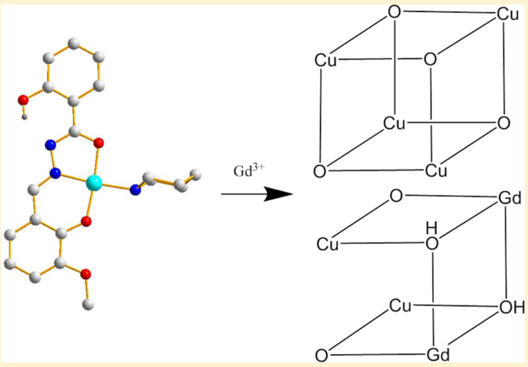
Inorganic Chemistry
Article
pubs.acs.org/IC

Synthesis, Structural Characterization, and Magnetic Properties of a Copper–Gadolinium Complex Derived from a Hydroxybenzohydrazide Ligand

Jean-Pierre Costes,*[†,‡] Carine Duhayon,[†,‡] and Laure Vendier[†,‡]

[†]Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France
[‡]Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France

Supporting Information



ABSTRACT: The reaction of hydroxybenzohydrazide with *o*-vanillin yields 2-hydroxy-*N*′-[(2-hydroxy-3-methoxyphenyl)methylidene]-benzohydrazide (LH_3), a ligand that is able to give mononuclear and tetranuclear copper complexes but also to associate copper and gadolinium ions in a Cu_2–Gd_2 heterotetranuclear complex. This synthesis is successful if the Gd ions, which are acidic in protic solvents, are introduced in a basic methanol solution of the mononuclear copper complex. In the absence of piperidine, the addition of Gd ions to a methanol solution of the mononuclear copper complex only yields a tetranuclear cubane-type copper complex. This work reports on the first structural characterization of a copper–gadolinium complex involving a benzohydrazide ligand. The resulting complex consists of two Cu–Gd pairs linked by a dihydroxo Gd–Gd bridge, in which the Cu and Gd ions are bridged by a nonsymmetric phenoxo–hydroxo bridge. The magnetostructural correlation between the ferromagnetic coupling constant and the hinge angle observed in symmetrical double-phenoxo Cu–Gd bridges remains valid for dissymmetric Cu–Gd bridges and confirms the preponderance of the structural factor over the nature of the bridge. This tetranuclear complex corresponds to two $S = 4$ units linked through a dihydroxo bridge introducing a weak antiferromagnetic Gd–Gd interaction and impeding the existence of a $S = 8$ ground state.

■ INTRODUCTION

Ligands possessing N and O donor atoms are of great interest in inorganic, biomimetic, and medicinal chemistry because they allow syntheses of mono-, homo-, and heteropolynuclear transition-metal complexes. Ligands associating transition- and lanthanide-metal ions have been largely used these last years for the syntheses of complexes possessing interesting magnetic properties, and several reviews dedicated to that particular research interest have appeared.[1] Among the possible ligands, it appeared to us that the potentiality of some of them has not been completely exploited. This is the case for ligands derived from benzohydrazide moieties. Benzohydrazide or hydroxybenzohydrazide synthons have been reacted with several organic reactants such as pyridinecarboxaldehyde,[2] 2-acetylpyridine,[3] carboxylic acids, or derivatives such as acetic anhydride or acyl chlorides,[4] or even more exotic sulfur-containing ligands[5] to yield mono- or polynuclear transition-metal complexes. Surprisingly, literature data furnish only a few examples making use of salicylaldehyde or *o*-vanillin as the reactant,[6] with structural determinations of the *N*′-[(2-hydroxy-3-methoxybenzylidene]benzohydrazide ligand and of its copper cubane complex. More recently, some structural determinations of dinuclear dysprosium complexes prepared with diverse benzohydrazide ligands have been described, along with their single-molecule-magnet properties.[7,8] Keeping these results in mind, we decided to prepare the ligand resulting from the reaction of hydroxybenzohydrazide with *o*-vanillin, (2-hydroxy-*N*′-[(2-hydroxy-3-methoxyphenyl)methylidene]benzohydrazide (LH_3), in order to prepare a heterometallic 3d–4f complex. The present work describes the characterization of the ligand (1D and 2D ^1H and ^{13}C NMR) and its reaction with Cu and Gd ions. The structural determinations of the resulting complexes do confirm the existence of mono- and tetranuclear copper complexes and, more interesting, the isolation of a genuine tetranuclear copper–gadolinium entity, which is the first example of a 3d–4f complex obtained with a benzohydrazide ligand.

■ EXPERIMENTAL SECTION

Materials. Hydrazine hydrate, phenyl salicylate, *o*-vanillin, tetramethylheptanedione (Hthd), triethylamine, piperidine, $Cu(OAc)_2 \cdot 2H_2O$, and $Gd(NO_3)_3 \cdot 6H_2O$ (Aldrich) were used as purchased. High-grade solvents [diethyl ether, tetrahydrofuran (THF), dichloromethane, acetone, and methanol (MeOH)] were used for the syntheses of ligands and complexes.

Received: November 15, 2013
Published: February 6, 2014

dx.doi.org/10.1021/ic4027283 | *Inorg. Chem.* 2014, 53, 2181–2187

Ligands. *2-Hydroxybenzohydrazide.* Phenyl salicylate (6.4 g, 3.0 × 10^{-3} mol) and hydrazine hydrate (2.0 g, 4.0 × 10^{-3} mol) were heated for 20 min. The addition of isopropyl alcohol (20 mL) induced cooling and the appearance of a white precipitate, which was filtered off, washed with a small amount of isopropyl alcohol, and dried. Yield: 2.9 g (66%). Anal. Calcd for $C_7H_8N_2O_2$ (152.1): C, 55.5; H, 5.3; N, 9.7. Found: C, 55.1; H, 5.1; N, 9.5. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.68 (s, l, 2 H, NH_2), 6.80 (t, J = 7.8 Hz, 1 H, CH-5), 6.87 (d, J = 7.8 Hz, 1 H, CH-3), 7.32 (t, J = 7.8 Hz, 1 H, CH-4), 7.80 (d, J = 7.8 Hz, 1 H, CH-6), 10.07 (s, l, 1 H, NH),12.45 (s, l, 1 H, OH). ^{13}C{^{1}H} NMR (100.63 MHz, DMSO-d_6): δ 115.51 (s, ArC-1), 117.99 (s, ArC-3), 118.27 (s, ArC-5), 128.00 (s, ArC-6), 133.54 (s, ArC-4), 160.78 (s, ArCOH), 168.14 (s, OCNH).

2-Hydroxy-N′-[(2-hydroxy-3-methoxyphenyl)methylidene]-benzohydrazide. The addition of *o*-vanillin (1.52 g, 1.0 × 10^{-3} mol) to a stirred MeOH solution (30 mL) of 2-hydroxybenzhydrazide (1.52 g, 1.0 × 10^{-3} mol), followed by 30 min of heating, induced the formation of a bulky white precipitate, which was filtered off after cooling, washed with MeOH and diethyl ether, and dried. Yield: 2.7 g (95%). Anal. Calcd for $C_{15}H_{14}N_2O_4$ (286.3): C, 62.9; H, 4.9; N, 9.8. Found: C, 62.7; H, 4.8; N, 9.7. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.83 (s, 3 H, CH_3), 6.88 (t, J = 8 Hz, 1 H, CH-5′), 6.97 (t, J = 7.8 Hz, 1 H, CH-5), 6.99 (d, J = 7.8 Hz, 1 H, CH-3), 7.05 (d, J = 8 Hz, 1 H, CH-4′), 7.18 (d, J = 8 Hz, CH-6′), 7.50 (t, J = 7.8 Hz, 1 H, CH-4), 7.90 (d, J = 7.8 Hz, 1 H, CH-6), 8.70 (s, 1 H, HC═N), 10.88 (s, 1 H, NH), 11.95 (s, 2 H, OH). ^{13}C{^{1}H} NMR (100.63 MHz, DMSO-d_6): δ 56.30 (s, OCH$_3$), 114.44, (s, ArC-4′), 116.09 (s, ArC-1′), 117.76 (s, ArC-3), 119.35 (s, ArC-1), 119.46 (s, ArC-5′), 119.55 (s, ArC-5), 121.18 (s, ArC-6′), 129.01 (s, ArC-6), 134.42 (s, ArC-4), 147.70 (s, ArC-3′), 148.43 (s, ArCOH′), 149.31 (s, HC═N), 159.52 (s, ArCOH), 164.99 (s, OCNH).

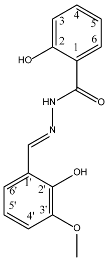
Complexes. *[LHCu(pip)]·$^1/_2$H$_2$O (**1**).* A mixture of H$_3$L (0.28 g, 1.0 × 10^{-3} mol), Cu(Ac)$_2$·H$_2$O (0.20 g, 1.0 × 10^{-3} mol), and piperidine (0.30 g, 3.5 × 10^{-3} mol) in MeOH (20 mL) was heated for 30 min, and a green precipitate appeared. It was filtered off, washed with MeOH, and dried. Slow diffusion of diethyl ether into a CH$_2$Cl$_2$ solution of the green precipitate yielded crystals suitable for X-ray diffraction (XRD). Yield: 0.36 g (84%). Anal. Calcd for $C_{20}H_{24}CuN_3O_{4.5}$ (442.0): C, 54.4; H, 5.5; N, 9.5. Found: C, 54.1; H, 5.1; N, 9.5. IR (ATR): 3601w, 3369w, 3262w, 2949w, 1621s, 1598s, 1519s, 1495s, 1449 ms, 1434m, 1383m, 1363m, 1299m, 1253m, 1240s, 1214s, 1159w, 1072w, 974w, 851w, 754m, 730m, 696w, 681w cm^{-1}.

*[LHCu]$_4$ (**2**).* A mixture of H$_3$L (0.28 g, 1.0 × 10^{-3} mol), Cu(Ac)$_2$·H$_2$O (0.20 g, 1.0 × 10^{-3} mol), and triethylamine (0.35 g, 3.5 × 10^{-3} mol) in MeOH (20 mL) was heated for 30 min, and a green precipitate appeared. It was filtered off, washed with MeOH and diethyl ether, and dried. Yield: 0.32 g (91%). Anal. Calcd for $C_{15}H_{12}CuN_2O_4$ (347.8): C, 51.8; H, 3.5; N, 8.0. Found: C, 51.4; H, 3.3; N, 7.9 . IR (ATR): 2948w, 1622m, 1601m, 1588m, 1514m, 1490s, 1450s, 1380s, 1360s, 1245s, 1218s, 1158m, 1099w, 1083w, 1070m, 970m, 924w, 790w, 750m, 736m, 699w, 681w, 650w cm^{-1}. The addition of Gd(NO$_3$)$_3$·5H$_2$O to a MeOH solution of **1** yielded crystals characterized by similar analytical and IR data.

*[LHCu(OH)Gd(thd)$_2$)]$_2$ (**3**).* To a mixture of H$_3$L (0.28 g, 1.0 × 10^{-3} mol) and tetramethylheptanedione (0.36 g, 2.0 × 10^{-3} mol) in MeOH (30 mL) were added Cu(Ac)$_2$·H$_2$O (0.20 g, 1.0 × 10^{-3} mol) and Gd(NO$_3$)$_3$·5H$_2$O (0.44 g, 1.0 × 10^{-3} mol) at once and eventually piperidine (0.30 g, 3.5 × 10^{-3} mol). The resulting solution was heated for 20 min and then left to cool with stirring, thus yielding a green precipitate that was filtered off and dried. Slow evaporation of a THF solution of the complex yielded crystals suitable for XRD. Yield: 0.61 g (70%). Anal. Calcd for $C_{74}H_{102}Cu_2Gd_2N_4O_{18}$ (1777.2): C, 50.0; H, 5.8; N, 3.1. Found: C, 49.7; H, 5.9; N, 3.1. IR (ATR): 2952m, 2865w, 1605m, 1592m, 1575m, 1551m, 1538m, 1493s, 1461m, 1395s, 1381s, 1357s, 1242m, 1218s, 1178w, 1144w, 1104w, 1065w, 965w, 869w, 794w, 756w, 736w, 629w cm^{-1}.

Physical Measurements. C, H, and N elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France. IR spectra were recorded with a Perkin-Elmer Spectrum 100 FTIR spectrometer using ATR mode. 1D and 2D ^{1}H and ^{13}C NMR spectra were acquired at 400.16 MHz (^{1}H) or 100.63 MHz (^{13}C) on a Bruker Avance 400 spectrometer using (CD$_3$)$_2$SO as the solvent. Chemical shifts are given in ppm versus tetramethylsilane (^{1}H and ^{13}C) with the numbering specified in Scheme 1. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 2−300 K temperature range under a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.[9] Isothermal magnetization measurements were performed up to 5 T at 2 K. The theoretical magnetic susceptibilities were computed through exact calculations of the energy levels associated with the spin Hamiltonian through diagonalization of the full matrix with a general program[10] and fitted by least-squares techniques[11] to the sets of experimental magnetic data for complexes **2** and **3**.

Scheme 1. LH$_3$ Ligand with the Numbering Scheme Retained for NMR Data (^{1}H and ^{13}C)



Crystallographic Data Collection and Structure Determination for Complexes 1−3. Crystals of **1**−**3** were kept in the mother liquor until they were dipped into oil. The chosen crystals were mounted on a Mitegen micromount and quickly cooled to 100 K (**1** and **2**) or 180 K (**3**). The selected crystals of **1** (red brown, 0.20 × 0.20 × 0.15 mm^3), **2** (green, 0.25 × 0.03 × 0.03 mm^3), and **3** (dark purple, 0.25 × 0.17 × 0.05 mm^3) were mounted on a Bruker Kappa Apex II (**1**) or an Oxford-Diffraction Gemini (**2** and **3**) using molybdenum (λ = 0.71073 Å, **1** and **3**) or copper radiation (λ = 1.54180, **2**) and equipped with an Oxford Cryosystems cooler device. The unit cell determination and data integration were carried out using *CrysAlis RED* or *SAINT* packages.[12−14] The structures have been solved using *SUPERFLIP*[15] or *SHELXS-97*[16] and refined by least-squares procedures using the software packages *CRYSTALS*[17] or *WinGX*, version 1.63.[18] Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[19] All H atoms were refined by using a riding model. When it was possible, all non-H atoms were anisotropically refined. Drawings of molecules are performed with the program *CAMERON*[20] with 30% probability displacement ellipsoids for non-H atoms.

*Crystal data for **1**:* $C_{20}H_{24}CuN_3O_{4.5}$, M = 441.97, monoclinic, Pn, Z = 8, a = 11.3862(4) Å, b = 19.1051(7) Å, c = 18.6796(7) Å, $\alpha = \gamma$ = 90°, β = 107.783(2)°, V = 3869.3(2) Å^3, 91884 collected reflections, 18806 unique reflections (R_{int} = 0.0338), R factor = 0.028, weighted R factor = 0.032 for 16585 contributing reflections [$I > 3\sigma(I)$]. The crystal was twinned. Data were treated with ROTAX, which gave the twin law between the two components (0.65:0.35).[21]

*Crystal data for **2**:* $C_{60}H_{48}Cu_4N_8O_{16}$, M = 1391.27, tetragonal, $P\bar{4}$, Z = 2, a = 16.8827(3) Å, b = 16.8827(3) Å, c = 12.6346(2) Å, $\alpha = \beta = \gamma$ = 90°, V = 3601.20(10) Å^3, 27154 collected reflections, 5425 unique reflections (R_{int} = 0.0382), R factor =0.074, weighted R factor = 0.085 for 4856 contributing reflections [$I > 3\sigma(I)$]. The asymmetric unit contains two independent half-molecules. For both molecules, the HL ligand is disordered over two positions with a 0.5:0.5 occupancy ratio.

*Crystal data for **3**:* $C_{74}H_{102}Cu_2Gd_2N_4O_{18}$, M = 1777.23, monoclinic, $P2_1/n$, Z = 4, a = 20.8730(11) Å, b = 17.923(3) Å, c = 26.0370(15) Å, β = 112.462 (5)°, V = 9001.6(17) Å^3, 18371 collected reflections, 16423 unique reflections (R_{int} = 0.1146), R factor = 0.0603, weighted R factor = 0.0694 for 6940 contributing reflections [$I > 2.8\sigma(I)$].

RESULTS

The reaction of 2-hydroxybenzohydrazide with *o*-vanillin yields the 2-hydroxy-*N*′-[(2-hydroxy-3-methoxyphenyl)methylidene]-benzohydrazide ligand, which is clearly characterized by 1D and 2D ^{1}H and ^{13}C NMR and chemical analysis. This ligand possesses three functions that can be deprotonated and two different coordination sites, so that it appears as a good candidate to give heterometallic complexes. In a first step, the reaction with transition-metal ions has been envisaged. Because the main coordination site involves three donor atoms, the ligand is reacted with copper acetate in the presence of an excess of piperidine (pip) as the deprotonating agent. Structural determination confirms the formation of a simple mononuclear complex, **1**, with pip being able to complete the copper coordination sphere. Replacement of pip by triethylamine gives an insoluble complex. The IR and analytical data confirm the absence of triethylamine, with triethylamine being unable to make a bond with the Cu ion. Structural characterization indicates that we are dealing with a tetranuclear complex, **2**. Surprisingly, the same complex can be prepared by the addition of a metal ion such as Gd to the mononuclear complex **1**. On the contrary, the reaction of the ligand with a mixture of copper acetate and gadolinium nitrate in a 1:1 ratio in the presence of an ancillary Hthd (Hthd = tetramethylheptanedione) ligand and a slight excess of pip yields a third complex in which the main ligand, thd, and Cu and Gd ions are in a 1:2:1:1 ratio, as in complex **3**. Structural determinations of these three complexes are described in the following. We can note the prominent role of pip in these preparations, being able to enter into the copper coordination sphere in complex **1** or to favor formation of the heterotetranuclear complex **3**, which cannot be isolated in an acidic medium.

Structural Determinations. The asymmetric unit of **1** includes four mononuclear [LHCu(pip)] neutral molecules and two water molecules. One of these molecules is represented in Figure 1, with selected bonds and angles appearing in the corresponding figure caption. The Cu ion is located in the main tridentate coordination site of the ligand, linked to two O and one N atoms of the ligand, with the fourth position being occupied by the piperidine N atom. Deprotonation of the hydrazide and of one phenol function yields a neutral copper complex, with the Cu ion in a square-planar environment. The 2-fold deprotonated ligand is not completely planar, while pip is in a unique chair conformation, as a consequence of the presence of an equatorial Cu−N bond that induces an axial position for the N−H bond. The mean planes of the main ligand and pip are roughly perpendicular. The Cu−N and Cu−O bonds for the four different molecules are very similar, with the shorter bonds involving the Cu−O and Cu−N bonds of the hydrazone part of the ligand [from 1.901(2) to 1.919(3) Å] and the Cu−O hydrazide bond being slightly larger [1.938(2)−1.945(2) Å] but shorter than the Cu−N piperidine bonds [1.993(3)−2.005(3) Å]. The nondeprotonated phenol function is involved in hydrogen bonding with the hydrazide N atom. A water molecule is hydrogen-bonded to the piperidine N atom and the methoxy and phenoxo O atoms of two different molecules positioned in a roughly perpendicular arrangement.

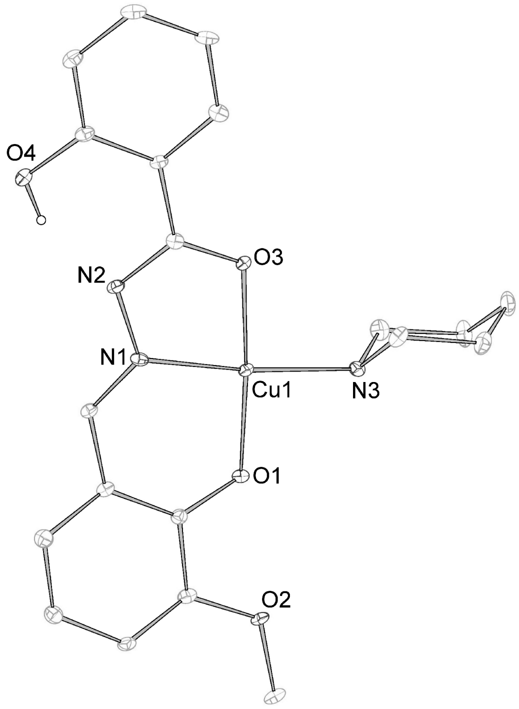


Figure 1. View of the mononuclear molecule **1**. Selected bond lengths (Å) and angles (deg): Cu1−N1 1.913(3), Cu1−N3 1.993(3), Cu1−O1 1.906(2), Cu1−O3 1.938(2), O1−Cu1−N3 91.8(1), O1−Cu1−N1 93.5(1), N1−Cu1−O3 81.7(1), O3−Cu−N3 93.1(1); Cu101−N101 1.916(3), Cu101−N103 1.991(3), Cu101−O101 1.901(2), Cu101−O103 1.941(2), O101−Cu101−N103 91.8(1), O101−Cu101−N101 93.6(1), N101−Cu101−O103 82.4(1), O103−Cu101−N103 92.4(1); Cu201−N201 1.915(3), Cu201−N203 2.005(3), Cu201−O201 1.911(2), Cu201−O203 1.942(2), O201−Cu201−N203 92.7(1), O201−Cu201−N201 93.7(1), N201−Cu201−O203 82.8(1), O203−Cu201−N203 92.0(1); Cu301−N301 1.919(3), Cu301−N303 1.999(3), Cu301−O301 1.915(2), Cu301−O303 1.945(2), O301−Cu301−N303 92.6(1), O301−Cu301−N301 93.4(1), N301−Cu301−O303 82.1(1), O303−Cu301−N303 92.2(1).

The asymmetric unit of **2** is made of two slightly different LHCu units. Application of symmetry operations to each LHCu leads to four LHCu units arranged to yield a cubane entity. Hence, the asymmetric unit contains a quarter of cubane 1 and cubane 2. The vertices of each cubane are alternately occupied by four phenoxo O atoms and four Cu ions in a six-coordinate environment. The molecular structure of a cubane is reported in Figure 2, while selected bond distances and angles are again given in the figure caption. Each Cu center is linked to three phenoxo O atoms, so that it can interact with the other three Cu ions. The head-to-tail ligand strand arrangement leads to a unique $CuNO_5$ chromophore, implying a hydrazone N atom, three phenoxo O atoms, and methoxy and hydrazide O atoms coming from three different ligands. As in complex **1**, each Cu ion is coordinated to three NO_2 donor atoms coming from the same ligand, to two O atoms (phenoxo and methoxy) from a second ligand, and to a phenoxo O atom from a third ligand. The Cu···Cu distances are homogeneous and vary from 3.281(1) to 3.343(2) Å. These cubane structures do present four faces characterized by Cu−O−Cu angles of 112.9(2) and 88.3(2)° (cubane 1) against 113.8(2) and 86.9(2)° (cubane 2), while the last two faces involve two identical Cu−O−Cu angles equal to respectively 90.4(2) and 88.6(2)°. We observe two short Cu−O bond lengths [1.966(4) and 1.970(4) Å and 1.963(5) and 1.981(4) Å] and one long Cu−O [2.686(5) and 2.755(5) Å for cubanes 1 and 2, respectively], so that these cubane structures can be classified as 4 + 2 (type II) cubanes.[22,23]

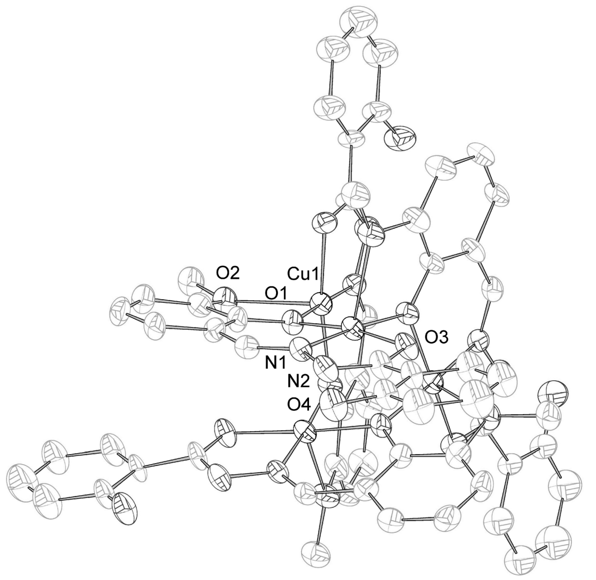


Figure 2. View of the tetranuclear copper complex **2**. Selected bond lengths and distances (Å) and angles (deg): Cu1–N1 1.910(5), Cu1–O1 1.970(4), Cu1–O3 1.948(4), Cu1–O1 4_757 1.966(4), Cu1–O1 3_775 2.686(5), Cu1–O2 4_757 2.298(4), Cu2–N21 1.914(5), Cu2–O21 1.963(5), Cu2–O23 1.953(4), Cu2–O220 4_656 2.275(4), Cu2–O21 4_656 1.981(4), Cu2–O22 4_656 2.248(4), Cu1–Cu1 4_757 3.281(1), Cu1–Cu1 2_577 3.281(1), Cu1–Cu1 3_775 3.343(2) Å, Cu2–Cu2 4_656 3.304(1), Cu2–Cu2 2_566 3.304(1), Cu2–Cu2 3_665 3.342(2), Cu1–O1–Cu1 2_577 112.9(2), Cu1 3_775–O1–Cu1 90.4(2), Cu1 3_775–O1–Cu1 2_577 88.3(2), Cu2 3_665–O21–Cu2 2_566 86.9(2), Cu2 3_665–O21–Cu2 88.6(2), Cu2 2_566–O21–Cu2 113.8(2).

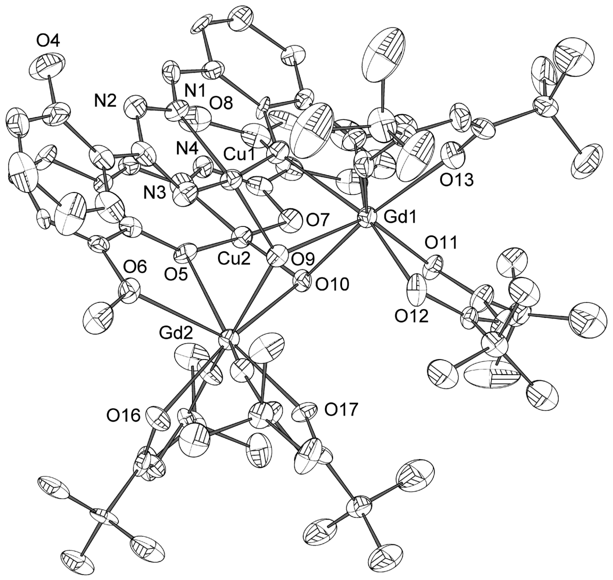


Figure 3. View of the tetranuclear $[LHCu(OH)Gd(thd)_2)]_2$ complex **3**. Selected bond lengths and distances (Å) and angles (deg): N1–Cu1 1.910(8), O9–Cu1 1.957(8), O3–Cu1 1.912(9), O1–Cu1 1.911(9), N3–Cu2 1.941(11), O10–Cu2 1.958(9), O5–Cu2 1.906(10), O7–Cu2 1.935(9), O2–Gd1 2.601(9), O9–Gd1 2.454(8), O1–Gd1 2.391(8), O10–Gd1 2.443(8), O11–Gd1 2.331(9), O12–Gd1 2.274(9), O13–Gd1 2.294(10), O14–Gd1 2.359(9), O9–Gd2 2.440(9), O10–Gd2 2.489(8), O5–Gd2 2.379(8), O6–Gd2 2.578(9), O15–Gd2 2.350(9), O16–Gd2 2.305(9), O17–Gd2 2.273(8), O18–Gd2 2.333(8), Cu1–Gd1 3.363(2), Cu2–Gd2 3.392(2), Gd1–Gd2 3.999(1), Cu1–O9–Gd1 99.3(4), Cu1–O9–Gd2 117.0(4), Cu1–O1–Gd1 102.2(4), Gd2–O9–Gd1 109.6(3), Gd1–O10–Gd2 108.4(3), Cu2–O10–Gd2 98.7(3), Cu2–O10–Gd1 116.6(4), Cu2–O5–Gd2 104.1(4).

The molecular structure of complex **3** appears in Figure 3 with again selected bond distances and angles reported in the figure caption. It consists of two $LHCu(OH)Gd(thd)_2$ units assembled through two hydroxo bridges, with each μ_3-OH bridge coordinating the Cu and Gd ions of one unit to the Gd ion of the second one. The Cu and Gd ions of one unit are connected by a nonsymmetric double bridge involving the phenoxo O atom of the LH ligand and the hydroxo O atoms. The Gd ions are thus bridged by a double hydroxo bridge, while a simple hydroxo bridge is operating between the Cu and Gd ions belonging to different units. There is no direct link between the Cu ions. As in complexes **1** and **2**, each Cu ion is linked to the same three donor atoms of the LH ligand (NO_2), and it completes its square-planar environment by the hydroxo anion. The Gd ion is eight-coordinate, with two O atoms originating from the LH ligand (methoxy and phenoxo), two from the hydroxo anions, and four from the two thd ancillary ligands. The Gd–O(thd) bond lengths [2.273(8)–2.359(9) Å] are shorter than the Gd–O(phenoxo) [2.379(8)–2.391(8) Å] and Gd–OMe [2.578(9)–2.601(9) Å] bond lengths. Three Gd–OH [2.440(9)–2.454(8) Å] bond lengths are different from the fourth one [2.489(8) Å], and the Gd···Gd distance is equal to 3.999(1) Å. The Cu···Gd distances through the phenoxo–hydroxo bridge are very similar [3.363(2)–3.392(2) Å], while the Cu···Gd distances through the single hydroxo bridge are larger [3.741(2)–3.753(2) Å]. The central $Gd-(OH)_2-Gd$ core of the molecule is surrounded on one side by the two main ligands and by two thd ligands on the other side, while the last two thd ligands are roughly in the plane of this core, so that the tetranuclear complexes are well isolated from the neighboring ones, with the shorter metal distances being larger than 10 Å.

Magnetic Properties. In agreement with structural determination, complex **1** presents no interest from the magnetic point of view, with the $\chi_M T$ product being constant and equal to from 300 to 2 K (Figure S1 in the Supporting Information). The magnetic behavior of complex **2** is reported in Figure 4 in the form of thermal variation of the $\chi_M T$ product (χ_M is the molar magnetic susceptibility of the tetranuclear copper complex corrected for diamagnetism of the ligands).[9] $\chi_M T$, which is equal to 1.16 cm^3 K mol^{-1} at 300 K decreases

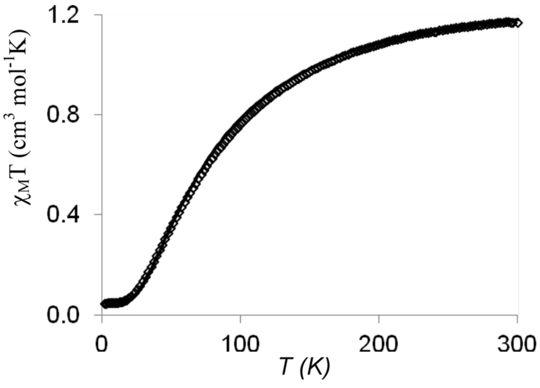


Figure 4. Temperature dependence of the $\chi_M T$ product for complex **2** at 0.1 T applied magnetic field. The solid line corresponds to the best data fit (see the text).

smoothly until 150 K (0.97 cm^3 K mol^{-1}) and then more abruptly until 2 K, where it is equal to 0.04 cm^3 K mol^{-1} (Figure 4). The $\chi_M T$ product at room temperature, lower than expected for four isolated Cu ions (1.5 cm^3 K mol^{-1} with $g = 2$) decreases from 300 to 2 K, thus indicating that an antiferromagnetic interaction through the phenoxo bridge is active, with the nonzero value at 2 K being due to the presence of a paramagnetic term. A qualitative analysis was first performed with a simple isotropic Hamiltonian $H = -2J(S_{Cu1}\cdot S_{Cu2} + S_{Cu2}\cdot S_{Cu3} + S_{Cu3}\cdot S_{Cu4} + S_{Cu1}\cdot S_{Cu4})$. The best fit yields an antiferromagnetic interaction parameter J_{CuCu} through the double phenoxo bridge equal to -36.8 cm^{-1}, with $g = 2.0$, a paramagnetic term of 1.7% and a correct agreement factor $R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{obs}]^2$ equal to 1×10^{-4}.

In view of the structure described above, two exchange coupling constants seem to be necessary to fit the magnetic data, and a qualitative analysis was performed with the following isotropic Hamiltonian $H = -2J_1(S_{Cu1}\cdot S_{Cu2} + S_{Cu3}\cdot S_{Cu4}) - 2J_2(S_{Cu1}\cdot S_{Cu4} + S_{Cu2}\cdot S_{Cu3} + S_{Cu1}\cdot S_{Cu3} + S_{Cu2}\cdot S_{Cu4})$. According to the structural determination, J_1 is associated with angles close to 90° and expected to be ferromagnetic while J_2, implying a larger Cu−O−Cu angle of 114°, must be antiferromagnetic. The best fit yields an antiferromagnetic interaction parameter J_2 through the double phenoxo bridge equal to -35.8 cm^{-1}, a ferromagnetic J_1 parameter of 5.9 cm^{-1} with $g = 2.0$, a paramagnetic term of 1.7%, and a correct agreement factor $R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{obs}]^2$ equal to 1×10^{-4}. These values are in complete agreement with those obtained with a similar cubane complex prepared with a Schiff base ligand resulting from the reaction of *o*-vanillin with an amino acid.[24]

Thermal variation of the $\chi_M T$ versus T plot of complex **3** is similar to what was observed for previously reported copper−gadolinium dinuclear complexes (Figure 5).[25] χ_M is the molar magnetic susceptibility of the tetranuclear complex, corrected for the diamagnetism of the ligands.[8] At 300 K, $\chi_M T$ is equal to 16.31 cm^3 K mol^{-1}, which is attributable to two Cu^{II} and two Gd^{III} uncoupled cations (16.5 cm^3 K mol^{-1} with $g = 2$). Upon a lowering of the temperature, $\chi_M T$ increases, reaching a maximum value of 19.18 cm^3 K mol^{-1} at 8 K, which is followed by a slight decrease to 18.49 cm^3 K mol^{-1} at 2 K. The maximum value is not far from that expected (20 cm^3 K mol^{-1}) for two pairs of ferromagnetically coupled Cu^{II} and Gd^{III} ions. A quantitative analysis using the Hamiltonian $H = -J_1(S_{Cu1}\cdot S_{Gd1} + S_{Cu2}\cdot S_{Gd2}) - J_2(S_{Cu1}\cdot S_{Gd2} + S_{Cu2}\cdot S_{Gd1}) - J_3(S_{Gd1}\cdot S_{Gd2})$ has been realized with the *MAGPACK* program[10] in order to take into account the three possible interaction pathways evidenced by the structural determination. The best fit leads to the parameter values $J_1 = 4.8$ cm^{-1}, $J_2 = -0.05$ cm^{-1}, $J_3 = -0.013$ cm^{-1}, and $g = 2.00$. The agreement factor $R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{obs}]^2 = 1 \times 10^{-4}$ is good. The ferromagnetic term J_1 does correspond to the Cu−Gd interaction through the nonsymmetric phenoxo−hydroxo bridge, while the Gd−Gd interaction through the double hydroxo bridge is antiferromagnetic and very weak, as expected. Eventually, our tetranuclear complex can be considered from the magnetic point of view as an assembly of two Cu−Gd dinuclear pairs governed by a ferromagnetic interaction. This conclusion is confirmed by the field dependence of magnetization M at 2 K, which is correctly fitted with these parameters (Figure 6).

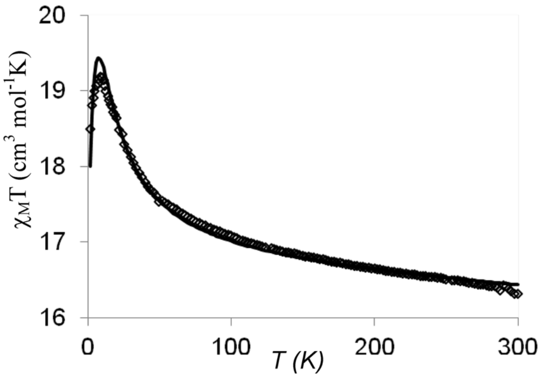


Figure 5. Temperature dependence of the $\chi_M T$ product for complex **3** at 0.1 T applied magnetic field. The solid line corresponds to the best data fit (see the text).

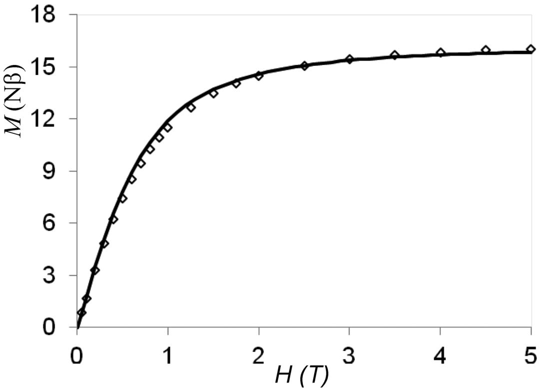


Figure 6. Field dependence of magnetization for complex **3**. The solid line corresponds to the best data fit (see the text).

Furthermore, increasing the field up to 5 T results in a magnetization close to the saturation value of 15.8Nβ units, consistent with a tetranuclear complex made of two $S = 4$ ($g = 2$) units.

■ DISCUSSION

Until now, 2-hydroxybenzohydrazide has been reacted with pyridinecarboxaldehyde[2] or 2-acetylpyridine[3] to yield ligands possessing two functions that can be deprotonated, but in the presence of 3d ions, only the NH hydrazide deprotonates. Introducing *o*-vanillin instead of pyridinecarboxaldehyde furnishes a new trianionic ligand with six potential donor atoms distributed in two coordination sites, so that complexation of 3d and 4f ions can be expected. A look at our three structural determinations shows that the phenol function not involved in the main coordination site never deprotonates. The addition of gadolinium nitrate to the monomeric complex **1** yields the tetranuclear species **2**, without complexation of Gd ions. This observation can be easily explained if we remember that positive metal ions yield acidic solutions in protic solvents.[26] Such an acidic ion protonates pip, thus leaving free the fourth coordination site and favoring formation of the tetranuclear complex. Replacement of pip by triethylamine gives directly the tetranuclear complex, with triethylamine being unable to enter in the copper coordination sphere.

If benzohydrazide ligands were first used to prepare mono- or polynuclear transition-metal complexes,[2−6] it was recently shown that picolinoylhydrazide ligands, with their supplementary pyridine N atom, were able to give dinuclear dysprosium complexes.[7,8] The possible preparation of homonuclear coordinate 3d and 4f complexes encouraged us to make an attempt to synthesize heteronuclear 3d−4f complexes, and more precisely Cu−Gd complexes. If Gd ions are added in the presence of an excess of pip, the solution remains basic, thus favoring the formation of hydroxo anions and chelation of Gd ions to the phenoxo methoxy part of the ligand. The same complex **3** is isolated when a mixture of Cu and Gd ions is mixed to a MeOH solution of the ligand and pip. The structural determination of complex **3** clearly shows that the Cu ion occupies the tridentate NO_2 coordination, as in the homonuclear copper complexes **1** and **2**, while each hydroxo anion is μ_3-bridged to the two Gd ions and to one Cu ion. The Gd ion is also linked to the phenoxo methoxy part of the ligand, and it completes its coordination sphere with two ancillary thd ligands and the two μ_3-hydroxo anions. The nondeprotonated phenol function is involved in hydrogen bonding with the close hydrazide N atom.

From the magnetic point of view, each Gd ion does interact with the other three ions (one Gd and two Cu ions), but there is no direct link between the Cu ions. Of course, the main Cu−Gd interaction involves the dissymmetric double phenoxo−hydroxo bridge. Some years ago, a similar dissymmetric bridge had been described.[25] The main difference between these two examples of dissymmetric bridges comes from the value of the hinge angle, defined as the angle between the CuOO and GdOO planes involving the metal ions and bridging O atoms. A hinge angle of 0.3(1)° is associated with an interaction parameter J value of 8.4 cm^{-1} in the previous case, while in the present complex, a hinge angle of 26.1(2)° [mean value for angles of 25.5(2) and 26.7(2)°] gives a lower J value of 4.8 cm^{-1}. The magnetostructural correlation between the coupling strength and hinge angle observed in symmetrical double phenoxo Cu−Gd bridges remains valid for dissymmetric Cu−Gd bridges and confirms the preponderance of the structural factor over the nature of the bridge.

The magnetic coupling in dinuclear gadolinium complexes bridged by two O atoms forming a four-membered Gd_2O_2 ring has been the subject of theoretical studies.[27] These complexes are divided into two classes, according to the type of functions involved in the bridges, carboxylate or phenolate functions that induce differences in their geometrical parameters: unequal Gd−O bond lengths and Gd−O−Gd angles larger than 113° in Ln_2O_2 carboxylate bridges, characterized by weak ferromagnetic interaction; nearly equal Gd−O bond lengths and Gd−O−Gd angles lower than 113° in Ln_2O_2 phenolate bridges giving weak antiferromagnetic interactions. In our complex **3**, the Gd−O_2−Gd core is not planar, with a hinge angle of 17.0(2)°, but the bond lengths [2.436(6)−2.450(7) Å], the angles at the oxygen bridgeheads [108.2(2) and 109.7(2)°], and the Gd···Gd distance [4.000(1) Å] do correspond to criteria favoring antiferromagnetic interactions. Our best fit yields a J_3 value of −0.013 cm^{-1}, in agreement with the structural parameters.

Because of the lack of literature data, it is more difficult to speak about the third interaction pathway corresponding to the single hydroxo bridge between the Cu ion of one dinuclear unit and the Gd ion of the second dinuclear unit. We found an example of μ_3-hydroxo anion bridging two Dy and one Cu ions[28] that gives no information on the Cu−OH−Dy interaction. When this interaction pathway was supposed as secondary, the presence of a ferromagnetic Cu−Gd interaction in the main dinuclear unit and of an antiferromagnetic Gd−Gd interaction should result in an antiferromagnetic interaction through the single hydroxo bridge. The J_2 best fit value of −0.05 cm^{-1} corresponds to what is expected and does agree with the absence of spin frustration in that complex **3**.

CONCLUSION

We have shown, with the help of structural determinations, that a hydrazide ligand can yield mononuclear copper complexes in the presence of coordinating amine ligands (pip) and tetranuclear copper complexes in a slightly acidic medium or in the presence of noncoordinating organic bases such as triethylamine. Furthermore, in a basic medium, this ligand is also able to associate Cu and Gd ions. The resulting complex corresponds to two Cu−Gd units with a dissymmetric phenoxo−hydroxo bridge that are associated through the Gd ions by a dihydroxo bridge. The two μ_3-hydroxo anions add a supplementary single hydroxo bridge between the Cu and Gd ions belonging to the different Cu−Gd units. The magnetic study confirms that the interaction through the dissymmetric bridge is ferromagnetic and that the magnetostructural correlation between the coupling strength and hinge angle observed in symmetrical double phenoxo Cu−Gd bridges remains valid for dissymmetric Cu−Gd bridges, thus confirming the preponderance of the structural factor over the nature of the bridge. This tetranuclear complex furnishes a nice example of Gd ions linked through a dihydroxo bridge introducing a weak antiferromagnetic Gd−Gd interaction, impeding the existence of a $S = 8$ ground state but consistent with a tetranuclear complex made of two $S = 4$ units. This work, reporting the first structural characterization of a copper−gadolinium complex involving a benzohydrazide ligand, confirms that such ligands can be used in the preparation of heteronuclear 3d−4f complexes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format and magnetism of complex **1** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jean-pierre.costes@lcc-toulouse.fr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by CNRS, MAGMANet (Grant NMP3-CT-2005-515767).

REFERENCES

(1) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369−2387. Huang, Y.-G.; Jiang, F.-L.; Hong, M.-C. *Coord. Chem. Rev.* **2009**, *253*, 2814−2834.

(2) Zhou, P.; Zhao, Y.-G.; Bai, Y.; Pang, K.-L.; He, C. *Inorg. Chim. Acta* **2007**, *360*, 3965−3970. Samanta, B.; Chakraborty, J.; Shit, S.; Batten, S. R.; Jensen, P.; Masuda, J. D.; Mitra, S. *Inorg. Chim. Acta* **2007**, *360*, 2471−2484.

(3) Barbazan, P.; Carballo, R.; Vazquez-Lopez, E. M. *CrystEngComm* **2007**, *9*, 668−675.

(4) Luo, W.; Wang, X.-T.; Meng, X.-G.; Cheng, G.-Z.; Ji, Z.-P. *Polyhedron* **2009**, *28*, 300−306. Luo, W.; Meng, X.-G.; Cheng, G.-Z.; Ji, Z.-P. *Inorg. Chim. Acta* **2009**, *362*, 551−555. Choi, J.; Park, J.; Park, M.; Moon, D.; Lah, M. S. *Eur. J. Inorg. Chem.* **2008**, 5465−5470. Luo,

W.; Meng, X.-G.; Xiang, J.-F.; Duan, Y.; Cheng, G.-Z.; Ji, Z.-P. *Inorg. Chim. Acta* **2008**, *361*, 2667–2676. Luo, W.; Wang, X.-T.; Meng, X.-G.; Cheng, G.-Z.; Ji, Z.-P. *Inorg. Chem. Commun.* **2008**, *11*, 1044–1047. Luo, W.; Wang, X.-T.; Cheng, G.-Z.; Song, G.; Ji, Z.-P. *Inorg. Chem. Commun.* **2008**, *11*, 769–771. John, R. P.; Park, M.; Moon, D.; Lee, K.; Hong, S.; Zou, Y.; Hong, C. S.; Lah, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 14142–14143. Moon, D.; Lee, K.; John, R. P.; Kim, G. H.; Suh, B. J.; Lah, M. S. *Inorg. Chem.* **2006**, *45*, 7991–7993. John, R. P.; Lee, K.; Kim, B. J.; Suh, B. J.; Rhee, H.; Lah, M. S. *Inorg. Chem.* **2005**, *44*, 7109–7121. Lin, S.; Liu, S.-X.; Chen, Z.; Lin, B.-Z.; Gao, S. *Inorg. Chem.* **2004**, *43*, 2222–2224. Lin, S.; Liu, S.-X.; Huang, J.-Q.; Lin, C.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 1595–1601. Liu, S.-X.; Lin, S.; Lin, C.-C.; Huang, J.-Q. *Angew. Chem., Int. Ed.* **2001**, *40*, 1084–1087.

(5) Beghidja, C.; Rogez, G.; Kortus, J.; Wesolek, M.; Welter, R. *J. Am. Chem. Soc.* **2006**, *128*, 3140–3141. Beghidja, C.; Wesolek, M.; Welter, R. *Inorg. Chim. Acta* **2005**, *358*, 3881–3888.

(6) Chakraborty, J.; Thakurta, S.; Pilet, G.; Luneau, D.; Mitra, S. *Polyhedron* **2009**, *28*, 819–825. Pouralimardan, O.; Chamayou, A.-C.; Janiak, C.; Hosseini-Monfared, H. *Inorg. Chim. Acta* **2007**, *360*, 1599–1608. Mohan, M.; Gupta, N. S.; Gupta, M. P.; Kumar, A.; Kumar, M.; Jha, N. K. *Inorg. Chim. Acta* **1988**, *152*, 25–36.

(7) Lin, P.-O.; Korobkov, I.; Burchell, T. J.; Murugesu, M. *Dalton Trans.* **2012**, *41*, 13649–13655. Lin, P.-O.; Burchell, T. J.; Clerac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848–8851.

(8) Zou, L.; Zhao, L.; Chen, P.; Guo, Y.-N.; Guo, Y.-N.; Li, Y.-H.; Tang, J. *Dalton Trans.* **2012**, *41*, 2966–2971. Guo, Y.-N.; Xu, G.-F.; Wernsdorfer, W.; Ungur, L.; Guo, Y.; Tang, J.; Zhang, Y.-N.; Chibotaru, L. F.; Powell, A. K. *J. Am. Chem. Soc.* **2011**, *133*, 11948–11951. Guo, Y.-N.; Chen, X.-H.; Xue, S.; Tang, J. *Inorg. Chem.* **2011**, *50*, 9705–9713. Guo, Y.-N.; Xu, G.-F.; Gamez, P.; Zhao, L.; Lin, S.-Y.; Tang, J.; Zhang, H.-J. *J. Am. Chem. Soc.* **2010**, *132*, 8538–8539.

(9) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5–70.

(10) Boudalis, A. K.; Clemente-Juan, J.-M.; Dahan, F.; Tuchagues, J.-P. *Inorg. Chem.* **2004**, *43*, 1574–1586.

(11) James, F.; Roos, M. *Comput. Phys. Commun.* **1975**, *10*, 343–367.

(12) *Xcalibur CCD system* and *CrysAlisPro Software system*, version 1.171.35.19; Agilent Technologies U.K. Ltd.: Oxford, U.K., 2011.

(13) *CrysAlis CCD and CrysAlis RED and associated programs*: Oxford Diffraction Program name(s); Oxford Diffraction Ltd.: Abingdon, England, 2006.

(14) *SAINT*; Bruker AXS Inc.: Madison, WI, 2007.

(15) *Superflip*: Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.

(16) Sheldrick, G. M. *SHELX97 [includes SHELXS97, SHELXL97, CIFTAB]: Programs for Crystal Structure Analysis*, release 97-2; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

(17) *CRYSTALS*: Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

(18) *WINGX 1.63 Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data*: Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837–840.

(19) *International Tables for X-ray crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. *IV*.

(20) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory: Oxford, England, 1996.

(21) Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Crystallogr.* **2002**, *35*, 168–174.

(22) Mergehenn, R.; Haase, W. *Acta Crystallogr.* **1977**, *B33*, 1877–1882.

(23) Tercero, J.; Ruiz, E.; Alvarez, S.; Rodriguez-Fortea, A.; Alemany, P. *J. Mater. Chem.* **2006**, *16*, 2729–2735.

(24) Puterova-Tokarova, Z.; Mrazova, V.; Kozisek, J.; Valentova, J.; Vranovicova, B.; Boca, R. *Polyhedron* **2014**, *70*, 52–58.

(25) Chiboub Fellah, F. Z.; Costes, J. P.; Dahan, F.; Duhayon, C.; Novitchi, G.; Tuchagues, J. P.; Vendier, L. *Inorg. Chem.* **2008**, *47*, 6444–6451.

(26) Hawkes, S. J. *J. Chem. Educ.* **1996**, *73*, 516–517.

(27) Roy, L. E.; Hughbanks, T. *J. Am. Chem. Soc.* **2006**, *128*, 568–575.

(28) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750–1755.