Electronic Supplementary Material for Dalton Transactions

Density functional studies on the exchange interaction of a dinuclear Gd(III)-Cu(II) Complex: Method assessment, magnetic coupling mechanism and magneto-structural correlations

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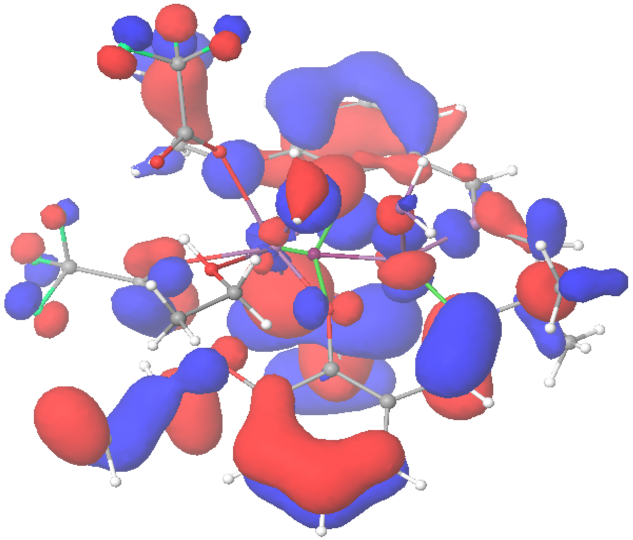
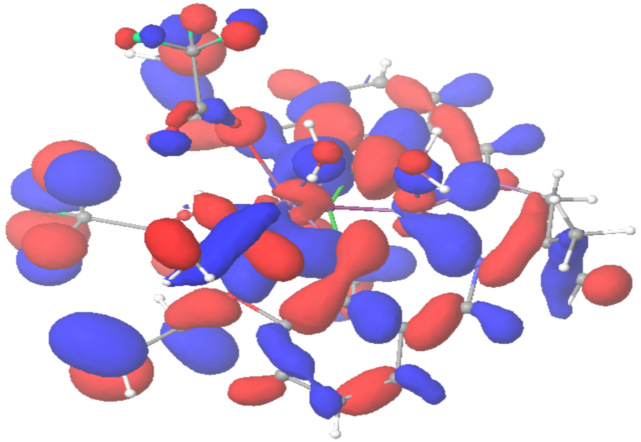
Supporting material:



Alpha 189th MO



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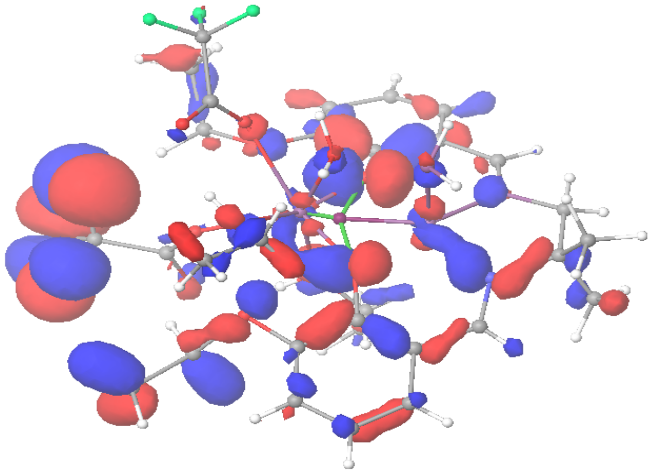

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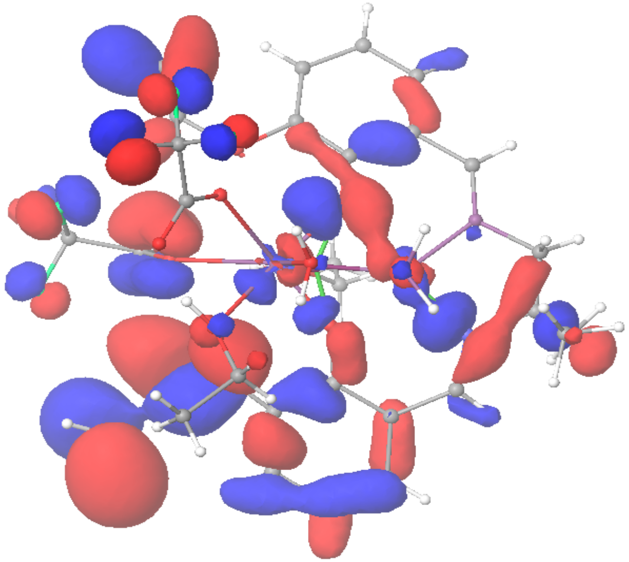

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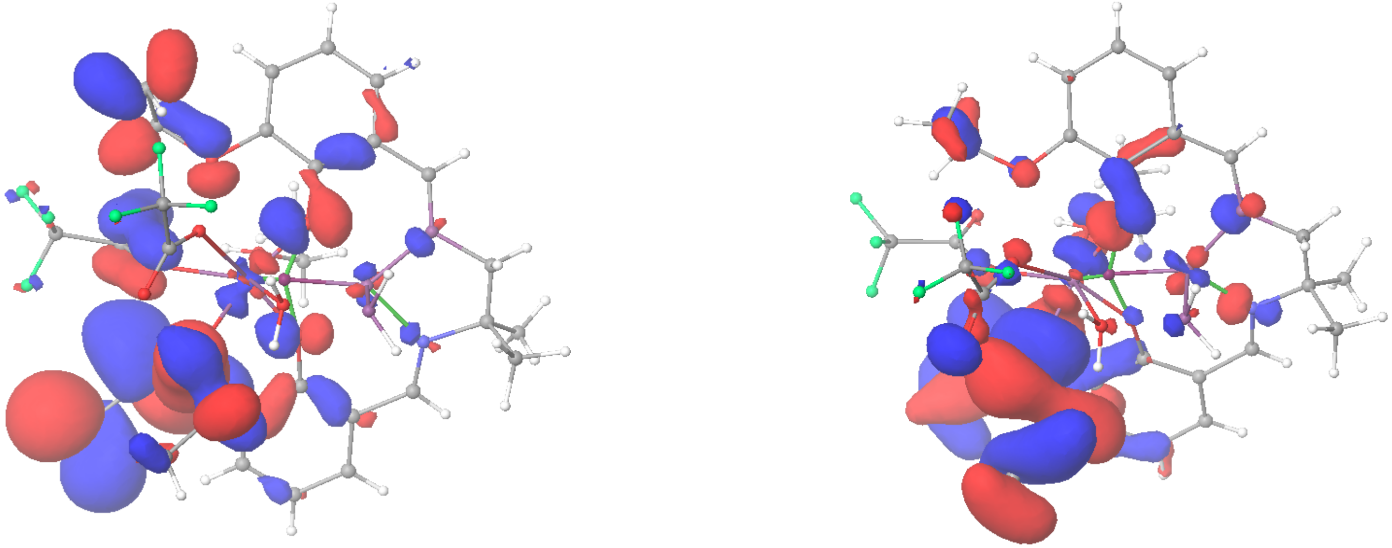
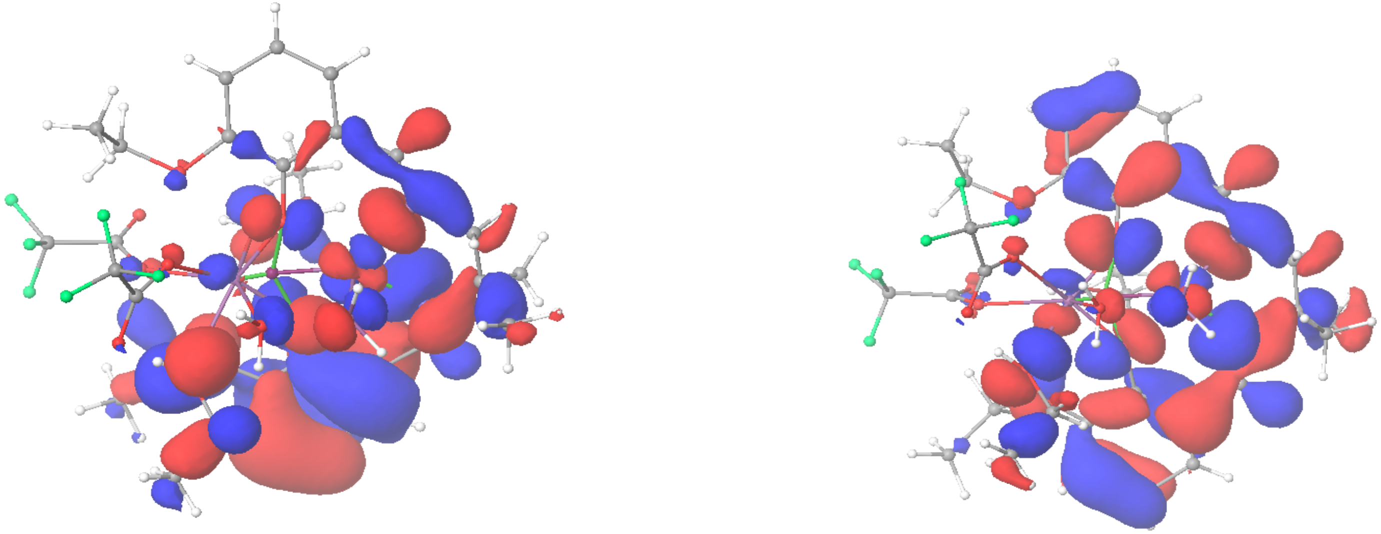


Alpha 197th MO

Alpha 200th MO



Alpha 204th MO

Alpha 205th MO

Figure S1. Selected alpha MOs of the model ***1c*** at an Gd-O-Cu angle of 90 deg having significant Cu(II) and Gd(III) character.

Table S1. Natural bond orbital coefficients of **1** on the S=4 state.

Occupancy (type)		Hybrid coefficients		
		p	d	f
1	0.02098 (RY*)	3.75	99.99	1.54
2	0.01879 (RY*)	7.65	99.99	8.05
3	0.01356 (RY*)	16.06	99.99	5.65
4	0.01277 (RY*)	3.06	99.99	1.34
5	0.00897 (RY*)	8.34	99.99	4.67

Table S2. Experimental *J* values for 26 different [GdCu] dinuclear complexes.

CSD code	Gd..Cu	Gd-O-Cu ang	O-Cu-O-Gd Dihedral	*J*	reference
AHICID	3.426	94.3085	27.27	-2.2	1
AWUQUE	3.443	103.56	16.609	-4.92	2
AXIGUJ	3.391	103.27	11.59	-4.42	3
BERPAQ	3.454	106.429	16.932	-5.5	4
CADLOJ	3.426	106.652	5.239	-6.94	5
EZAPAW	3.473	107.4225	10.208	-7.4	6
FAKLOT	3.454	106.9815	9.76	-8.5	7
GANFEH	3.433	103.738	17.353	-4.5	8
GANFIL	3.498	108.179	8.243	-7.6	8
JCQTEO	3.473	103.8685	16.462	-4.2	9
KEQRED	3.512	108.733	1.51	-10.1	10
KEZWES	3.414	103.435	1.1	-7.6	11
LOYTOI	3.400	105.168	3.705	-8.08	12
MIDHIQ	3.252	97.08	36.629	-1.91	13
NAMDIP	3.475	107.0195	11.107	-7.3	13
NEVHEB	3.484	107.7585	10.898	-7	14
NEVHIF	3.523	108.08	14.95	-4.8	14
OFELAM	3.288	97.48	26.568	-1.21	14
OFELEQ	3.274	96.3045	34.992	-1.47	15
OFELIU	3.288	97.3495	32.577	-1.25	16
QEMYAI	3.425	109.405	10.729	-5.6	16
RINQAG	3.230	95.033	39.632	-1.02	17
RINQIO	3.252	96.6635	32.185	-1.4	18
WIXYIL	3.224	97.0595	25.721	-4.33	19
XAYTIB	3.346	102.4415	17.708	-3.36	20
ZUVTIT	3.428	106.6195	11.687	-6.9	21

Discussion on chosen functionals: For the evaluation of suitable functional, as a GGA functional, we have tested BLYP[2223] and one of the functional in the new families of functionals developed by Handy and co-workers called HCTH407[2425]. As expected both pure functionals having no HF (Hartree-Fock) exchange overestimates the computed *J* values (See Table 1). As hybrid functionals we have employed the popular B3LYP, B3P86 where the only difference is on the non-local correlation part which is provided here by Perdew 86[26] instead of the LYP[23] correlation in B3LYP, X3LYP[27] functional developed by Xu and co-workers that has a modified exchange functional combined with the LYP correlation, the mPW1PW91 that uses the modified Perdew-Wang exchange and Perdew-Wang 91 correction[28], the B98 functional proposed by Becke[29] using the G2 test set to the fit the parameters, the B97-1[30] modification to the B97 of Becke by Hamprecht et al[30] and the SB98 functional[31] that can be considered as a meta-GGA extension of B98 functional. These entire set functional have varying percentage of HF exchange between 20 to 25 %. The computed *J* values with different hybrid functionals are very similar and are in good agreement with the experiment. We have also performed calculations on other hybrid functionals incorporating higher percent of HF exchange, namely the BHandH having 50% HF exchange and LYP correlation and BHandHLYP with modified exchange functional yield the *J* value with similar accuracy to hybrid functional but on the lower end. The computed spin density on the (Table 1) Gd(III) does not vary significantly across the column, however the spin density on the Cu(II) vary from 0.462 to 0.724 with different functionals. This is associated with the well-known problem of DFT where all the standard pure and hybrid functionals over-estimate the covalancy of Cu(II) and one should require higher percent HF exchange to obtain satisfactory bonding description for Cu(II) complexes[32]. To obtain unique and reliable methodology for the calculation of *J* for the molecules containing rare earth-radical or 3*d*-4*f* exchange, the standard hybrid functionals yields good numerical estimates of *J*. Although in the present case the "half-and-half" functional provide similar accuracy, this is possibly related to the presence of Cu(II).

References

1. F.Avecilla, C.Platas-Iglesias, R.Rodriguez-Cortinas, G.Guillemot, J.-C.G.Bunzli, C.D.Brondino, C.F.G.C.Geraldes, A.de Blas, T.Rodriguez-Blas, *J.Chem.Soc.,Dalton Trans.* 2002,4658
2. J.-P.Costes, F.Dahan, G.Novitchi, V.Arion, S.Shova, J.Lipkowski, *Eur.J.Inorg.* 2004, 1530.
3. G.Novitchi, S.Shova, A.Caneschi, J.-P.Costes, M.Gdaniec, N.Stanica, *Dalton Trans.*2004, 1194.
4. G.Novitchi, J.-P.Costes, B.Donnadieu, *Eur.J.Inorg.Chem.* , 2004, 1808.
5. J.-P.Costes, F.Dahan, *C.R. Acad.Sci.,Ser II:chim.*,2001, 97.
6. A.Elmali, Y.Elerman, *Z.Naturforsch.,B:Chem.Sci.* ,2004, 535.
7. J.-P.Costes, G.Novitchi, S.Shova, F.Dahan, B.Donnadieu, J.-P.Tuchagues, *Inorg.Chem.* 2004, 7792.
8. S.kine, T.Matsumoto, T.Taniguchi, T.Nabeshima, *Inorg.Chem.*, 2005, 3270.
9. M.Sasaki, H. Hoiruchi, M.Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, Y. Sodaoka, M. Ohba, H. Okawa, *Chem. Lett.*,1998, 911.
10. J.-P.Costes, F.Dahan, A.Dupuis, J.-P.Laurent, *New J.Chem.*, 1998,1525.
11. J.-P.Costes, F.Dahan, A.Dupuis, *Inorg.Chem.* , 2000, 165.
12. T.Hamamatsu, K.Yabe, M.Towatari, N.Matsumoto, N.Re, A.Pochaba, J.Mrozinski, *Bull.Chem.Soc.Jpn.*, 2007, 523.
13. S.Mohanta, Hsin-Huang Lin, Chin-Jhan Lee, Ho-Hsiang Wei, *Inorg.Chem.Commun.*, 2002, 585.
14. C.Brewer, G.Brewer, W.R.Scheidt, M.Shang, E.E.Carpenter, *Inorg.Chim.Acta* , 2001, 65.
15. J.-P.Costes, F.Dahan, A.Dupuis, J.-P.Laurent, *Inorg.Chem.*, 1997, 3429.
16. M.Ryazanov, V.Nikiforov, F.Lloret, M.Julve, N.Kuzmina, A.Gleizes, *Inorg.Chem.* 2002,1816.
17. H.Kara, Y.Elerman, K.Prout, *Z.Naturforsch.,B:Chem.Sci.*, 2000, 1131.
18. I.Ramade, O.Kahn, Y.Jeannin, F.Robert, *Inorg.Chem.*, 1997,930.
19. M.L.Kahn, T.M.Rajendiran, Y.Jeannin, C.Mathoniere, O.Kahn, *C.R.Acad.Sci.,Ser.IIc:Chim.* , 2000, 131.
20. Feng He, Ming-Liang Tong, Xiao-Ming Chen, *Inorg.Chem.* 2005, 8285.
21. J.-P.Costes, F.Dahan, A.Dupuis, J.-P.Laurent, *Inorg.Chem.*, 1996, 2400.
22. A. D. Becke, *Phys. Rev. A* **1998**, 38, 3098.
23. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
24. F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, *J. Chem.Phys.* **1998**, 109, 6264.
25. A. D. Boese, N. L. Doltsinis, N. C. Handy, and M. Sprick, *J. Chem. Phys.* **2000**, 112, 1670.
26. K. Burke, J. P. Perdew, and Y. Wang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, Ed. J. F. Dobson, G. Vignale, and M. P. Das (Plenum, **1998**).
27. X. Xu, W. A. Goddard III, *Proc. Natl. Acad. Sci.* **2004**,101 2673.
28. C. Adamo and V. Barone, *J. Chem. Phys.* **1998** 108, 664.
29. H. L. Schmider and A. D. Becke, *J. Chem. Phys.* **1998,** 108, 9624.
30. A. D. Becke, *J. Chem. Phys* **1997**, 107, 8554. F. A. Hamprecht, A. J. Cohen, D. J.

Tozer, and N. C. Handy, *J. Chem. Phys.* **1998** 109, 6264.

31. H. L. Schmider and A. D. Becke, *J. Chem. Phys.* **1998** 108, 9624.
32. M. Atanasov, P. Comba, B. Martin, V. Muller, G. Rajaraman, H. Rohwer, S. Wunderlich, *J. Comp. Chem.*, **2006**, 27, 1263