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# Dinuclear Co^II/Gd^III and Co^III/Gd^III Complexes Derived from Hexadentate Schiff Bases: Synthesis, Structure, and Magnetic Properties

## Jean-Pierre Costes,*[a] Françoise Dahan,[a] and Javier García-Tojal[b]

**Abstract:** Two heterodimetallic complexes of formulae [LCo(MeOH)Gd(NO$_3$)$_3$] (**1**) and [LCo(AcO)$_2$Gd(NO$_3$)$_2$] (**2**) (H$_2$L = 1,3-bis[(3-methoxysalicyli-dene)amino]-2,2′-dimethylpropane) have been synthesized and characterized. The structure of **1** consists of discrete dinuclear entities. The cobalt(II) ion exhibits a square-pyramidal geometry, in which the basal plane is formed by the N$_2$O$_2$ set of the inner Schiff base site and the apical position is occupied by the methanol oxygen atom. The gadolinium(III) ion is ten-coordinate to three bidentate nitrate groups and the four oxygen atoms of the Schiff base. The phenolate oxygen atoms act as a bridge between both metal ions. Complex **2** is also formed by isolated dinuclear species. The cobalt(III) ion shows a distorted octahedral geometry in which the equatorial plane is formed by the N$_2$O$_2$ set of the Schiff base, and the axial positions are occupied by two oxygen atoms from both acetate groups. The gadolinium(III) ion is ten-coordinate to two bidentate nitrate groups, two oxygen atoms of the acetate groups, and the four oxygen atoms of the Schiff base. The metal ions are bridged through both the phenolate oxygens and the acetate groups, the latter acting as $\mu_2$ ligands. Magnetic measurements on compound **1** allowed, for the first time, a quantitative evaluation of the $J$(Co,Gd) ferromagnetic interaction parameter ($J = 0.90$ cm$^{-1}$). The Co$^{II}$ zero-field splitting has to be taken into account to fit the experimental data at low temperature ($D = 4.2$ cm$^{-1}$). In complex **2**, the magnetically isolated gadolinium center obeys a Curie law.

**Keywords:** cobalt · lanthanides · magnetic properties

## Introduction

The preparation of heteronuclear complexes containing both 4f and 3d ions has attracted special attention in view of their magnetic and electronic properties.[1] In this sense, the synthesis of discrete heterodinuclear compounds can be relevant, because they represent the simplest models for the understanding of how the mutual influences of two different metal centers modulate the electronic, magnetic, and electrochemical properties of such compounds. The use of compartmental ligands, in particular those with two phenolic oxygens as an endogenous bridge, has been developed due to the specific stereochemical preferences exhibited by the two different metal ions.[2] In this sense, the methoxy derivatives of salen (H$_2$salen = N,N′-bis(salicylidene)ethylenediamine) contain an inner site with N- and O-donor chelating centers suitable for the linkage to d-block ions. The outer coordination site with its O-donor atoms is greater than the inner one and can incorporate larger ions, such as lanthanides.[3]

In the last years, we have studied several heterodinuclear complexes of salen derivatives that contain orbitally non-degenerate Cu$^{II}$/Gd$^{III}$, V$^{IV}$/Gd$^{III}$, and Ni$^{II}$/Gd$^{III}$ and orbitally degenerate Fe$^{II}$/Gd$^{III}$ systems.[4] Now we have focused the research on the heterodinuclear Co/Gd complexes as an extension of our work to compounds that exhibit more complex magnetic interactions. It is well known that [Co$^{II}$(salen)] and its analogues show reactivity toward dioxygen;[5] some of them have been proposed as models of organo-cobalamins[6] and applied in asymmetric catalysis.[7] We have found few structural studies on cobalt/gadolinium hetero-polynuclear complexes[8] and few magnetic studies on hetero-dinuclear entities.[9] Furthermore, as far as we are aware the Co/Gd/salen system is unexplored up to date. Herein we report the synthesis and crystal structures of two Co$^{II}$Gd$^{III}$ (**1**) and Co$^{III}$Gd$^{III}$ (**2**) complexes derived from H$_2$L (1,3-bis[(3-methoxysalicylidene)amino]-2,2′-dimethylpropane) together with their magnetic properties.

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## Results and Discussion

**[LCo(MeOH)Gd(NO$_3$)$_3$] (1)**: A view of the molecular structure is shown in Figure 1. The most relevant interatomic distances and angles are listed in Table 1. The cobalt(II) ion exhibits a very slightly distorted square-pyramidal geometry,
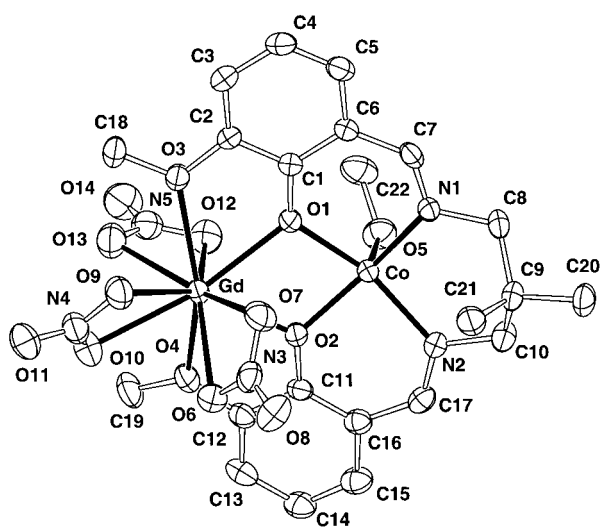
Figure 1. Molecular structure of [LCo(MeOH)Gd(NO₃)₃] (**1**) with thermal ellipsoids at 50 % probability level.

Table 1. Selected bond lengths [Å], angles [°], and hydrogen bonding contacts A−H···B for [LCo(MeOH)Gd(NO₃)₃] (**1**).[a]

| Co−O1 | 2.021(2) | Gd−O3 | 2.542(2) |
|---|---|---|---|
| Co−O2 | 1.995(2) | Gd−O4 | 2.506(2) |
| Co−N1 | 2.031(2) | Gd−O6 | 2.497(2) |
| Co−N2 | 2.074(2) | Gd−O7 | 2.483(2) |
| Co−O5 | 2.0546(19) | Gd−O9 | 2.488(2) |
| | | Gd−O10 | 2.566(2) |
| Gd−O1 | 2.379(1) | Gd−O12 | 2.590(2) |
| Gd−O2 | 2.333(1) | Gd−O13 | 2.523(2) |
| O1-Gd-O2 | 65.48(5) | Gd-O1-Co | 106.46(6) |
| O1-Co-O2 | 78.78(6) | Gd-O2-Co | 109.07(6) |
| $\alpha$ | 4.2(4) | | |

| | A−H [Å] | A···B [Å] | H···B [Å] | A−H···B [°] |
|---|---|---|---|---|
| O5−H5A···O12ⁱ | 1.04(3) | 2.918(3) | 1.96(3) | 152(2) |
| O5−H5A···O14ⁱ | 1.04(3) | 3.401(3) | 2.51(3) | 143(2) |

[a] Symmetry transformation i: $1-x, -y, 1-z$.

and the value of the Addison's parameter is $\tau = 0.02$.[10] It is surrounded by two nitrogen and two phenolato oxygen atoms belonging to the Schiff base ligand, while the O5 oxygen atom of the methanol molecule occupies the apical position. The cobalt(II) ion is located 0.2972(3) Å out of the basal plane formed by the four chelating centers of the ligand toward the oxygen atom of methanol. The gadolinium(III) ion is ten-coordinate, bonded to two phenolato and two methoxy oxygen atoms of the Schiff base and three nitrate groups acting as bidentate ligands ($\eta^2$ coordination). The Gd−O bond lengths range from 2.333(1) to 2.590(2) Å; the shorter ones correspond to those involving the phenolate oxygen atoms that act as a bridge between the cobalt(II) and the gadolinium(III) ions. The Co···Gd intramolecular distance is 3.5310(2) Å. The dihedral angle $\alpha$ between the O1CoO2 and O1GdO2 planes is 4.2(4)°. The hydrogen bonds that stabilize the framework are those which involve both the methanol molecule and one of the nitrate groups. The shortest Co···Co, Co···Gd, and Gd···Gd intermolecular distances are to 6.7845(6), 7.2369(3), and 8.6924(1) Å, respectively, so that the dinuclear entities can be considered as well insulated.

As far as we are aware, this is the first example of pentacoordinate cobalt in cobalt–lanthanide complexes. The Co···Gd intramolecular distance is very similar to that of 3.583 Å in a CoII···PrIII related compound,[9b] while the shortest CoII···GdIII distance referenced is 3.383(3) Å.[8b]

**[LCo(AcO)₂Gd(NO₃)₂] (2):** A view of one of the two crystallographic independent molecules (i.e., molecule A) is shown in Figure 2. Significant interatomic dimensions are
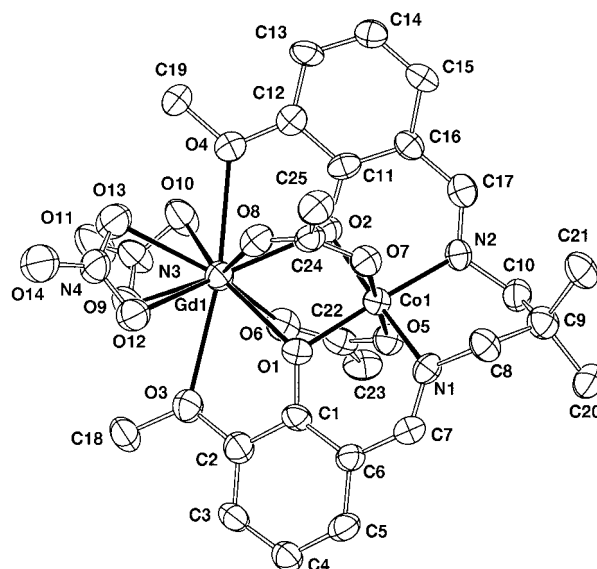


Figure 2. Molecular structure of [LCo(AcO)₂Gd(NO₃)₂] (**2**) (molecule A) with thermal ellipsoids at 40 % probability level.

given in Table 2. The cobalt(III) ion has a distorted octahedral geometry. The N1N2O1O2 set of the Schiff base chelating centers forms the equatorial plane around the metal ion, while the O5 and O7 oxygen atoms belonging to two different acetate groups are linked in the axial positions. The cobalt(III)

Table 2. Selected bond lengths [Å] and angles [°] for [LCo(AcO)₂Gd (NO₃)₂] (**2**).

| | Molecule A | Molecule B |
|---|---|---|
| Gd−O1 | 2.351(2) | 2.341(2) |
| Gd−O2 | 2.356(3) | 2.347(2) |
| Gd−O3 | 2.702(2) | 2.612(3) |
| Gd−O4 | 2.613(3) | 2.658(3) |
| Gd−O6 | 2.462(3) | 2.407(3) |
| Gd−O8 | 2.424(3) | 2.434(3) |
| Gd−O9 | 2.485(3) | 2.531(3) |
| Gd−O10 | 2.521(3) | 2.510(3) |
| Gd−O12 | 2.498(3) | 2.497(3) |
| Gd−O13 | 2.492(3) | 2.512(3) |
| Co−O1 | 1.909(3) | 1.916(3) |
| Co−O2 | 1.923(3) | 1.913(3) |
| Co−O5 | 1.907(3) | 1.912(3) |
| Co−O7 | 1.891(3) | 1.880(3) |
| Co−N1 | 1.926(3) | 1.944(3) |
| Co−N2 | 1.914(3) | 1.895(3) |
| O1-Gd-O2 | 70.52(9) | 70.55(9) |
| O1-Co-O2 | 90.3(1) | 90.0(1) |
| Gd-O1-Co | 99.9(1) | 99.8(1) |
| Gd-O2-Co | 99.3(1) | 99.6(1) |

ion is placed out of the equatorial plane, 0.0111(5) Å in molecule A and 0.0060(5) Å in molecule B. The gadolinium(III) ion is also ten-coordinate, linked to the four oxygen atoms belonging to the outer coordination site of the Schiff base, two bidentate nitrate groups, and two oxygen atoms from both acetate groups. The Gd−O bond lengths vary from 2.351(2) to 2.702(4) Å in molecule A and from 2.341(2) to 2.658(3) Å in molecule B. Again the shorter Gd−O distances correspond to those involving the phenolate oxygen atoms. Four bridges are present between the cobalt(III) and gadolinium(III) ions, two of them linking the metal centers through the phenolate oxygens of the Schiff base and the two other ones involving both oxygen atoms of each acetate group. The Co···Gd intramolecular distance is 3.2726(5) and 3.2672(5) Å for A and B, respectively. The $CoO_2Gd$ core is planar, the dihedral angles $\alpha$ between the O1CoO2 and O1GdO2 planes being 0.5(4) and 0.0(10)° for A and B, respectively. The shortest Co···Co, Co···Gd, and Gd···Gd intermolecular distances are to 10.5679(7), 7.5605(5) and 8.8259(3) Å, respectively, so that the dinuclear entities can be considered as well insulated.

It is worth mentioning the different shapes in the molecular structures of **1** and **2** due to the orientation of both the phenolate rings and the carbon chain of the diimine moiety. In compound **2** the ligand is more deformed than in compound **1**, the angles defined by the phenolate rings and the mean cobalt coordination plane N1N2O1O2 being 7.2 and 8.9° for **1** and 31.1 and 35.0° or 35.2 and 40.7° for molecules **2A** and **2B**, respectively.

Existence of four bridges between metal ions is an unusual structural feature in the 3d – 4f heterodinuclear complexes. As a consequence the Co···Gd intramolecular distance in compound **2** represents the shortest Co···Ln distance in coordination compounds up to date. Although cobalt(II) is reluctant to form carboxylate-bridged di- and trinuclear complexes,[11] cobalt(III) is prone to give such bonds.

**Magnetic properties:** The magnetic susceptibility $\chi_M$ of complexes **1** and **2** was measured in the 2 – 300 K temperature range in a 0.8 T applied magnetic field, while isothermal magnetization measurement as a function of the external magnetic field for **1** was performed up to 5 T at 2 K. The data obtained for complex **1** are given in Figure 3. At 300 K the
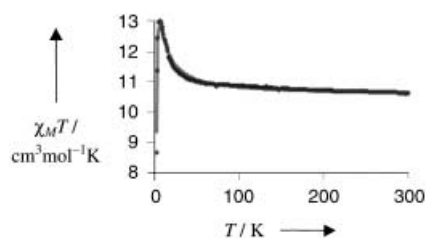


Figure 3. Thermal dependence of $\chi_M T$ for complex **1**. The solid line represents the best data fit (see text).

$\chi_M T$ product is equal to 10.57 cm³mol⁻¹ K, which is slightly larger than the expected 9.75 cm³mol⁻¹ K value for non-interacting $S = 3/2$ (Co) and $S = 7/2$ (Gd) spins. As the temperature is lowered, $\chi_M T$ gradually increases to

13 cm³mol⁻¹ K at 7 K, indicating the presence of a ferromagnetic interaction, and then abruptly decreases to 8.69 cm³mol⁻¹ K at 2 K. In the case of complex **2** the $\chi_M T$ product is constant from room temperature to 2 K with a $\chi_M T$ value of 7.89 cm³mol⁻¹ K, which corresponds to the expected value (7.87 cm³mol⁻¹ K; Figure 4). Indeed the contribution
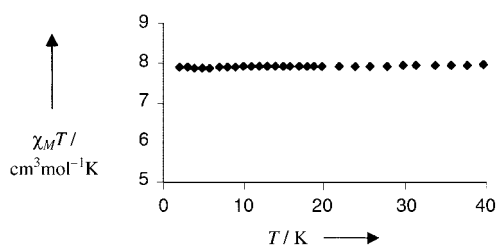


Figure 4. Thermal dependence of $\chi_M T$ for complex **2**.

only comes from the insulated gadolinium centers, the cobalt(III) ions being diamagnetic. This result emphasizes that the dinuclear (Co^III, Gd) units are well isolated from each other and that the $\chi_M T$ variation observed for complex **1** originates exclusively from the insulated (Co^II, Gd) dinuclear units. Owing to the orbital degeneracy of high-spin cobalt(II) ($S = 3/2$), application of an isotropic spin Hamiltonian is not rigorous for these complexes. The Kotani expressions,[12] appropriate with isolated cobalt(II) centers, are not suitable here because of the Co−Gd magnetic interaction. The exchange phenomenon in the presence of orbital degeneracy is an open problem for which no general solution is available. It has been previously shown that the orbital contribution is significantly quenched when the iron(II) environment deviates from ideal octahedral geometry.[13] This is the case of complex **1** in which the cobalt(II) center is pentacoordinate with a square-pyramidal geometry; in such a case, the orbital degeneracy can only weakly affect the temperature dependence of the $\chi_M T$ product.[14, 15] Attempts to fit the data by using the simplified $H = -JS_{Co}S_{Gd}$ Hamiltonian failed, indicating that zero field splitting (ZFS) of cobalt(II) cannot be neglected. The energy levels and magnetic properties of spin systems including the anisotropic cobalt(II) usually require consideration of single ion ZFS terms. This ZFS term includes the anisotropy that originates from the orbital contribution. The simpler spin Hamiltonian that may be used is $H = -JS_{Co}S_{Gd} + D_{Co}S^2_{zCo} + \Sigma_{i,j}g_i\beta H_jS_{ij}$ in which the first term gauged by the parameter $J$ accounts for the spin exchange interaction, the second one gauged by $D$ accounts for axial single ion ZFS of cobalt(II), and the third one accounts for the Zeeman contributions in which $i = $ Co, Gd and $j = x,y,z$. The temperature dependence of $\chi_M T$ was fitted by using the above Hamiltonian. Analytical expressions for eigenvalues and susceptibility can not be derived due to the ZFS term. To calculate the energy levels and magnetic properties, diagonalization of the full matrix was carried out.[16] The best fit for complex **1** (Figure 3) was obtained for the following set of parameters, $J = 0.90$ cm⁻¹, $D = 4.23$ cm⁻¹, $g = 2.07$. The occurrence of a ZFS term, for which the magnitude $D$ is similar or larger to that of the exchange parameter $J$, is responsible for the unusual profile of the $\chi_M T$ versus $T$ plot.

The 2 K magnetization data was then satisfactorily simulated with this set of parameters, as illustrated in Figure 5, confirming simultaneous operation of ferromagnetic Co–Gd
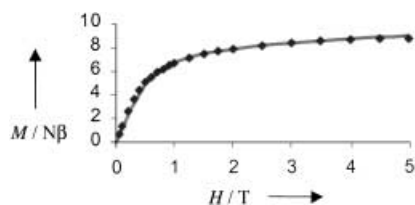


Figure 5. Field dependence of the magnetization for complex **1**. The solid line is obtained from the best fit of the $\chi_M T$ curve.

exchange interactions and single Co$^{II}$ ion ZFS.[17] Eventually, we have to stress that a model with an effective cobalt spin of ½ is not able to reproduce the experimental magnetization and susceptibility data.

## Conclusion

We have seen above that the complex **1** has a higher planarity than complex **2**. This result is probably due to the change in the cobalt oxidation number. Indeed the cobalt(III) ion has a smaller ionic radius than the cobalt(II) ion. As a consequence, the N1···N2 distance decreases in **2** (2.67(1) Å) in comparison to **1** (3.06(1) Å) and this decrease induces an increase of the O1···O2 distance (2.72(1) Å for **2** instead of 2.55(1) Å for **1**) and an even more pronounced increase for the O3···O4 distance (5.30(2) and 4.89(2) Å for **2** and **1**, respectively). The net result is an increased size of the outer O$_4$ coordination site. This observation can explain why it is the first example of a structurally characterized (M$^{III}$, Gd$^{III}$) heterodinuclear complex with such compartmental Schiff base ligands.

With use of this ligand, we have been able to isolate the heterodinuclear (Cu$^{II}$,Gd), (Ni$^{II}$,Gd), (Co$^{II}$,Gd), and (Fe$^{II}$,Gd) complexes, to solve the structural determinations of the $\eta^2$-coordinated nitrate entities, and to study their magnetic behaviors. In a previous work,[4c] it has been shown for Cu/Gd pairs that the sign and magnitude of the exchange interaction are dependent on the bending of the {CuO$_2$Gd} core gauged by the dihedral angle $\alpha$, going from 4.8 cm$^{-1}$ for $\alpha = 16.6(2)°$ to 10.1 cm$^{-1}$ for $\alpha = 1.7(2)°$. For the three Ni, Co, and Fe complexes, these dihedral angles are very similar: 4.2(5)°, 4.2(4)°, and 6.2(7)°, respectively. The $J$(M,Gd) coupling constants, reported to the Hamiltonian $H = -J S_M S_{Gd}$, are all ferromagnetic and respectively equal to 3.6, 0.9, and 1.0 cm$^{-1}$, respectively, while a $J$(Cu,Gd) coupling constant of 8 cm$^{-1}$ is expected for a dihedral angle around 5°. Considering that the exchange mechanism is affected by the increased number of active d electrons (from one (Cu$^{II}$) to two (Ni$^{II}$), three (Co$^{II}$) and four (Fe$^{II}$)), these $J$(M,Gd) values correspond to the expected ones, although values around 2 cm$^{-1}$ should be expected for the (Co,Gd) and (Fe,Gd) couples. This situation may originate from presence of two antagonist effects in these complexes, that is, ferromagnetic interaction and single Co$^{II}$ or Fe$^{II}$ ion ZFS.

## Experimental Section

**Preparation of the complexes**: Starting materials were purchased from Acros Organics (o-vanillin) and Aldrich (1,3-diamino-2,2′-dimethylpropane, cobalt(II) acetate tetrahydrate and gadolinium nitrate hexahydrate), and used without further purification. The ligand was prepared as described in the literature.[18] The complexes were synthesized as follows. All complexation reactions and sample preparations for physical measurements were carried out in a purified nitrogen atmosphere within a glovebox (Vacuum Atmospheres H.E.43.2) equipped with a dry-train (Jahan EVAC 7).

**[LCo(MeOH)Gd(NO$_3$)$_3$] (1):** Cobalt(II) acetate (1 mmol, 0.25 g) was added as a solid to a solution of the Schiff base (1 mmol, 0.37 g) in methanol (10 mL). The dark red solution was stirred for 15 minutes. Then, an equimolar amount of gadolinium nitrate (1 mmol, 0.45 g) was added, and the color of the solution turned into orange. Orange crystals suitable for X-ray studies were obtained by slow evaporation of the solvent. Elemental analysis calcd (%) for C$_{22}$H$_{28}$CoGdN$_5$O$_{14}$: C 32.9, H 3.5, N 8.7; found: C 33.3, H 3.5, N 8.3; selected IR bands: $\tilde{\nu} = 3401$ (m, br), 2956 (m), 2916 (m, sh), 1619 (vs), 1562 (m), 1470 (vs, br; ligand + NO$_3$), 1294 (s; ligand + NO$_3$), 1243 (m), 1226 (s), 739 cm$^{-1}$ (s).

**[LCo(AcO)$_2$Gd(NO$_3$)$_2$] (2)**: The reaction was carried out in air. Cobalt(II) acetate (1 mmol, 0.25 g) was added as a solid to a suspension of the ligand (1 mmol, 0.37 g) in methanol (10 mL). After stirring the dark solution for 15 minutes, gadolinium nitrate (1 mmol, 0.45 g) was added. The solution was stirred overnight. A green precipitate was obtained, washed with methanol, and dried under vacuum. Yield 49%. Dark green crystals suitable for X-ray analysis were obtained by slow evaporation of the mother liquor. The same results were obtained taking the solution of [LCo(MeOH)Gd(NO$_3$)$_3$] off the dry box and allowing slow evaporation of the solvent. Elemental analysis calcd (%) for C$_{25}$H$_{30}$CoGdN$_4$O$_{14}$: C 36.3, H 3.7, N 6.8; found: C 36.4, H 3.3, N 6.7; selected IR bands: 3435 (m, br), 2958 (w), 1642 (s, C=O), 1609 (w), 1591 (s), 1506 (s), 1477 (vs; ligand + NO$_3$), 1384 (vs),1291 (vs; ligand + NO$_3$), 1251 (s), 744 (m), 734 cm$^{-1}$ (m).

**Physical measurements:** Elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse (France) for C, H, and N. IR spectra were recorded on a GX system 2000 Perkin–Elmer spectrophotometer. Samples were run as KBr pellets.

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. All samples were 3 mm diameter pellets molded in the glove box from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 0.8 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.[19] Isothermal magnetization measurements as a function of the external magnetic field were performed up to 5 T at 2 K. The magnetic susceptibility was computed by exact calculation of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry,[20] and with the MAGPACK program package[16] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.[17]

**Crystal data for 1 and 2:** Single crystals suitable for X-ray analysis were mounted on glass fibers. X-ray intensities were measured at 193 K for **1** and 293 K for **2** with Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation on a STOE-IPDS diffractometer. Integrated intensities including Lorentz and polarization effects and numerical absorption corrections were obtained using the STOE programs.[21, 22] For further crystal and data collection details see Table 3.

Crystal structures were solved by direct methods using the SHELXS-97 program.[23] . The function $w(F_o^2 - F_c^2)^2$ was minimized by using full-matrix least-squares refinement implemented in the SHELXL-97 program.[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and were allowed to ride on the corresponding parent atom with isotropic displacement parameters 1.1 times that of the parent atom, except that bonded to the oxygen methanol in compound **1**, which was allowed to vary. The scattering factors and anomalous dispersion coefficients were taken from International Tables for Crystallography.[25] A summary of the results is given in Table 3 ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = \{\Sigma w(F$

Table 3. Crystal data and structure refinement for [LCo(MeOH)Gd$(NO_3)_3$] (**1**) and [LCo(AcO)$_2$Gd(NO$_3$)$_2$] (**2**).

| | 1 | 2 |
|---|---|---|
| formula | $C_{22}H_{28}CoGdN_5O_{14}$ | $C_{25}H_{30}CoGdN_4O_{14}$ |
| $M_r$ | 802.67 | 826.71 |
| crystal habit | orange plate | red plate |
| crystal dimensions [mm] | $0.50 \times 0.15 \times 0.10$ | $0.40 \times 0.30 \times 0.15$ |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/n$ (No. 14) | $Pc$ (No. 7) |
| $a$ [Å] | 9.5318(7) | 11.4353(12) |
| $b$ [Å] | 14.0508(13) | 20.9665(19) |
| $c$ [Å] | 21.3711(16) | 13.0248(14) |
| $\beta$ [°] | 97.134(9) | 97.796(12) |
| $V$ [Å$^3$] | 2840.1(4) | 3093.9(5) |
| $Z$ | 4 | 4 |
| $F(000)$ | 1592 | 1644 |
| $\lambda$ [Å] | 0.71073 | 0.71073 |
| $T$ [K] | 193(2) | 293(2) |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.877 | 1.775 |
| $\mu$ [mm$^{-1}$] | 2.976 | 2.734 |
| transmission range | 0.3179 – 0.7824 | 0.5066 – 0.7830 |
| $\theta$ limits [°] | 2.60 – 25.98 | 2.04 – 26.13 |
| reflections collected | 22463 | 24763 |
| independent refls | 5417 | 11 397 |
| $R_{int}$ | 0.0304 | 0.0311 |
| observed reflections [$I > 2\sigma(I)$] | 4643 | 9657 |
| parameters | 391 | 811 |
| GOF on $F^2$ | 0.981 | 1.036 |
| observed reflections | 4469 | 3425 |
| $R$ [$I > 2\sigma(I)$] | 0.0260 | 0.0273 |
| $wR2$ (all data) | 0.0586 | 0.0560 |
| Flack parameter | – | – 0.010(5) |
| $(\Delta/\rho)$max/min [e Å$^{-3}$] | 1.106/ – 1.024 | 0.789/ – 1.320 |

$^2_o - F^2_c)^2]/\Sigma[w(F^2_o)^2]\}^{1/2}$, GOF $= \{\Sigma[w(F^2_o - F^2_c)^2]/(n-p)]\}^{1/2}$, where $n$ is the number of reflections and $p$ is the number of parameters).

CCDC 183351 (**1**) and CCDC 183352 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

## Acknowledgements

[1] a) R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, *27*, 447; b) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347; c) M. Sakamoto, K. Manseki, H. Okawa, *Coord. Chem. Rev.* **2001**, *219 – 221*, 379.
[2] H. Okawa, H. Furutachi, D. E. Fenton, *Coord. Chem. Rev.* **1998**, *174*, 51, and references therein.
[3] a) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Chem. Eur. J.* **1998**, *4*, 1616; b) D. Cunningham, P. McArdle, M. Mitchell, N. N. Chonchubhair, M. O'Gara, F. Franceschi, C. Floriani, *Inorg. Chem.* **2000**, *39*, 1639; c) M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba, H. Okawa, *J. Chem. Soc. Dalton Trans.* **2000**, 259; d) T. Kido, S. Nagasato, Y. Sunatsuki, N. Matsumoto, *Chem. Commun.* **2000**, 2113.
[4] a) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1996**, *35*, 2400; b) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 4284; c) J.-P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* **2000**, *39*, 165; d) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **2000**, *39*, 169; e) J.-P. Costes, F. Dahan, B. Donnadieu, J. García-Tojal, J.-P. Laurent, *Eur. J. Inorg. Chem.* **2001**, 363; f) J.-P. Costes, J. M. Clemente-Juan, F. Dahan, F. Dumestre, J. P. Tuchagues, *Inorg. Chem.* **2002**, *41*, 2886 .
[5] a) E. Eichhorn, A. Rieker, B. Speiser, *Z. Anorg. Allg. Chem.* **1997**, *623*, 810; b) H. Furutachi, S. Fujinami, M. Suzuki, H. Okawa, *J. Chem. Soc. Dalton Trans.* **2000**, 2761.
[6] J. Gomes, B. de Castro, *Inorg. Chem.* **2000**, *39*, 1994.
[7] D. A. Annis, E. N. Jacobsen, *J. Am. Chem. Soc.* **1999**, *121*, 4147.
[8] a) T. Yi, S. Gao, B. G. Li, *Polyhedron* **1998**, *17*, 2243; b) B.-Q. Ma, S. Gao, O. Bai, H.-L. Sun, G.-X. Xu, *J. Chem. Soc. Dalton Trans.* **2000**, 1003.
[9] a) E. K. Brechin, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1997**, 1665; b) J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *C. R. Acad. Sci. Ser IIc.* **1998**, *1*, 417; c) S. Rigault, C. Piguet, G. Bernardinelli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **2000**, 4587; d) Y. Cui, G. Chen, J. Ren, Y. Qian, J. Huang, *Inorg. Chem.* **2000**, *39*, 4165.
[10] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
[11] a) W. Clegg, P. A. Hunt, B. P. Straughan, M. A. Mendiola, *J. Chem. Soc. Dalton Trans.* **1989**, 1127; b) R. C. Mehrotra, R. Bohra, *Metal Carboxylates*, Academic Press, London and New-York, **1983**, p. 271.
[12] M. Kotani, *J. Phys. Soc. Japan* **1949**, *4*, 293.
[13] J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii, B. S. Tsukerblat, *J. Phys. Chem. A* **1998**, *102*, 200.
[14] R. L. Carlin, *Magnetochemistry*, Springer, New York, **1986**.
[15] *Theory and Applications of Molecular Magnetism* (Eds.: E. A. Boudreaux, L. N. Mulay), Wiley-Interscience: New York, **1976**.
[16] a) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, *Inorg. Chem.* **1999**, *38*, 6081; b) J. J.; Borrás-Almenar, J. M.; Clemente-Juan, E. Coronado, B. S. Tsukerblat, *J. Comput. Chem.* **2001**, *22*, 985.
[17] MINUIT Program: A System for Function Minimization and Analysis of the Parameters Errors and Correlations: F. James, M. Roos, *Comput. Phys. Commun.* **1975**, *10*, 345.
[18] P. Guerriero, S. Tamburini, P. A. Vigato, U. Russo, C. Benelli, *Inorg. Chim. Acta* **1993**, *213*, 279.
[19] P. Pascal, *Ann. Chim. Phys.* **1910**, *19*, 5.
[20] a) P. Garge, R. Chikate, S. Padhye, J.-M. Savariault, P. de Loth, J.-P. Tuchagues, *Inorg.Chem.* **1990**, *29*, 3315; b) J. Aussoleil, P. Cassoux, P. de Loth, J.-P. Tuchagues, *Inorg. Chem.* **1989**, *28*, 3051.
[21] Stoe, IPDS Manual, Version 2.93, Stoe & Cie, Darmstadt (Germany), **1997**.
[22] Stoe, X-SHAPE, Crystal Optimisation for Numerical Absorption Correction, Revision 1.01, Stoe & Cie, Darmstadt (Germany), **1996**.
[23] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, (Germany), **1990**.
[24] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Göttingen (Germany), **1997**.
[25] *International Tables for Crystallography, Vol. C*, Kluwer Academic, Dordrecht (The Netherlands), **1992**.