Two New Diphenoxo-Bridged Discrete Dinuclear $Cu^{II}Gd^{III}$ Compounds with Cyclic Diimino Moieties: Syntheses, Structures, and Magnetic Properties

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Two Schiff base compartmental ligands, H_2L^1 and H_2L^2, derived from the condensation of 3-ethoxysalicylaldehyde with 1,2-diaminocyclohexane and orthophenylenediamine, respectively, have been utilized to isolate two diphenoxo-bridged discrete dinuclear $Cu^{II}Gd^{III}$ complexes, $[Cu^{II}(H_2O)L^1Gd^{III}(NO_3)_3]$ (**3**) and $[Cu^{II}L^2Gd^{III}(NO_3)_3]$ (**4**). This is the first report on the 3d-4f compounds derived from compartmental Schiff base ligands with cyclic diamines. The compounds **3** and **4** crystallize in the triclinic $P\bar{1}$ and orthorhombic $Pna2(1)$ space groups, respectively, with the following unit cell parameters – **3**: a = 8.8713(2) Å, b = 12.8399(3) Å, c = 14.0067(3) Å, α = 80.6649(5)°, β = 77.4059(5)°, γ = 76.8879(5)°, and Z = 2; **4**: a = 9.2210(1) Å, b = 16.5407(2) Å, c = 19.9248(4) Å, and Z = 4. Structural analysis reveals that both are discrete dinuclear complexes. In **3**, one water molecule is coordinated to the copper(II) ion to result in a square-pyramidal coordination geometry, while the geometry of the coppe(II) center in **4** is square planar. In both complexes, the gadolinium(III) center has an O_{10} coordination environment. In contrast to expectation, although the N_2O_2 cavity affords a better planar environment for the copper(II) center in **4**, the bridging moiety in complex **3** is more planar than that in **4** or in most of the previously reported examples (the dihedral angle between two CuO_2Gd planes: 2.1° for **3** and 7.1° for **4**). Variable-temperature and variable-field magnetic measurements reveal that the metal centers in both the complexes are ferromagnetically coupled (J values: 6.3 cm^{-1} for **3** and 5.4 cm^{-1} for **4**; $H = -2JS_{Cu}\cdot S_{Gd}$). Interestingly, complex **3** exhibits strongest ferromagnetic interaction among the related compounds.

Introduction

With the exception of a few examples of carboxylate-bridged dimers,[1] all other reported discrete dinuclear 3d-4f complexes have been derived from Schiff base ligands.[2–19] In these Schiff base compounds, the steric effects imposed by complete encapsulation of the dinuclear core,[2,3] alkyl substituents on the lateral diiminoalkane chain,[4–16] the presence of an apical fifth ligand (1-methyl imidazole, methanol or acetone) coordinated to the square-planar copper(II) center,[6,17] or the distortion of the copper(II) environment from a square plane to tetrahedron have been argued to be the governing factors that stabilize the discrete dinuclear cores.[18]

Costes et al. reported a number of discrete 3d-4f compounds derived from the compartmental Schiff base ligands obtained on condensation of 3-methoxy/ethoxysalicylaldehyde with diaminoalkanes that have alkyl substituents on the lateral alkane chain.[4–16] There is also a recent example in which a discrete $Cu^{II}Gd^{III}$ compound has been synthesized by using the planar diamino chain provided by *S*-methylisothiosemicarbazide.[19] We reported a $Cu^{II}Gd^{III}$ compound derived from *N*,*N′*-ethylenebis(3-ethoxysalicylaldimine) with no alkyl substituent on the lateral chain.[20] In this complex, although the metal ions are well separated, there exists a weak intermolecular antiferromagnetic interaction, probably due to the semicoordination of one nitrate oxygen of one molecule to the copper(II) center of another dinuclear unit. The studies of the reported compounds reveal that although the nature of interaction is ferromagnetic in most cases,[2–20] the ferromagnetic behavior is not intrinsic; it depends on the environment of the metal ions and the structural parameters, and the behavior may also be antiferromagnetic.[14,15] It has also been realized that the dihedral angle between the CuO_2 and LnO_2 planes plays the crucial role in determining the nature and magnitudes of the exchange interactions.[10,17]

Although several acyclic diamines have been used to prepare Schiff base ligands that can stabilize discrete 3d-4f

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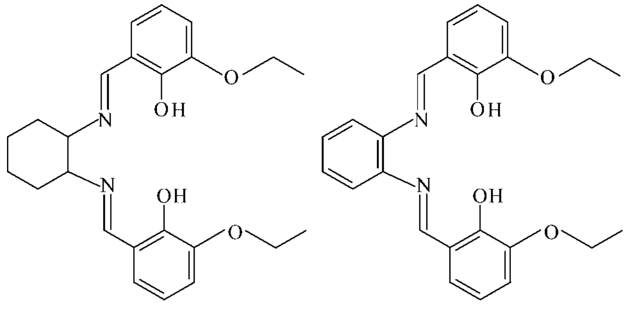
complexes, cyclic diamines such as 1,2-diaminocyclohexane or orthophenylenediamine have still not been utilized. By using two compartmental Schiff base ligands, H_2L^1 and H_2L^2, derived from the condensation of 3-ethoxysalicylaldehyde with 1,2-diaminocyclohexane and orthophenylenediamine, respectively, we have isolated two new heteronuclear $Cu^{II}Gd^{III}$ complexes, $[Cu^{II}(H_2O)L^1Gd^{III}(NO_3)_3]$ (**3**) and $[Cu^{II}L^2Gd^{III}(NO_3)_3]$ (**4**) (Scheme 1). We were particularly interested in the designed syntheses of 3d-4f systems that exhibit ferromagnetic interactions of different strengths.



H_2L^1 H_2L^2

Scheme 1. Chemical structures of H_2L^1 and H_2L^2.

Results and Discussion

Description of the Structures of 3 and 4

The X-ray crystal structures of the two complexes show that both are dinuclear neutral complexes of copper(II) and gadolinium(III). ORTEP representations of **3** and **4** along with atom labels are shown in Figure 1 and Figure 2, respectively. The selected bond lengths and angles are listed in Table 1. In **3**, the cyclohexane moiety exists in a diequatorial *trans* configuration indicating that the condensation takes place with the diequatorial *trans* form of the diamine. The metal centers in both the complexes are doubly bridged by two phenoxo oxygen atoms provided by the ligands. The inner N_2O_2 cavity is occupied by copper(II), while gadolinium(III) occupies the open and larger position of the dinucleating compartmental ligands, $[L^1]^{2-}$ or $[L^2]^{2-}$. Because of the significant difference in size, the bond lengths of copper(II) and gadolinium(III) with bridging phenoxo oxygen atoms are significantly different [**3**: Cu–O(1) = 1.915(2), Cu–O(2) = 1.909(2), Gd–O(1) = 2.380(2), Gd–O(2) = 2.343(2) Å; **4**: Cu–O(1) = 1.884(4), Cu–O(2) = 1.903(5), Gd–O(1) = 2.368(5), Gd–O(2) = 2.419(4) Å].

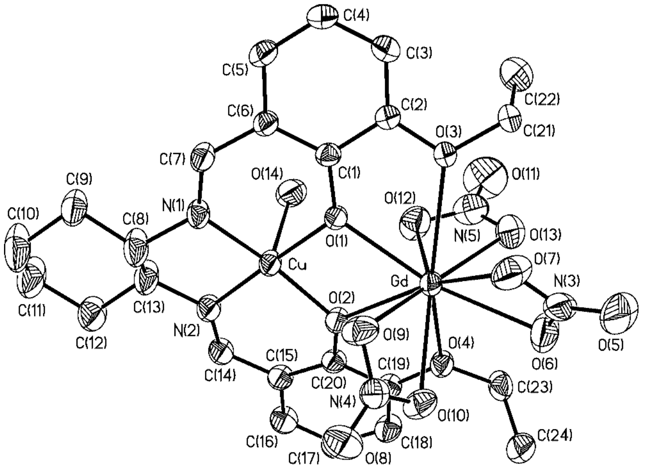


Figure 1. ORTEP representation (40% thermal ellipsoids) of **3** with atom-labeling schemes.

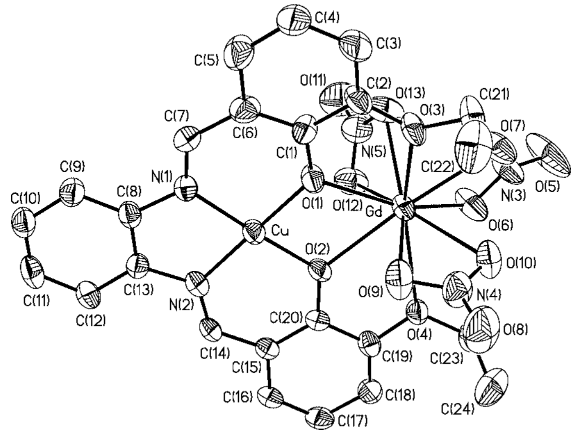


Figure 2. ORTEP representation (40% thermal ellipsoids) of **4** with atom-labeling schemes.

The gadolinium(III) ion in both compounds has an O_{10} coordination environment. In addition to the phenoxo groups, two ethoxy oxygen atoms coordinate to this metal center. Two oxygen atoms each from the three nitrate groups chelate to gadolinium(III) to complete the decacoordination geometry. There are, as usual, three sets of Gd–O bond lengths.[4–13,18] The shortest and longest bonds involve the linking of the lanthanide with the bridging phenoxo oxygen atoms [**3**: Gd–O(1) = 2.380(2), Gd–O(2) = 2.343(2) Å; **4**: Gd–O(1) = 2.368(5), Gd–O(2) = 2.419(4) Å] and the ethoxy moieties [**3**: Gd–O(3) = 2.712(2), Gd–O(4) = 2.568(2) Å; **4**: Gd–O(3) = 2.544(4), Gd–O(4) = 2.701(4) Å], respectively, while the Gd–O(nitrates) separations [**3**: 2.450(3)–2.554(3) Å; **4**: 2.441(6)–2.551(5) Å] are of intermediate length. The Gd–O (ethoxy, nitrate or phenoxo) bond lengths are almost similar to the bond lengths observed in previously reported examples.[6–15,20]

As mentioned before, copper(II) occupies the N_2O_2 cavities of the compartmental ligands in **3** and **4**. The ranges of the *cisoid* [84.23(9)°–96.82(11)°] and *transoid* [178.41(11)° and 168.44(12)°] angles in the N_2O_2 cavity, and the dihedral angles between the CuN(1)N(2) and CuO(1)O(2) planes (δ_1, 11.5°) or the CuN(1)O(1) and CuN(2)O(2) planes (δ_2, 11.7°) indicate that the N_2O_2 moiety affords an approximate square plane to copper(II) in **3**; the donor centers are alternatively above and below the mean N_2O_2 plane by an average of 0.086 Å, while the copper(II) is 0.1 Å below this square plane. In contrast, the N_2O_2 environment in **4** is more planar. Although the range of the *cisoid* angles [83.0(2)°–96.1(2)°] in **4** is similar to that in **3**, the *transoid*

Table 1. Selected bond lengths [Å] and angles [°] for **3** and **4**.

	3	4
Cu–O(1)	1.915(2)	1.884(4)
Cu–O(2)	1.909(2)	1.903(5)
Cu–N(1)	1.918(3)	1.916(6)
Cu–N(2)	1.922(3)	1.913(5)
Cu–O(14)	2.535(3)	
Gd–O(1)	2.380(2)	2.368(5)
Gd–O(2)	2.343(2)	2.419(4)
Gd–O(3)	2.712(2)	2.544(4)
Gd–O(4)	2.568(2)	2.701(4)
Gd–O(Nitrate)	2.450(3)–2.554(3)	2.441(6)–2.551(5)
Cu–O(1)–Gd	104.18(9)	107.9(2)
Cu–O(2)–Gd	105.77(9)	105.28(18)
O(14)–Cu–O((1)	89.56(10)	
O(14)–Cu–O((2)	94.65(10)	
O(14)–Cu–N((1)	96.82(11)	
O(14)–Cu–N((2)	91.60(12)	
δ[a]	2.1	7.1
δ_1[a]	11.5	1.8
δ_2[a]	11.7	1.9
Cu···Gd[b]	3.401	3.449
Cu···Cu[b]	6.469	6.695
Cu···Gd[b]	7.657	7.192
Gd···Gd[b]	8.871	9.221

[a] δ, δ_1, δ_2 are the dihedral angles between CuO(1)O(2) and GdO(1)O(2), CuN(1)N(2) and CuO(1)O(2), and CuN(1)O(1) and CuN(2)O(2) planes, respectively. [b] Intramolecular interaction. [c] Shortest intermolecular interaction.

angles deviate only by a small degree from 180°. In addition, the dihedral angles δ_1 (1.8°) and δ_2 (1.9°) are close to 0°, which indicates an almost planar copper(II) environment afforded by the hexadentate ligand in **4**; the deviations of the donor centers and the metal ion is 0.01 Å (average). As expected, the copper(II) environment in the N_2O_2 cavity is more planar in **4**. However, interestingly, the planarity of the bridging moieties does not parallel our expectation; the dihedral angles (δ) between the CuO(1)O(2) and GdO(1) O(2) planes in **3** and **4** are 2.1° and 7.1°, respectively. Among the diphenoxo-bridged $M^{II}Ln^{III}$ complexes reported so far, the bridging moiety in one $Cu^{II}Gd^{III}$ complex that has a δ value of 1.7° is more planar than that in **3**.[10] The dihedral angles in other related compounds range from 4.7° to 47.4°.[7–16,20]

In addition to the four donor centers provided by the Schiff base ligand, one water molecule is coordinated to the apical position of the copper(II) center in **3** to result in a square-pyramidal coordination environment. As expected, due to Jahn–Teller distortion, the Cu–O(water) bond length [2.535(3) Å] is much longer than the bond lengths [1.909(2)–1.922(3) Å] of the metal ion with the donor centers in the equatorial plane. The bond angles of the Cu–O(water) axis with the planar Cu–N or Cu–O bonds lie between 89.56(10)° and 96.82(11)° indicating the square-pyramidal geometry of the copper(II) ion in **3**. In contrast, the coordination environment in **4** is square planar.

There exist several types of common intra- and intermolecular hydrogen bonds in both **3** and **4** that result in self-assembled supramolecular structures (one-dimensional for **4** and two-dimensional for **3**; see supporting information for discussion and figures). However, the shortest intermolecular metal···metal distances in **3** (Gd···GdA = 8.871 Å, Cu···GdA = 7.657 Å, Cu···CuC = 6.469 Å; symmetry: A, *x* – 1, *y*, *z*; C, 1 – *x*, –*y*, 1 – *z*) or **4** (Cu···CuA = 6.695 Å, Cu···GdA = 7.192 Å, Gd···GdB = 9.221 Å; symmetry: A, *x* – 0.5, 0.5 – *y*, *z*; B, *x* – 1, *y*, *z*) are long enough to consider the dinuclear cores in both complexes as discrete.

Magnetic Properties

The variable-temperature (2–300 K) magnetic behavior of **3** and **4** are shown in Figure 3 and Figure 4, respectively, in the form of $\chi_M T$ versus T plots. The $\chi_M T$ values at 300 K for both complexes (8.51 $cm^3 mol^{-1} K$ for **3** and 8.34 $cm^3 mol^{-1} K$ for **4**) are slightly higher than the calculated value (8.25 $cm^3 mol^{-1} K$) for two uncoupled spins with $g = 2$. With a decrease in temperature from 300 K to 85 K, the $\chi_M T$ values slowly increase to reach 8.80 $cm^3 mol^{-1} K$ and 8.55 $cm^3 mol^{-1} K$ for **3** and **4**, respectively. On further lowering of the temperature, $\chi_M T$ increases sharply to 10.31 $cm^3 mol^{-1} K$ at 10 K for **3** and 9.97 $cm^3 mol^{-1} K$ at 2 K

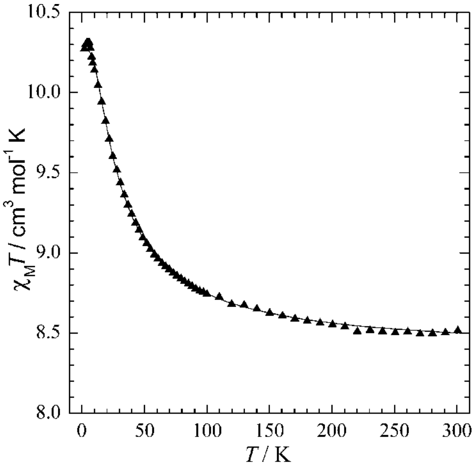


Figure 3. Experimental (triangles) and calculated (solid lines) $\chi_M T$ vs. T plots for $[Cu^{II}(H_2O)L^1Gd^{III}(NO_3)_3]$ (**3**).

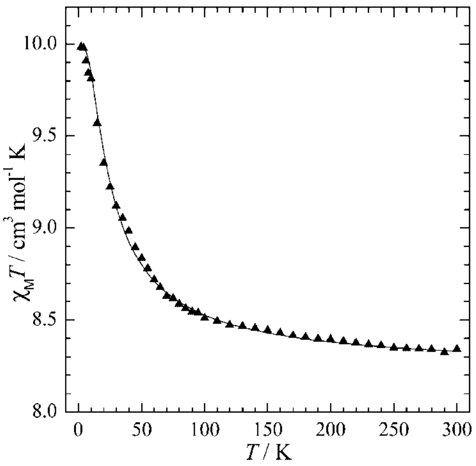


Figure 4. Experimental (triangles) and calculated (solid lines) $\chi_M T$ vs. T plots for $[Cu^{II}L^2Gd^{III}(NO_3)_3]$ (**4**).

for **4**. Below 10 K, the $\chi_M T$ values of **3** are practically constant. As there is no orbital contribution in the ground state of Gd^{III}, the trends for the magnetic behavior indicate a ferromagnetic interaction between the metal centers in both complexes. The higher value of $\chi_M T$ at 300 K is also consistent with the ferromagnetic interaction between the spin carriers. For **4**, the larger value of $\chi_M T$ at 300 K is also associated with the larger value of g_{Cu} (vide infra).

Using the spin-only HDVV Hamiltonian [$H = -2JS_{Cu}\cdot S_{Gd} + \beta(g_{Cu}\cdot S_{Cu} + g_{Gd}\cdot S_{Gd})H$], the theoretical expression of χ_M for the $Cu^{II}Gd^{III}$ system may be derived as:

$$\chi_M = \frac{4N\beta^2}{k(T-\theta)} \times \frac{7g_3{}^2 + 15g_4{}^2\exp(8J/kT)}{7+9\exp(8J/kT)} \qquad (1)$$

where g_4 and g_3 are the g values of the pair states $S_T = 4$ and $S_T = 3$, respectively, which, in turn, are related to the local g values as:

$$g_3 = \frac{9g_{Gd} - g_{Cu}}{8}$$

$$g_4 = \frac{7g_{Gd} + g_{Cu}}{8}$$

Least-squares fitting of the experimental data with Equation (1) leads to $J = 6.3\ cm^{-1}$, $g_{Gd} = 2.008$, $g_{Cu} = 2.15$ for **3** and $J = 5.4\ cm^{-1}$, $g_{Gd} = 1.997$, $g_{Cu} = 2.0$ for **4**;[21] the agreement factor defined as $[\sum\{(\chi_M T)_{obs} - (\chi_M T)_{calc}\}^2 / \sum(\chi_M T)_{obs}{}^2]$ is 1.9×10^{-3} and 2.9×10^{-3} for **3** and **4**, respectively.

The field dependence of magnetization (up to 60000 G for **3** and 55000 G for **4**) at 5 K was measured. In Figure 5 and Figure 6, the magnetization data have been compared with the sum of the Brillouin functions of isolated Gd^{III} and Cu^{II}, as well as with the Brillouin function of the $S_T = 4$ state. The experimental magnetization is always greater than the sum of the noncorrelated spin system and matches well with the calculated values of the $S_T = 4$ state. The analysis confirms the existence of ferromagnetic exchange interactions between Cu^{II} and Gd^{III} in both complexes.

Kahn suggested that because the coupling is dependent on the exchange transfer integral between the 3d orbital of copper(II) and the 4f orbitals of gadolinium(III), the magnitude of J in systems with a CuO_2Gd moiety, like in **3** and **4**, should be a function of the dihedral angle (δ) between the CuO_2 and GdO_2 planes.[17] Later, on analyzing the coupling constants of a limited numbers of structurally characterized diphenoxo-bridged complexes, Costes proposed an exponential relationship, $2J = Ae^{-B\delta}$ ($A = 11.5$, $B = 0.054$).[10] According to this correlation, J should be $5.15\ cm^{-1}$ for **3** ($\delta = 2.1°$) and $3.9\ cm^{-1}$ for **4** ($\delta = 7.1°$). The experimental values of $6.3\ cm^{-1}$ (**3**) and $5.4\ cm^{-1}$ (**4**) are not very different from this hypothesis. For the $Cu^{II}Gd^{III}$ complex with the smallest dihedral angle (1.7°) reported so far, J is $5\ cm^{-1}$.[10] However, compound **4** with a dihedral angle of 2.1° exhibits the strongest ferromagnetic interaction among the reported examples.

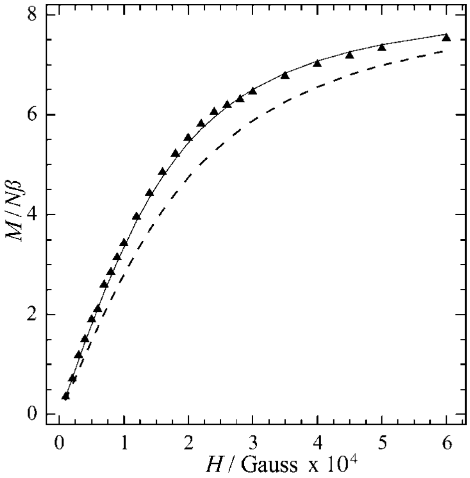


Figure 5. Field dependence of the magnetization at 5 K for $[Cu^{II}(H_2O)L^1Gd^{III}(NO_3)_3]$ (**3**). The solid and dashed lines represent the theoretical magnetization curves for the $S_T = 4$ state and the isolated spin system, respectively.

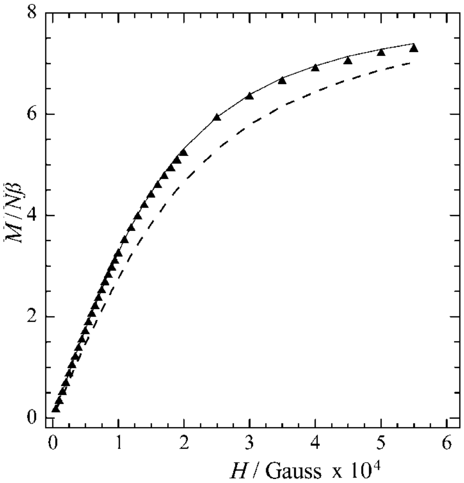


Figure 6. Field dependence of the magnetization at 5 K for $[Cu^{II}L^2Gd^{III}(NO_3)_3]$ (**4**). The solid and dashed lines represent the theoretical magnetization curves for the $S_T = 4$ state and the isolated spin system, respectively.

Conclusions

Two Schiff base compartmental ligands, H_2L^1 and H_2L^2, derived from the condensation of 3-ethoxysalicylaldehyde with 1,2-diaminocyclohexane and orthophenylenediamine, respectively, have been utilized to isolate two diphenoxo-bridged dinuclear $Cu^{II}Gd^{III}$ complexes, $[Cu^{II}(H_2O)L^1Gd^{III}(NO_3)_3]$ (**3**) and $[Cu^{II}L^2Gd^{III}(NO_3)_3]$ (**4**). Cyclic diamines have for the first time been utilized to obtain discrete dinuclear 3d-4f complexes. We expected that **3** would be a discrete $Cu^{II}Gd^{III}$ complex with high δ value that would exhibit a weak ferromagnetic interaction. In contrast, as $[L^2]^{2-}$ should afford a better square plane to copper(II), we expected a more planar bridging moiety in **4** so that this complex would exhibit a stronger ferromagnetic interaction. In contrast to our expectation, although the N_2O_2 cavity affords a better square plane to the copper(II) center in **4**, the bridging moiety in complex **3** is more planar than that in **4** or in most of the previously reported examples. Complex **3** exhibits the strongest ferromagnetic interaction (J = 6.3 cm^{-1}; $H = -2JS_{\mathrm{Cu}}\cdot S_{\mathrm{Gd}}$) among the related compounds reported so far.

Experimental Section

Materials and Physical Methods: All the reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H, N) analyses were performed with a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Perkin–Elmer RXIFT spectrophotometer with samples as KBr disks. Variable-temperature (2–300 K) magnetic susceptibility measurements under a fixed field strength of 0.5 T and the field-dependence magnetization experiments (up to 60000 G for **3** and 55000 G for **4**) at 5 K were carried out with a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

Synthesis of the Complexes

[Cu^{II}L^1]·H$_2$O (1): A methanol solution (10 mL) of an equimolar mixture of *cis*- and *trans*-1,2-diaminocyclohexane (0.475 g, 5 mmol) was mixed with a methanol solution (30 mL) of 3-ethoxysalicylaldehyde (1.66 g, 10 mmol), and the mixture was refluxed for 30 min. After cooling to room temperature, an aqueous solution (10 mL) of copper(II) acetate monohydrate (1.0 g, 5 mmol) was added dropwise to the resulting brown solution with stirring. An ash-colored precipitate was separated immediately. After stirring for 1 h, the compound was collected by filtration and air dried. Recrystallization from dimethylformamide resulted in a brown crystalline compound. Yield: 2.1 g (86%). $C_{24}H_{30}N_2O_5Cu$ (490.06): calcd. C 58.82, H 6.17, N 5.71; found C 58.68, H 6.25, N 5.83. IR (cm^{-1}, KBr): ν_{OH}(water), 3541 (m), 3501 (m); ν_{CH}(cyclohexane), 3048 (w), 2985 (w), 2931 (m), 2867 (w); $\nu_{\mathrm{C=N}}$, 1623 (s).

[Cu^{II}L^2]·H$_2$O (2): This compound was prepared in a similar way to **1**, except with *o*-phenylenediamine instead of 1,2-diaminocyclohexane. Color: brown. Yield: 2.18 g (90%). $C_{24}H_{24}N_2O_5Cu$ (484.01): calcd. C 59.55, H 4.99, N 5.78; found C 59.67, H 4.90, N 5.71. IR (cm^{-1}, KBr): ν_{OH}(water), 3506 (w), 3461 (w); $\nu_{\mathrm{C=N}}$, 1606 (s).

[Cu^{II}(H$_2$O)L^{1}Gd^{III}(NO$_3$)$_3$] (3): To a stirred suspension of 1 (0.122 g, 0.25 mmol) in acetone (20 mL) was added a methanol solution (10 mL) of gadolinium(III) nitrate hexahydrate (0.135 g, 0.3 mmol). The color of the solution changed to red. After 20 min of stirring, the solution was filtered to remove the suspended particles and was kept at room temperature for slow evaporation. After a few days, an orange crystalline compound containing diffractable single crystals appeared that was collected by filtration and air dried. Yield: 0.1 g (48%). $C_{24}H_{30}N_5O_{14}CuGd$ (833.32): calcd. C 34.59, H 3.63, N 8.40; found C 34.70, H 3.55, N 8.31. IR (cm^{-1}, KBr): ν_{OH}(water), 3500 (w), 3480 (w); $\nu_{\mathrm{C=N}}$, 1632 (s); ν_{Nitrate}, 1393 (s).

[Cu^{II}L^{2}Gd^{III}(NO$_3$)$_3$] (4): This compound was prepared in a similar way to **3**, except with **2** instead of **1**. Color: orange. Yield: 0.14 g (69%). $C_{24}H_{22}N_5O_{13}CuGd$ (809.26): C 35.62, H 2.74, N 8.65; found: C 35.53, H 2.81, N 8.72. IR (cm^{-1}, KBr): $\nu_{\mathrm{C=N}}$, 1608 (s); ν_{Nitrate}, 1388 (s).

Crystal Structure Determination: Pertinent crystallographic data of both complexes are summarized in Table 2. Diffraction data for **3** and **4** were collected on a Bruker SMART CCD and a NONIUS Kappa CCD diffractometer, respectively, in the ω–2θ scan mode using graphite monochromated Mo-K_α radiation with λ = 0.71073 Å. The accurate unit cells were obtained by means of least-squares fittings of 25 centered reflections. The intensity data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections were made from ψ-scans. A total of 20780 reflections were collected for **3** in the range 2θ = 3.0–55.0° with $-11 \le h \le 11$, $-16 \le k \le 16$, and $-18 \le l \le 18$, of which 6930 independent reflections (R_{int} = 0.0275) were used for structure determinations. In the case of **4**, among 18891 of the total reflections collected in the 2θ range of 4.92–55.0° with $-11 \le h \le 11$, $-21 \le k \le 21$, and $-25 \le l \le 25$, 6767 were independent (R_{int} = 0.0612). The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods based on F^2 with the programs SHELXS-97 and SHELXL-97.[22,23] The final least-squares refinements ($R1$) based on $I > 2\sigma(I)$ converged to 0.0255 for **3** and 0.0425 for **4**. CCDC-250133 (**3**) and CCDC-250132 (**4**) contain the supple-

Table 2. Crystallographic data for **3** and **4**.

	3	**4**
Formula	$C_{24}H_{30}N_5O_{14}CuGd$	$C_{24}H_{22}N_5O_{13}CuGd$
Molecular weight	833.32	809.26
Crystal color	orange	orange
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pna*2(1)
a [Å]	8.8713(2)	9.2210(1)
b [Å]	12.8399(3)	16.5407(2)
c [Å]	14.0067(3)	19.9248(4)
α [°]	80.6649(5)	90.00
β [°]	77.4059(5)	90.00
γ [°]	76.8879(5)	90.00
V [Å^3]	1505.77(6)	3038.97(8)
Z	2	4
$D_{\mathrm{calcd.}}$ [g cm^{-3}]	1.838	1.769
F(000)	828	1592
μ [cm^{-1}]	2.966	2.934
Crystal size [mm]	0.37 × 0.25 × 0.08	0.15 × 0.07 × 0.02
Temperature [K]	295(2)	295(2)
Final R indices [$I > 2\sigma(I)$]	$R1$[a] = 0.0255, w$R2$[b] = 0.0556	$R1$[a] = 0.0425, w$R2$[b] = 0.0820
R indices (all data)	$R1$[a] = 0.0400, w$R2$[b] = 0.0679	$R1$[a] = 0.0804, w$R2$[b] = 0.0979

[a] $R1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

mentary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Y.-Y. Yang, Y.-L. Wu, L.-S. Long, X.-M. Chen, *J. Chem. Soc., Dalton Trans.* **1999**, 2005.
[2] S. J. Archibald, A. J. Blake, S. Parsons, M. Schroder, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* **1997**, 173.
[3] Q.-Y. Chen, Q.-H. Luo, Z.-L. Wang, J.-T. Chen, *J. Chem. Soc. Chem. Commun.* **2000**, 1033.
[4] R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, 447.
[5] M. Sakamoto, K. Manseki, H. Ōkawa, *Coord. Chem. Rev.* **2001**, 219–221, 379.
[6] J.-P. Costes, A. Dupuis, J.-P. Laurent, *Chem. Eur. J.* **1998**, 1616.
[7] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1996**, *35*, 2400.
[8] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 3429.
[9] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 4284.
[10] J.-P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* 2000, *39*, 165.
[11] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *New J. Chem.* **1998**, *22*, 1525.
[12] J.-P. Costes, A. Dupuis, J.-P. Laurent, *Eur. J. Inorg. Chem.* **1998**, 1543.
[13] J.-P. Costes, A. Dupuis, J.-P. Laurent, *J. Chem. Soc., Dalton Trans.* **1998**, 735.
[14] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **2000**, *39*, 169.
[15] J.-P. Costes, F. Dahan, B. Donnadieu, J. Garcia-Tojal, J.-P. Laurent, *Eur. J. Inorg. Chem.* **2001**, 363.
[16] G. Novitchi, S. Shova, A. Caneschi, J.-P. Costes, M. Gdaniec, N. Stanica, *J. Chem. Soc., Dalton Trans.* **2004**, 1194.
[17] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930.
[18] M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Nishida, Y. Sakiyama, M. Sakai, Y. Sadaoka, M. Ohba, H. Ōkawa, *J. Chem. Soc., Dalton Trans.* **2000**, 259.
[19] J.-P. Costes, F. Dahan, G. Novitchi, V. Arion, S. Shova, J. Lipkowski, *Eur. J. Inorg. Chem.* **2004**, 1530.
[20] S. Mohanta, H.-H. Lin, C.-J. Lee, H.-H. Wei, *Inorg. Chem. Commun.* **2002**, *5*, 585.
[21] Global minimization takes place with $g = 2.15$. If the value of g is forced to be smaller, the quality of the simulation becomes more and more poor.
[22] G. M. Sheldrick, *SHELXS-97: A Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.
[23] G. M. Sheldrick, *SHELXL-97: A Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

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