DOI: 10.1002/ejic.201100311

Antiferromagnetic Co–Gd Interactions in a Tetranuclear $[CoGd]_2$ Complex with Low-Spin Square-Planar Co Ions – Role of the Singly Occupied 3d Co Magnetic Orbital

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Keywords: Coordination compounds / Cobalt / Gadolinium / Magnetic properties / Lanthanides

A trianionic ligand H_3L [2-hydroxy-*N*-(2-{[(2-hydroxyphenyl)-methylene]amino}-2-methylpropyl)benzamide] with an inner N_2O_2 coordination site and an oxygen atom coming from an amide function not involved in this site yields a monoanionic LCo-pipH$^+$ complex, in which the Co^{II} ion is in a square-planar environment and a low-spin state $S = 1/2$. Further reaction with $GdCl_3·6H_2O$ and tetramethylheptanedione (Hthd) yields a dinuclear Co–Gd complex that self-assembles into a tetranuclear species, as demonstrated by the structural determination of the $[LCoGd(thd)_2(MeOH)]_2$ complex. This genuine entity is the first example in which a Co^{II} ion in a low-spin state is associated with a gadolinium ion. The magnetic studies confirm that two antiferromagnetic interactions are active through the double phenoxo bridge ($J = -1.0\ cm^{-1}$) and through the single amide bridge ($j = -0.1\ cm^{-1}$). Contrary to the large majority of 3d–Gd complexes that present ferromagnetic interactions, the involvement of a d_{xy} or d_{yz} cobalt orbital is responsible for the presence of an antiferromagnetic interaction.

Introduction

The magnetic interaction in 3d–Gd complexes is still a puzzling problem. Despite extensive experimental work mainly directed toward Cu–Gd complexes,[1] there are only a few reports centered on the theoretical evaluation of the magnetic exchange J and the understanding of the coupling mechanism.[2] The synthesis of well-isolated heterodinuclear Cu–Gd complexes has put forward the widespread occurrence of a ferromagnetic interaction, but a few examples governed by an antiferromagnetic coupling have been reported.[3] Some examples involving other 3d ions, such as Ni^{II},[4] Co^{II},[5] Fe^{II},[6] Mn^{II},[7] are also known. Although weaker than those in the Cu–Gd complexes, the magnetic interactions are still ferromagnetic. In these examples, the 3d ions are in a six-coordinate octahedral or a five-coordinate square-pyramidal environment. These five ions possess a common particularity, that is, the σ-type orbitals are singly occupied, whatever the 3d ion involved. Quantum chemical calculations within the C_{2v} symmetry have evidenced that the ferromagnetic coupling in Cu–Gd complexes originates from an orthogonal orbital exchange pathway, the dominating interaction operating between the $b_2[Cu^{II}L]$ and $a_2[Gd^{III}]$ orbitals.[2] The involved molecular orbitals are not genuine Cu and Gd orbitals, but molecular orbitals containing a small tail of Gd origin for the orbital located mainly on the $[Cu^{II}L]$ side as well as a slight mixing of the 4f and 5d atomic orbitals of gadolinium. The partially occupied 5d-type Gd^{III} orbitals gain their spin density from charge transfer from the 3d Cu orbitals and from the 4f delocalization.[2] Schiff base ligands with their strong equatorial ligand field yield square-planar Ni^{II} or Co^{II} complexes.[8] If the diamagnetic Ni^{II} complexes with their unoccupied $d_{x^2-y^2}$ orbital are not interesting from the magnetic point of view, the corresponding Co^{II} complexes, which have been the subject of a lot of work in the past, are much more interesting, as their five 3d orbitals are split into a single σ-type highly antibonding orbital, $d_{x^2-y^2}$, and a set of four closely spaced nonbonding or weakly interacting orbitals containing seven electrons. Furthermore, it has been established that the singly occupied orbital is not a σ-type orbital, contrary to the result given by the conventional angular overlap model.[9] Some years ago, we prepared a mixed amide–imine ligand that was able to yield square-planar Cu or Ni complexes,[10] due to the presence of three functions (two phenol and one amide) that can be deprotonated once they are chelated to the Cu or Ni ion. Of course, this deprotonated ligand constitutes the equatorial plane of the isolated complexes. Keeping this idea in mind, we have tried to synthesize first the equivalent Co^{II} complex and then to introduce the Gd ion in order to check the magnetic behavior of the resulting entity. This communica-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100311.

tion is devoted to the synthesis of these Co and Co–Gd complexes, the determination of their X-ray structures, and the study of their magnetic properties.

Results and Discussion

The synthetic work was carried out under a nitrogen atmosphere in a glove box. The ligand H_3L was prepared as described previously[11] by reaction of *N*-(2-amino-2-methylpropyl)-2-hydroxybenzamide and salicylaldehyde (1:1 molar ratio) in methanol, followed by addition of $Co(Ac)_2\cdot 4H_2O$ and piperidine (1:3). Orange red crystals of the [LCo]pipH complex **1** appeared from the filtered solution ten days later. Addition of $GdCl_3\cdot 6H_2O$, tetramethylheptanedione (Hthd) (1:2), and piperidine (1:3) to the previous solution before crystallization yielded the tetranuclear $[LCoGd(thd)_2(MeOH)]_2$ complex **2** as a yellow orange solid.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction. The structure of **1** consists of a mononuclear anionic LCo^{II} unit with the Co^{II} ion located in the N_2O_2 site of the triply deprotonated L^{3-} ligand, along with a piperidinium entity (Figure 1). The Co ion only deviates by 0.0179(4) Å from the mean coordination plane defined by the four donor atoms. The strongest hydrogen bond involves the oxygen atom of the amide function. Two LCo^{II} units are positioned in a head-to-tail arrangement by two sets of symmetrical hydrogen bonds, the nitrogen atoms of each piperidinium cation along with the amide oxygen atom of one LCo^{II} unit on the one hand and the O1 phenoxo oxygen atom of the second LCo^{II} unit on the other hand (Figure S1). These hydrogen bonds yield dinuclear entities in which the Co ions are separated by 6.337(1) Å. The ligand is not strictly planar, the two benzene rings making an angle of 3.87(7)°, while the five-membered cycle implying the diamino chain is in a δ gauche conformation. The Co–N bonds [1.858(2) and 1.859(2) Å] and Co–O bonds [1.857(2) and 1.871(2) Å] are short, as expected for a cobalt ion in a square-planar environment.

In complex **2** two heteronuclear Co–Gd entities are assembled through the oxygen atoms of the amide groups to form a double (Co–N–C–O–Gd) bridge, which leads to a tetranuclear entity, as represented in Figure 2. In each Co–Gd unit, the cobalt ion, still in a square-planar coordination in the inner N_2O_2 site, is doubly bridged by two phenoxo oxygen atoms to the gadolinium ion. This bridging network, $Co–(O)_2–Gd$ is not planar, as the dihedral angle between the (OCoO) and (OGdO) planes is equal to 41.6(1)°, thus giving a Co–Gd distance of 3.3355(5) Å. The gadolinium ion is eight-coordinate; in addition to the two bridging phenoxo oxygen atoms, four oxygen atoms coming from two bidentate η^2-coordinated thd diketone ligands, the amide oxygen not involved in the Co coordination site, and one methanol oxygen atom complete its environment. The Gd–O bond lengths vary from 2.228(3) to 2.553(3) Å, depending on the nature of the oxygen atoms. Inside the tetranuclear complex, the Co···Co and Gd···Gd distances are equal to 5.5484(7) and 7.9338(4) Å, respectively. Due to the absence of intra- or intermolecular hydrogen bonds, these tetranuclear entities are well-isolated from each other; the shortest intermolecular Gd···Gd distances are 13.637(1) Å, which precludes any significant interaction of magnetic nature between these tetranuclear units. The Co–N and Co–O bond lengths are quite similar to those of the starting unit, which agrees with the low-spin state of the Co ions.

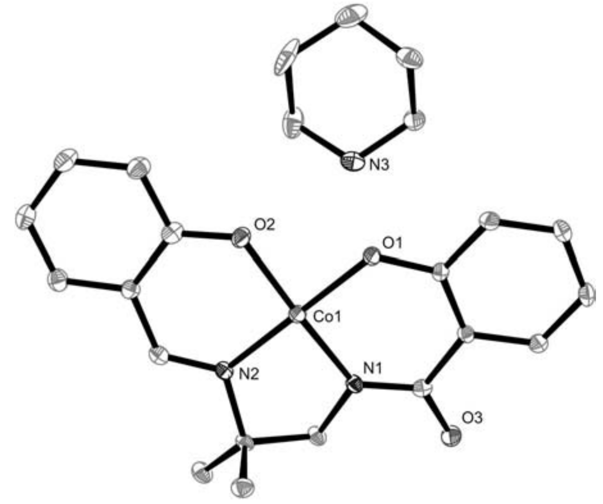

Figure 1. Plot of the asymmetric unit for **1** with the ellipsoids drawn at the 30% probability level and hydrogen atoms suppressed for clarity.

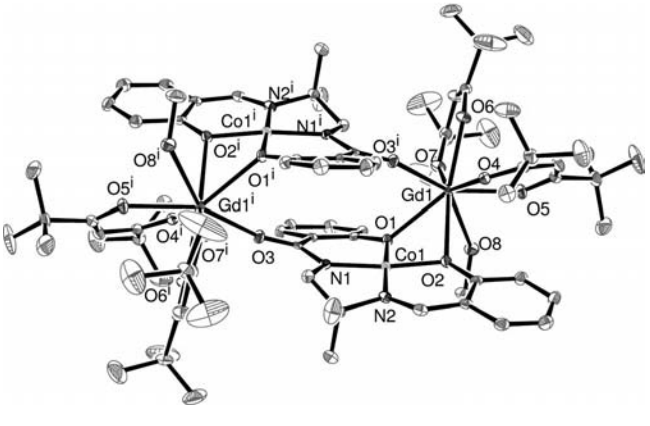

Figure 2. View of the tetranuclear $[CoGd]_2$ unit.

The $\chi_M T$ product reported in Figure S2 for compound **1** varies in a regular way from 0.74 $cm^3 mol^{-1} K$ at 300 K to 0.56 $cm^3 mol^{-1} K$ at 2 K. These values, corresponding to 2.40 and 2.11 μ_B, respectively, confirm that the square-planar cobalt ion is in a low-spin state ($S = 1/2$), as could be expected from such a geometry of the cobalt ion. Literature data confirm that magnetic moments varying from 2.2 to 2.7 μ_B are observed for such complexes.[12]

The $\chi_M T$ product reported in Figure 3 for compound **2** is equal to 17.3 $cm^3 mol^{-1} K$ at 300 K. From 300 to 50 K, a slight decrease to 16.7 $cm^3 mol^{-1} K$ is observed, followed by a sharp decrease to 13.78 $cm^3 mol^{-1} K$ at 2 K. The $\chi_M T$ at room temperature is slightly larger than that expected for two isolated Co and two Gd ions (16.5 $cm^3\,mol^{-1}\,K$) with $g = 2$, but it evidences that the cobalt ion is still in a low-spin state. The experimental data indicate the occurrence of an overall antiferromagnetic interaction in complex **2**. In view of the structural data, the magnetic susceptibility has been computed by exact calculation of the energy levels associated with the spin Hamiltonian $H = -J_{CoGd}(S_{Co1}\cdot S_{Gd1} + S_{Co2}\cdot S_{Gd2}) - j_{CoGd}(S_{Co1}\cdot S_{Gd2} + S_{Co2}\cdot S_{Gd1})$ through diagonalization of the full energy matrix.[13] The best fit yields the following data, $J_{CoGd} = -1.0\ cm^{-1}$, $j_{CoGd} = -0.10\ cm^{-1}$, $g = 2.04$, with an R factor equal to 1.0×10^{-5}, $R = \Sigma[(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2/\Sigma[(\chi_M T)^{obs}]^2$. In order to check the validity of these results, the Magpack program has been used to fit the experimental magnetization curve at low temperature.[14] The J value appears to be slightly overestimated for the 2–5 T part of the curve, a better fit being obtained with a lower J value, –0.8 cm^{-1} (Figure S3). This slight difference could be due to the estimation of the second j parameter corresponding to the magnetic interaction through the amido bridge. Nevertheless, it is clear that the global interaction is antiferromagnetic.

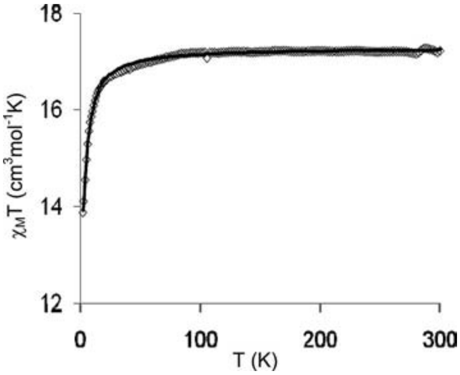

Figure 3. Temperature dependence of the $\chi_M T$ product for complex **2**. The solid line corresponds to the best data fit (see text).

For the first time a cobalt ion with a $S = 1/2$ spin state is associated to a gadolinium ion in a tetranuclear complex with alternate Co–Gd interactions through the double phenoxo bridge and through the single amidato bridge. From Figure 3, it is clear that an overall antiferromagnetic interaction is active. A strong equatorial ligand field causes a splitting of the five d orbitals into a single highly antibonding orbital ($d_{x^2-y^2}$), and a set of four closely spaced orbitals. In a low-spin Co^{II} complex, seven electrons fill these four orbitals. A previous work[9] has clearly demonstrated that the singly occupied orbital is the d_{xy} or d_{yz} orbital. A few Co–Gd complexes have appeared in the literature,[5] but they involve high-spin Co^{II} ions in a square-pyramidal or deformed octahedral environment, so that the $d_{x^2-y^2}$ and d_{z^2} orbitals are singly occupied in these examples. The change in the singly occupied 3d orbital has a drastic consequence on the magnetic interaction, changing it from ferro- to antiferromagnetic. A previous magnetic study of the Cu_2–Gd_2 tetranuclear entity, synthesized with the ligand used in the present work, confirmed that the two interaction pathways through the double phenoxo and the single amidato bridges are ferromagnetic.[15] These two Cu_2–Gd_2 and Co_2–Gd_2 complexes, which crystallize in the same space group $P2_1/n$, have similar geometric parameters, but they differ by the active magnetic orbitals of the 3d ions, a $d_{x^2-y^2}$ orbital for the copper ion against a d_{xy} or a d_{yz} orbital for the cobalt ion. If these observations do not elucidate the 3d–Gd interaction mechanism, they clearly indicate that the σ-type $d_{x^2-y^2}$ orbital must be responsible for the presence of a ferromagnetic 3d–Gd coupling.

Conclusions

Up to now, theoretical studies on Cu–Gd interactions were implemented to understand the quasi-general ferromagnetic coupling between copper(II) and gadolinium(III) ions. CASSCF calculations revealed that incorporation of the Gd 5d orbitals into the active space is necessary to reproduce the experimental J values.[2] It was shown that these 5d orbitals, initially supposed to be unoccupied, are partially populated by two phenomena, a charge transfer from the 3d ion orbital and a delocalization from the 4f orbitals toward the 5d orbitals. Furthermore, the charge transfer is more efficient when the unpaired electrons of the 3d ions are in a σ-type orbital.[2] So it appears that the 3d–5d orbital interaction plays a prominent role on the coupling, along with the symmetry of the complex. In the present case, a comparison of the equivalent Cu_2–Gd_2 and Co_2–Gd_2 complexes should eliminate the symmetry factor and emphasize the preponderant influence of the 3d–5d orbital interaction, the ferromagnetic interaction being associated to the presence of the unpaired electron in a σ-type orbital. This experimental result corroborates the conclusion of theoretical works related to Cu–Gd complexes. Further synthetic work making use of different mixed amide–imine ligands is in progress.

Experimental Section

1: The reaction was performed in a glove box. To a mixture of *N*-(2-amino-2-methylpropyl)-2-hydroxybenzamide (0.104 g, 0.5 mmol) and salicylaldehyde (0.061 g, 0.5 mmol) in MeOH (10 mL) was first added $Co(Ac)_2\cdot 4H_2O$ (0.125 g, 0.5 mmol) and eventually piperidine (0.127 g, 1.5 mmol). Stirring at room temperature for 30 min yielded an orange red solution that was filtered off and kept undisturbed. Orange crystals appeared ten days later. Some of them were put into grease for X-ray analysis, while the rest was collected by filtration and dried before taking out of the glove box. $C_{23}H_{29}CoN_3O_3$ (454.43): calcd. C 60.79, H 6.43, N 9.25; found C 60.46, H 6.32, N 9.10. Selected IR data (ATR) for **1**: $\tilde{\nu}$ = 3040 (w), 2959 (m), 2925 (w), 2859 (w), 2684 (w), 2589 (w), 2484 (w), 2407 (w), 1597 (s), 1568 (s), 1515 (s), 1440 (s), 1386 (s), 1335 (m), 1322 (m), 1308 (s), 1270 (m), 1258 (m), 1192 (m), 1143 (m), 1036 (m), 889 (m), 856 (w), 762 (m), 754 (s), 700 (m), 678 (w), 610 (w) cm^{-1}.

2: The reaction was first performed as for **1**, in the glove box. Then, to the solution of **1** were added $GdCl_3\cdot 6H_2O$ (0.188 g, 0.5 mmol), a MeOH solution containing tetramethylheptanedione (0.184 g, 1 mmol), and piperidine (0.085 g, 1 mmol). From the stirred solution a yellowish orange precipitate was filtered off two hours later and dried in the glove box. $C_{82}H_{118}Co_2Gd_2N_4O_{16}$ (1848.22): calcd. C 53.29, H 6.44, N 3.03; found C 53.25, H 6.42, N 3.10. The filtrate was kept and crystals appeared one month later. Selected IR data (ATR) for **2**: $\tilde{\nu}$ = 2965 (m), 2951 (m), 2864 (w), 1602 (m), 1594 (m), 1569 (s), 1526 (m), 1504 (s), 1446 (m), 1402 (s), 1381 (s), 1357 (s), 1284 (w), 1240 (m), 1225 (m), 1141 (m), 888 (w), 869 (w), 862 (w), 793 (w), 758 (m), 702 (w), 676 (w), 608 (w) cm^{-1}.

Crystal Structure Data for 1: $C_{23}H_{29}CoN_3O_3$, crystal size: $0.2\times0.12\times0.03\ mm^3$, orthorhombic, *Pbca*, a = 16.223(3) Å, b = 12.765(5) Å, c = 20.663(2) Å, V = 4279(2) $Å^3$, T = 180(2) K, Z = 8, ρ_{calc} = 1.411 $g\,cm^{-3}$, μ = 0.832 mm^{-1} (λ = 0.71073 Å), 21977 reflections collected, 4348 unique (R_{int} = 0.0638), $R1$ = 0.0422 and $wR2$ = 0.0873 using 2760 reflections with $I > 2\sigma(I)$.

Crystal Structure Data for 2: $C_{82}H_{118}Co_2Gd_2N_4O_{16}$, crystal size: $0.15\times0.15\times0.02\ mm^3$, monoclinic, $P2_1/c$, a = 13.6366(5) Å, b = 18.3717(5) Å, c = 17.8198(6) Å, β = 106.938(4)°, V = 4270.7(2) $Å^3$, T = 180(2) K, Z = 2, ρ_{calc} = 1.431 $g\,cm^{-3}$, μ = 1.978 mm^{-1} (λ = 0.71073 Å), 37409 reflections collected, 8696 unique (R_{int} = 0.0587), $R1$ = 0.0315 and $wR2$ = 0.0600 using 5367 reflections with $I > 2\sigma(I)$.

CCDC-813231 (**1**) and -813232 (**2**) contain the supplementary crystallographic data for this communication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figure showing the hydrogen bonds in complex **1**, temperature dependence of the $\chi_M T$ product for **1**, and field dependence of magnetization for **2** are presented.

Acknowledgments

This work was supported by Centre National de la Recherche Scientifique (CNRS), MAGMANet (Grant NMP3-CT-2005-515767), the Ministerio de Ciencia e Innovación of Spain through the project CTQ2009-07264/BQU and the Comissio Interdepartamental de Recerca I Innovacio Tecnologica de la Generalitat de Catalunya CIRI T (2009-SGR1454). V. G. is grateful to the Ministerio de Ciencia e Innovación for the PhD grant BES-2007-15668. The authors are grateful to Dr. A. Mari for technical assistance.

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Received: March 25, 2011