuclear complexes containing two La^{III} ions has been performed and this has been specifically done to extract the 1,3 interaction. Unlike the J_1 and J_2 interactions, the J_3 interaction sign and the strength varies across the series with a ferromagnetic J_3 for Cu(II) and weak and non-negligible antiferromagnetic $[10b]J_3$ for Ni(II) and antiferromagnetic and nearly negligible J_3 for Mn(II). The 1,3 interaction is generally small and negligible in transition metal complexes, however in lanthanides, this interaction is important for two reasons (i) the 1,2 interactions are generally weak and therefore even small 1,3 interactions cannot be neglected (ii) mechanism of exchange mediates via empty 5d/6s orbitals of Gd^{III} ions and participation of these diffuse orbitals in the 1,3 interaction lead to relatively large values. Although for the 1,2 interactions the Gd^{III} 5d orbitals are found to play a prominent role, the role of 5d/6s orbitals on the 1,3 interactions are not fully understood and this will be our target of study in the future. Obtaining an antiferromagnetic 1,3 interaction is also a good recipe for molecular coolants as this decrease the gap between ground state and excited state and thus lead to eventual increase in the ΔS_m values.

The computed spin density plots for **2**, **4**, **6** and **7** are shown in Fig. 4. In general, the spin densities of the 3d-metal ions are delocalized to the coordinating atoms while the Gd^{III} exhibits polarization where it gains significant densities from the coordinating atoms. Similar to dinuclear cases, the Gd^{III} has a spin density of 7.02 while the magnitude and shape of the spin densities on the 3d element varies. Spin densities on the bridging oxygen atoms are found to be related to the computed J values, with stronger ferromagnetic exchange with larger spin densities on oxygen atoms, for example, in the case of complex **6**.

4. Conclusions

Mechanistically well understood {NiGd} dimer complex has been chosen and the Ni²⁺ ion in the dimer was replaced with a series of first row transition metal ions such as Cr^{III}, Fe^{II}, Mn^{II}, and Cu^{II} to assess the nature of exchange interaction upon metal substitution. Among the isomorphous model complexes, the {CuGd} dimer is found to show strong ferromagnetic exchange and this is found to electronically correlate to the d-orbital occupation. Unpaired spins in e_g orbitals yields stronger ferromagnetic interaction compared to unpaired spins in t_{2g} orbital. As the e_g orbitals promote spin delocalization, a greater extent of spin densities are transferred to 5d orbital of Gd^{III} and this in turn results in stronger ferromagnetic coupling. Our studies suggest that metal ions possessing unpaired electrons in t_{2g} orbitals are better candidates

for molecular refrigeration as this application demands very weak intramolecular exchange. Studies on trimeric {3d-Gd-3d} complexes reveals that in all the cases studied the 1,2 interaction is found to be ferromagnetic and this corroborates with our findings on the dimeric models. The sign of the 1,3 interaction however is found to vary from ferromagnetic interaction to antiferromagnetic interaction for different metal ions. This is likely to correlate to the 3d-Gd-3d angles and efforts to understand this behavior is underway in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2013.02.037>.

References

- [1] (a) S.-D. Jiang, B.-W. Wang, G. Su, Z.-M. Wang, S. Gao, *Angew. Chem., Int. Ed.* 49 (2010) 7448; (b) M.A. Aldamen, J.M. Clemente-Juan, E. Coronado, C. Martil-Gastaldo, A. Gaita-Arinflo, *J. Am. Chem. Soc.* 130 (2008) 8874; (c) N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, *J. Phys. Chem. B* 108 (2004) 11265; (d) P.-H. Lin, T.J. Burchell, L. Ungur, L.F. Chibotaru, W. Wernsdorfer, M. Murugesu, *Angew. Chem., Int. Ed.* 48 (2009) 9489.
- [2] (a) M.N. Leuenberger, D. Loss, *Nature* 410 (2001) 789; (b) S. Hill, R.S. Edwards, N. Aliaga-Alcalde, G. Christou, *Science* 302 (2003) 1015; (c) R.E.P. Winpenny, *Angew. Chem., Int. Ed.* 47 (2008) 7992; (d) F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco, R.E.P. Winpenny, *Phys. Rev. Lett.* 94 (2005) 207208.
- [3] (a) M. Evangelisti, O. Roubeau, E. Palacios, A. Camon, T.N. Hooper, E.K. Brechin, J.J. Alonso, *Angew. Chem., Int. Ed.* 50 (2011) 6606; (b) M. Affronte, A. Ghirri, S. Carretta, G. Amoretti, S. Piligkos, G.A. Timco, R.E.P. Winpenny, *Appl. Phys. Lett.* 84 (2004) 3468.
- [4] (a) A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* 107 (1985) 8128; (b) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, L. Pardi, *Inorg. Chem.* 29 (1990) 1750.
- [5] (a) J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, *Inorg. Chem.* 39 (2000) 169; (b) J.P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* 39 (2000) 5994; (c) J.-P. Costes, F. Dahan, J. Garcia-Tojal, *Chem. Eur. J.* 8 (2002) 5430; (d) T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Brefuel, J.-P. Tuchagues, L. Vendier, W. Wernsdorfer, *Inorg. Chem.* 49 (2010) 9125; (e) J.-P. Costes, J.M. Clemente-Juan, F. Dahan, F. Dumestre, J.-P. Tuchagues, *Inorg. Chem.* 41 (2002) 2886; (f) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* 36 (1997) 4284; (g) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* 35 (1996) 2400.
- [6] M.J. Martinez-Perez, S. Cardona-Serra, C. Schlegel, F. Moro, P.J. Alonso, H. Prima-Garcia, J.M. Clemente-Juan, M. Evangelisti, A. Gaita-Arino, J. Sese, J. van Slageren, E. Coronado, F. Luis, *Phys. Rev. Lett.* 108 (2012) 1759.
- [7] A. Borta, E. Jeanneau, Y. Chumakov, D. Luneau, L. Ungur, L.F. Chibotaru, W. Wernsdorfer, *New J. Chem.* 35 (2011) 1270.
- [8] (a) C. Zimm, A. Jastrab, A. Sternberg, V.K. Pecharsky Jr., K. Gschneidner, M. Osborne, I. Anderson, *Adv. Cryog. Eng.* 43 (1998) 1759; (b) V.K. Pecharsky Jr., K.A. Gschneidner, *J. Magn. Magn. Mater.* 200 (1999) 44; (c) K.A. Gschneidner Jr., V. Pecharsky, *Int. J. Refrig.* 31 (2008) 945; (d) M. Manoli, R.D.L. Johnstone, S. Parsons, M. Murrice, M. Affronte, M. Evangelisti, E.K. Brechin, *Angew. Chem., Int. Ed.* 46 (2007) 4456.
- [9] (a) E. Cremades, S. Gomez-Coca, D. Aravena, S. Alvarez, E. Ruiz, *J. Am. Chem. Soc.* 134 (2012) 10532; (b) S.K. Langley, L. Ungur, N.F. Chilton, B. Moubaraki, L.F. Chibotaru, K.S. Murray, *Chem. Eur. J.* 17 (2011) 9209; (c) J. Cirera, E. Ruiz, *C. R. Chim.* 11 (2008) 1227.
- [10] (a) G. Rajaraman, F. Totti, A. Bencini, A. Caneschi, R. Sessoli, D. Gatteschi, *Dalton Trans.* (2009) 3153; (b) S.K. Singh, N.K. Tibrewal, G. Rajaraman, *Dalton Trans.* 40 (2011) 10897; (c) T. Rajeshkumar, G. Rajaraman, *Chem. Commun.* 48 (2012) 7856;

- (d) S.K. Singh, G. Rajaraman, Dalton Trans. 42 (2013) 3623;
(e) T. Rajeshkumar, S.K. Singh, G. Rajaraman, Polyhedron, 2013, <http://dx.doi.org/10.1016/j.poly.2012.06.017>.
- [11] T.N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti, E.K. Brechin, Angew. Chem., Int. Ed. 51 (2012) 4633.
- [12] (a) C. Lescop, E. Belorizky, D. Luneau, P. Rey, Inorg. Chem. 41 (2002) 3375;
(b) Z.-G. Gu, Y.-F. Xu, L.-C. Kang, Y.-Z. Li, J.-L. Zuo, X.-Z. You, Inorg. Chem. 48 (2009) 5073.
- [13] (a) S. Piligkos, G. Rajaraman, M. Soler, N. Kirchner, J. van Slagereen, R. Bircher, S. Parsons, H.-U. Guedel, J. Kortus, W. Wernsdorfer, G. Christou, E.K. Brechin, J. Am. Chem. Soc. 127 (2005) 5572;
(b) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 20 (1999) 1391;
(c) E. Ruiz, A. Rodriguez-Fortea, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 24 (2003) 982;
(d) G. Rajaraman, J. Cano, E.K. Brechin, E.J.L. McInnes, Chem. Commun. (2004) 1476;
(e) P. Christian, G. Rajaraman, A. Harrison, M. Helliwell, J.J.W. McDouall, J. Raftery, R.E.P. Winpenny, Dalton Trans. (2004) 2550.
- [14] G. Rajaraman, M. Murugesu, E.C. Sanudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S.J. Teat, G. Christou, E.K. Brechin, J. Am. Chem. Soc. 126 (2004) 15445.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09 R.A.01, Gaussian, Inc., Wallingford, CT, 2009.
- [16] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [17] T.R. Cundari, W.J. Stevens, J. Chem. Phys. 98 (1993) 5555.
- [18] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270;
(b) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299;
(c) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 284.
- [19] (a) R. Ditchfield, W.J. Herre, J.A. Pople, J. Chem. Phys. 54 (1971) 724;
(b) V.A. Rassolov, M.A. Ratner, J.A. Pople, P.C. Redfern, L.A. Curtiss, J. Comput. Chem. 22 (2001) 976.
- [20] (a) H.-Z. Kou, S. Gao, C.-H. Li, D.-Z. Liao, B.-C. Zhou, R.-J. Wang, Y. Li, Inorg. Chem. 41 (2002) 4756;
(b) A.N. Georgopoulou, R. Adam, C.P. Raptopoulou, V. Psycharis, R. Ballesteros, B. Abarcab, A.K. Boudalis, Dalton Trans. 40 (2011) 8199;
(c) A.N. Georgopoulou, R. Adam, C.P. Raptopoulou, V. Psycharis, R. Ballesteros, B. Abarcab, A.K. Boudalis, Dalton Trans. 39 (2010) 5020.
- [21] (a) J.-H. Wang, P.-F. Yan, G.-M. Li, J.-W. Zhang, P. Chen, M. Suda, Y. Einaga, Inorg. Chim. Acta 363 (2010) 3706;
(b) T. Yamaguchi, Y. Sunatsuki, M. Kojima, H. Akashi, M. Tsuchimoto, N. Re, S. Osa, N. Matsumoto, Chem. Commun. 148 (2004);
(c) Q.-Y. Chen, Q.-H. Luo, L.-M. Zheng, Z.-L. Wang, J.-T. Chen, Inorg. Chem. 41 (2002) 605.
- [22] (a) V. Chandrasekhar, B.M. Pandian, R. Boomishankar, A. Steiner, J.J. Vittal, A. Hourri, R. Clerac, Inorg. Chem. 47 (2008) 4918;
(b) V. Chandrasekhar, B.M. Pandian, R. Boomishankar, A. Steiner, R. Clerac, Dalton Trans. (2008) 5143;
(c) S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, Inorg. Chem. 44 (2005) 3270.