

## Synthesis, Structure, and Magnetic Properties of Heterometallic Dicyanamide-Bridged Cu–Na and Cu–Gd One-Dimensional Polymers

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The monometallic precursors  $L^1Cu$  and  $L^2Cu$  ( $L^1H_2$  standing for 1,3-bis((3-ethoxysalicylidene)amino) propane and  $L^2H_2$  standing for 1,2-bis((3-methoxysalicylidene)amino) ethane) react with sodium dicyanamide (dca) ( $NaN_3C_2$ ), a mixture of gadolinium nitrate, and sodium dicyanamide to yield heterodinuclear  $L^2CuNa(NCNCN)$  and  $L^1CuGd(NO_3)(NCNCN)_2$  entities. The structural determination shows that two Cu–Na entities are linked by dca with an original  $\mu_{1,1}$  coordination mode, evidenced here for the first time, to yield tetranuclear complexes. Two hydrogen bonds operate between the water molecule coordinated to one of the sodium ions and the free nitrogen atoms of two dca ligands, yielding infinite zigzag chains. The structural determination of the Cu–Gd entities indicates that they are held together by two dca ligands, bridging alternately Cu to Gd and Gd to Gd cations, in the more common  $\mu_{1,5}$  mode to yield a one-dimensional (1D) network. The dca ligands are not able to transmit interaction between the magnetically active centers in these chains, which are the unique example of structurally characterized Cu–Gd complexes involving dca ligands.

### Introduction

Polymeric coordination compounds built from paramagnetic cations and cyanide units such as monocyanide<sup>1</sup> ( $CN^-$ ,  $S-CN^-$ ,  $O-CN^-$ ), dicyanamide<sup>1c,2</sup>  $[N(CN)_2]^-$ , silver(I) and copper(I) cyanide,<sup>1b,3</sup> tricyanomethanide<sup>1c,4</sup>  $[C(CN)_3]^-$ , tetracyanometalates<sup>1d,5</sup>  $[M(CN)_4]^{2-}$ , hexacyanometalates<sup>1,6</sup>  $[M(CN)_6]^{3-}$  ( $M = Fe, Cr, Mn$ ), heptacyanometalates ( $[Mo(CN)_7]^{4-}$ ), and other polycyanide anions or organic radicals (such as  $TCNQ^-$  (tetracyano-*p*-quinodimethanide) or  $TCNE^-$  (tetracyanoethylenide))<sup>7</sup> are the focus of intense research.

The dicyanamide ligand  $N(CN)_2^-$ , abbreviated as dca, has attracted continuous attention in the past four years for the buildup of interesting extended architectures.<sup>1,2</sup> Its versatile

coordination behavior and its ability to organize solids into polymeric structures with a rich diversity of magnetic properties have attracted interest toward this research area.

We have previously shown that compartmental Schiff base ligands, resulting from the reaction of 3-methoxysalicylaldehyde with different diamines, may yield discrete heterodinuclear 3d/alkali-metal and 3d/4f complexes<sup>8</sup> with the 3d ion coordinated in the  $N_2O_2$  site and the alkali-metal cation or the 4f ion in the  $O_2O_2$  site. The isolated complexes are formulated  $LMM'X$  or  $LMLnX_3$ ,  $L$  standing for the ligand,  $M$  for the 3d ion (mainly  $Ni^{2+}$  and  $Cu^{2+}$ ),  $M'$  for  $Na^+$ ,  $Li^+$ ,  $K^+$ ,  $Ln$  for the 4f ion, and  $X$  for the anionic species (mainly  $NO_3^-$  or  $ClO_4^-$ ). Recently, we have obtained polymeric heterometallic 3d/4f complexes by using anionic species such as thiocyanates and hexacyanometalates, and we have shown that their magnetic behavior is dominated by ferromagnetic interactions.<sup>9</sup> In the present study, we report on the syntheses, crystal structures, and magnetic properties of an original heterometallic (3d/4f) coordination polymer based on  $Cu^{II}-Gd^{III}$  units linked by dicyanamide ligands and of one tetranuclear  $[Cu^{II}-Na^I]_2$  species that contains a bridging dicyanamide acting in the  $\mu_{1,1}$  end-on fashion.

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## Experimental Section

All starting materials and solvents were purchased from Aldrich and were used without further purification.  $L^1Cu$  and  $L^2Cu$  complexes were prepared as described earlier<sup>8a</sup> using of 1,3-diaminopropane or 1,2-diaminoethane as diamine reactants.

**$L^1Cu \cdot H_2O$ .** Anal. Found: C, 56.3; H, 5.6; N, 6.1. Calcd for  $C_{21}H_{26}CuN_2O_5$ : C, 56.5; H, 5.8; N, 6.2. IR (4000–400  $cm^{-1}$  KBr):  $\nu(OH)$  3549, 3506;  $\nu(C=N)$  1624, 1610;  $\nu(C=C)$  1548;  $\nu(C_{Ph}-O)$  1244, 1223.

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- $L^2Cu \cdot H_2O$ .** Anal. Found: C, 53.1; H, 5.0; N, 6.8. Calcd for  $C_{18}H_{20}CuN_2O_5$ : C, 53.0; H, 4.9; N, 6.9. IR (4000–400  $cm^{-1}$  KBr):  $\nu(OH)$  ~3459;  $\nu(C=N)$  1644, 1602;  $\nu(C=C)$  1546;  $\nu(C_{Ph}-O)$  1241, 1217.
- $[(L^2CuNa(NCNCN))_2(H_2O)]$  (1).** A mixture of  $NaN(CN)_2$  (0.1 g, 1 mmol) and  $L^2Cu \cdot H_2O$  (0.41 g, 1 mmol) in methanol (5 mL) yielded a red solution that was filtered and set aside. The dark-red crystals that appeared 5 days later were filtered off and air-dried. Anal. Found: C, 49.0; H, 3.8; N, 14.2. Calcd for  $C_{40}H_{38}Cu_2N_{10}Na_2O_9$ : C, 49.2; H, 3.9; N, 14.4. IR (4000–400  $cm^{-1}$  KBr):  $\nu(OH)$  ~3435;  $\nu(C=N)$  2251, 2242, 2201, 2145;  $\nu(C=N)$  1628;  $\nu(C=C)$  1545;  $\nu(C_{Ph}-O)$  1242, 1219.
- $\{[L^1CuGd(NO_3)(NCNCN)_2](CH_3)_2CO\}_n$  (2).**  $NaN(CN)_2$  (0.27 g, 3 mmol) in  $H_2O$  (1.5 mL) was added to a solution of  $Gd(NO_3)_3 \cdot 6H_2O$  (0.45 g, 1 mmol) in acetone (100 mL). The solution was refluxed for 2 h, cooled to room temperature, and filtered off. To this solution was added  $L^1Cu \cdot H_2O$  (0.45 g, 1 mmol) dissolved in 80 mL of acetone. The resulting green solution was set aside. Its slow evaporation at room temperature yielded green-brown crystals 3 days later; they were isolated by filtration and air-dried. Anal. Found: C, 40.12; H, 3.41; N, 14.85. Calcd for  $C_{28}H_{30}CuGdN_9O_8$ : C, 39.97; H, 3.59; N, 14.98. IR (4000–400  $cm^{-1}$  KBr):  $\nu(OH)$  ~3408;  $\nu(C=N)$  2319, 2281, 2246, 2228, 2195, 2166;  $\nu(C=O)$  1716;  $\nu(C=N)$  1622;  $\nu(C=C)$  1564, 1559;  $\nu(C_{Ph}-O)$  1249, 1222, 1204;  $\nu_{as}(NO_2)$  1468;  $\nu_s(NO_2)$  1296;  $\nu(NO)$  1084.
- $[L^1CuGd(NO_3)_3(CH_3)_2CO]$  (3).**  $L^1Cu \cdot H_2O$  (0.24 g, 0.5 mmol) dissolved in acetone (50 mL) was slowly added to an acetone solution (20 mL) of  $Gd(NO_3)_3 \cdot 6H_2O$  (0.23 g, 0.5 mmol) under vigorous stirring. After partial evaporation of the solvent, the blue-green crystals that appeared were separated by filtration, washed with cold acetone, and air-dried. Anal. Found: C, 35.06; H, 3.46; N, 8.35. Calcd for  $C_{24}H_{30}CuGdN_5O_{14}$ : C, 34.59; H, 3.63; N, 8.40. IR (4000–400  $cm^{-1}$  KBr):  $\nu(OH)$  ~3408;  $\nu(C=N)$  1616;  $\nu(C=C)$  1558, 1540;  $\nu(C_{Ph}-O)$  1249, 1222, 1204;  $\nu_{as}(NO_2)$  1471;  $\nu_s(NO_2)$  1320;  $\nu(NO)$  1078.
- Physical Measurements.** Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse, France. Infrared spectra (4000–400  $cm^{-1}$ ) 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 superconducting quantum interference device (SQUID) magnetometer. All samples were 3-mm diameter pellets molded from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 0.5 (1) or 0.1 T (2, 3) applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.<sup>10a</sup> Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibility has been 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<sup>10b</sup> and with the MAGPACK program package<sup>10c,d</sup> in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-
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**Table 1.** Summary of Crystal Data and Refinement Details for **1**, **2**, and **3**

compound	<b>1</b>	<b>2</b>	<b>3</b>
empirical formula	C <sub>40</sub> H <sub>38</sub> Cu <sub>2</sub> N <sub>10</sub> Na <sub>2</sub> O <sub>9</sub>	C <sub>28</sub> H <sub>30</sub> CuGdN <sub>9</sub> O <sub>8</sub>	C <sub>24</sub> H <sub>30</sub> CuGdN <sub>5</sub> O <sub>14</sub>
<i>M</i>	975.86	841.40	833.32
temperature, K	293	180	180
wavelength, Å	0.71073	0.71073	0.71073
space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
<i>a</i> , Å	21.5284(17)	9.1546(18)	9.522(5)
<i>b</i> , Å	17.046(2)	13.015(3)	15.774(5)
<i>c</i> , Å	22.928(2)	13.400(3)	20.347(5)
$\alpha$ , deg	90	79.23(3)	90
$\beta$ , deg	90	85.15(3)	93.503(5)
$\gamma$ , deg	90	89.84(3)	90
<i>V</i> , Å <sup>3</sup>	8414.0(15)	1562.7(5)	3050(2)
<i>Z</i>	8	2	4
$\rho_{\text{(calcd)}}$ , Mg/m <sup>3</sup>	1.541	1.788	1.815
$\mu_{\text{Mo}}$ , mm <sup>-1</sup>	1.100	2.849	2.928
<i>F</i> (000)	4000	836	1656
crystal size, mm	0.50 × 0.45 × 0.40	0.60 × 0.60 × 0.20	0.30 × 0.30 × 0.20
$\theta$ range, deg	1.76 to 25.97	3.19 to 25.50	2.31 to 26.08
index ranges	0 ≤ <i>h</i> ≤ 26 0 ≤ <i>k</i> ≤ 20 0 ≤ <i>l</i> ≤ 28	−11 ≤ <i>h</i> ≤ 22 −15 ≤ <i>k</i> ≤ 15 −16 ≤ <i>l</i> ≤ 16	−10 ≤ <i>h</i> ≤ 11 −19 ≤ <i>k</i> ≤ 19 −25 ≤ <i>l</i> ≤ 24
number of reflections			
measured	8245	10899	23572
unique	8245	5797( <i>R</i> <sub>(int)</sub> =0.0595)	5599( <i>R</i> <sub>(int)</sub> =0.0302)
number of refined parameters	576	428	410
max and min transmission	0.999 and 0.869	0.600 and 0.280	0.861 and 0.614
GOF for <i>F</i> <sup>2</sup>	0.923	1.042	1.072
<i>R</i> <sup>a</sup>	0.0301	0.0392	0.0265
<i>wR</i> <sup>b</sup>	0.0499	0.1031	0.0744
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ , eÅ <sup>3</sup>	0.218 and −0.226	1.995 and −1.499	0.542 and −1.064

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}.$$

minimization program MINUIT.<sup>10e</sup> X-band EPR spectra were recorded with a Bruker 200TT spectrometer operating at 9.4–9.5 GHz.

**X-ray Crystallography.** The selected crystal (dark-red parallelepiped, 0.50 × 0.45 × 0.40 mm<sup>3</sup>) of **1** was mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. A total of 8245 reflections were collected up to 52° in the  $\omega$ –2 $\theta$  scan mode. Data reduction was made with the MolEN package.<sup>11a</sup> Absorption corrections from  $\psi$  scans were applied.<sup>11b</sup>

Crystallographic measurements for **2** were carried out with the Oxford-Diffraction XCALIBUR CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The crystal was placed 60 mm from the CCD detector. More than a hemisphere of reciprocal space was covered by combination of four sets of exposures; each set had a different  $\varphi$ -angle (0, 90, 180, 270°). Coverage of the unique set is completed at 99.6%, up to 2 $\theta = 52^\circ$ . The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.<sup>12a</sup> Intensity data were corrected for the Lorentz and polarization effects.

The X-ray data for compound **3** were collected on a Stoe Imaging Plate Diffractometer System (IPDS) equipped with an Oxford

Cryosystems cooler device using a graphite monochromator ( $\lambda = 0.71073$  Å). Data were collected<sup>12b</sup> using  $\varphi$  rotation movement with the crystal-to-detector distance equal to 70 mm ( $\varphi = 0.0$ – $200^\circ$ ,  $\Delta\varphi = 2.0^\circ$ ). The absorption corrections for **2** and **3** were introduced by semiempirical methods based on equivalent reflections using the program MULTISCAN.<sup>12c</sup>

All structures were solved by direct methods using SHELXS-97<sup>12d</sup> and refined by full-matrix least squares on *F*<sub>o</sub><sup>2</sup> with SHELXL-97<sup>12e</sup> with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in calculations in idealized positions (*d*<sub>CH</sub> = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of the relevant atom. Positional parameters of the H atoms of water molecule in structure **1** were obtained from difference Fourier syntheses and verified by the geometric parameters of corresponding hydrogen bonds. Scattering factors and anomalous dispersion terms were taken from ref 12f. Molecular plots were obtained using the ZORTEP program.<sup>12g</sup> The crystallographic data together with the refinement details for the three structures are summarized in Table 1.

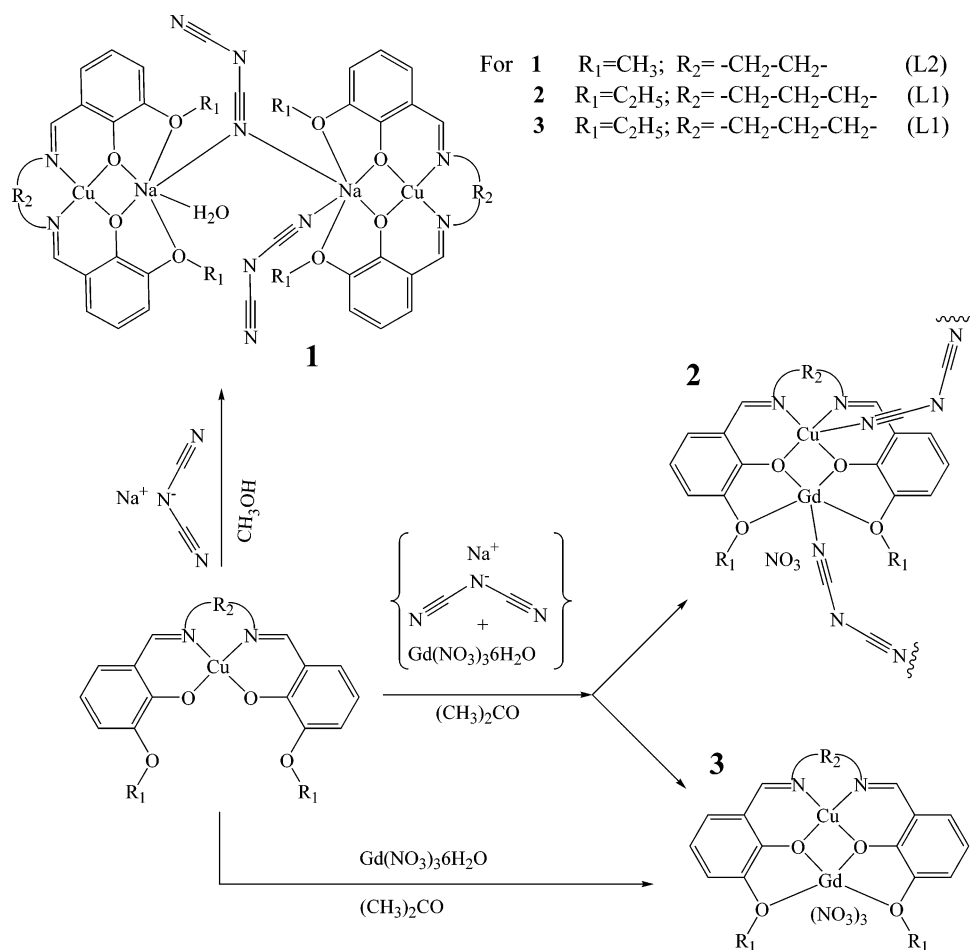
## Results

**Synthesis and IR Characterization.** The reaction of 3-ethoxysalicylaldehyde or 3-methoxysalicylaldehyde and 1,3-diaminopropane or 1,2-diaminoethane in a 2:1 molar ratio with methanol as solvent, followed by addition of CuOAc<sub>2</sub>·H<sub>2</sub>O, yielded the “compartmental complex-ligands” **L**<sup>*i*</sup>·Cu·H<sub>2</sub>O (*i* = 1, 2).<sup>8a</sup> These complexes possess a convenient O<sub>2</sub>O<sub>2</sub> donor set (two phenoxo and two ethoxo oxygen atoms) able to accommodate alkaline or 4f ions. The heterometallic Cu<sup>II</sup>–Gd<sup>III</sup> complex was synthesized by reaction of the mononuclear 3d-complexes **L**<sup>*i*</sup>·Cu·H<sub>2</sub>O dissolved in acetone with a warm acetone solution containing 1 equiv of Gd(NO<sub>3</sub>)<sub>3</sub>·

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Scheme 1



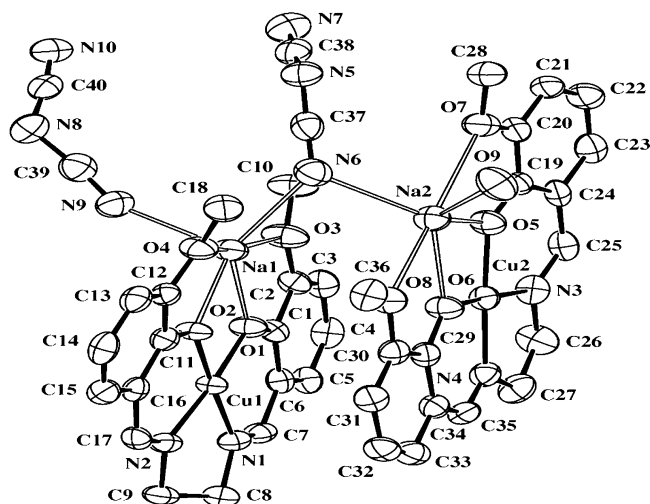
$6\text{H}_2\text{O}$  and 3 equiv of  $\text{NaN}(\text{CN})_2$  previously dissolved in a minimum of water. Two days later, the first crystals of the polymeric compound **2** that appeared were separated by filtration. From the resulting solution, new crystals corresponding to complex **3** were isolated later, along with a few more crystals of **2**. In another experiment, pure compound **3** was obtained by reaction of  $\text{L}^1\text{Cu}\cdot\text{H}_2\text{O}$  with  $\text{Gd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (1:1 molar ratio) in acetone. The heterometallic  $\text{Cu}^{\text{II}}-\text{Na}$  complex **1** was obtained in a similar way with use of methanol as solvent. The full set of reactions is summarized in Scheme 1.

The dicyanamide anion has three characteristic IR absorptions located in the  $2300-2170\text{ cm}^{-1}$  region ( $\nu_s + \nu_{\text{as}}(\text{C}-\text{N}) = 2263$ ;  $\nu_{\text{as}}(\text{C}\equiv\text{N}) = 2217$ ;  $\nu_s(\text{C}\equiv\text{N}) = 2168\text{ cm}^{-1}$  for  $\text{KN}(\text{CN})_2$ <sup>13a,b</sup> and  $2287$ ,  $2229$ ,  $2182\text{ cm}^{-1}$  for  $\text{NaN}(\text{CN})_2$ ) that are attributed to valence oscillations associated with delocalization of the triple bonds. Complex **2** exhibits six strong absorption bands ( $\nu_s + \nu_{\text{as}}(\text{C}-\text{N}) = 2319$ ,  $2281$ ;  $\nu_{\text{as}}(\text{C}\equiv\text{N}) = 2246$ ,  $2228$ ;  $\nu_s(\text{C}\equiv\text{N}) = 2195$ ,  $2166\text{ cm}^{-1}$ ) attributed to two different coordination modes of the dicyanamide ligands. Complex **1** exhibits lower absorptions at  $2251$ ,  $2242$ ,  $2201$ , and  $2145\text{ cm}^{-1}$ , indicating different coordination modes of the dca ligands. Large and strong bands at  $1471$  for **2** and

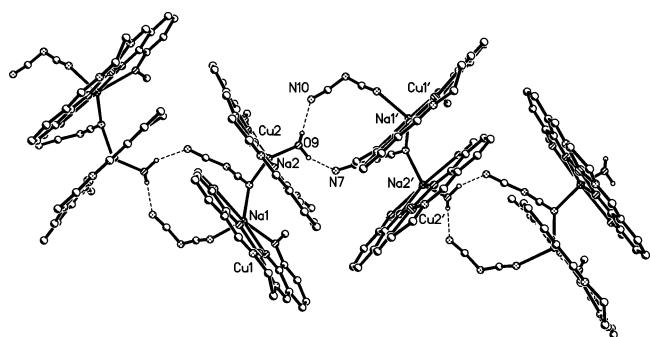
$1468\text{ cm}^{-1}$  for **3** ( $\nu_{\text{as}}(\text{NO}_2)$ ) confirm the presence of nitrate ions. Their  $\nu_s(\text{NO}_2)$  counterparts appear at  $1296$  (**2**) and  $1320\text{ cm}^{-1}$  (**3**), respectively. The difference between the two vibrations ( $\Delta\nu = 172$  and  $151\text{ cm}^{-1}$ ) is consistent with an  $\eta^2$  bidentate chelation of the nitrate ion and indirectly supports their coordination to the gadolinium ion.<sup>13c</sup>

**Structures.** The asymmetric unit of **1** is made of a tetranuclear cluster involving two copper and two sodium metal atoms. The molecular structure of this complex is illustrated in Figure 1. The dinuclear  $\text{L}^2\text{CuNaH}_2\text{O}$  and  $\text{L}^2\text{CuNaN}(\text{C}-\text{N})-\text{C}-\text{N}$  entities are linked through an additional bridging dicyanamide acting in the  $\mu_{1,1}$  end-on fashion. The  $\text{Na}(1)-\text{N}(6)$  and  $\text{Na}(2)-\text{N}(6)$  bond distances are equal to  $2.441(3)$  and  $2.494(3)\text{ \AA}$ , respectively, whereas the  $\text{Na}\cdots\text{Na}$  separation is equal to  $3.733(2)\text{ \AA}$ . This dca bridge yields tetranuclear  $\text{Cu}-\text{Na}-\text{Na}-\text{Cu}$  entities in which the planes defined by the equatorial  $\text{N}_2\text{O}_2$  donor atoms afforded by the ligands  $\text{L}^2$  to each copper ion are roughly parallel. It is noteworthy that despite the large diversity of dca coordination modes already described<sup>1c</sup> this type of dca bridging has not yet been observed. The structure of each dinuclear moiety is quite similar except for the coordination of the sodium atoms. Both of them are coordinated to four oxygen atoms from the compartmental ligand  $\text{L}^2$  and to the nitrogen atom  $\text{N}(6)$  of the bridging dicyanamide anion. The sixth position of the coordination octahedron is occupied by

(13) (a) Kohler, H.; Kolbe, A.; Lux, G. Z. *Anorg. Allg. Chem.* **1977**, *428*, 103. (b) Kohler, H. Z. *Anorg. Allg. Chem.* **1964**, *331*, 236. (c) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997.

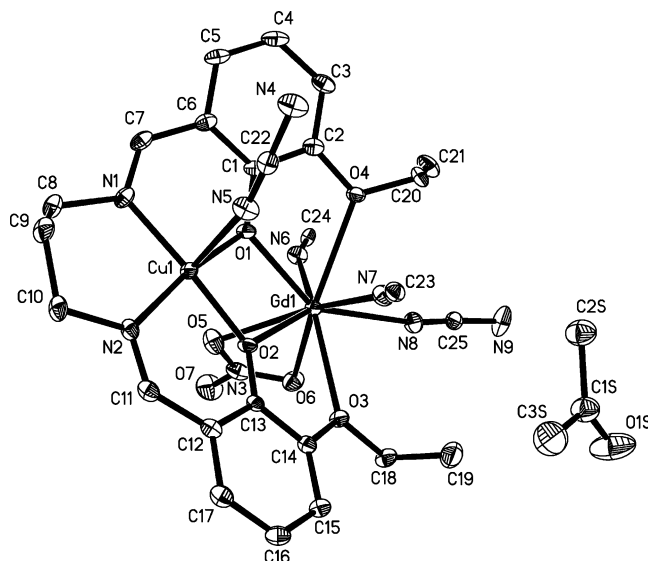


**Figure 1.** Molecular structure of the complex **1** with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.



**Figure 2.** A 1D H-bonded chain in the crystal structure of compound **1**.

a water molecule for Na(2) with a Na(2)–O(9) bond length of 2.311(3) Å and by a monodentate dicyanamide ligand for Na(1) atom with a Na(1)–N(9) bond length of 2.415(3) Å. An additional particularity originates from the Cu–N–C–C–N five-membered ring that has a  $\lambda$  gauche conformation for Cu(1) although it is practically planar for Cu(2) with a minute  $\delta$  gauche conformation. This conformation difference results in a decrease of the central C–C bond (C(26)–C(27)) = 1.473(4) Å for Cu(2); C(8)–C(9) = 1.522(4) Å for Cu(1) and of the C–N bonds (1.457(4) and 1.451(3) Å for Cu(2) compared to 1.474(3) and 1.474(3) Å for Cu(1)) whereas the C=N bonds increase (1.291(3) and 1.292(3) Å for Cu(2) compared to 1.270(3) and 1.279(3) Å for Cu(1)). The strongest intermolecular contacts between tetranuclear units are realized through two hydrogen bonds, including the coordinated water molecule and the noncoordinated nitrogen atoms of the two dicyanamide ligands with O(9)–H(9D) = 0.90(4), H(9D)···N(10) = 2.07(4), O(9)···N(10) = 2.949(4), O(9)–H(9C) = 0.94(4), H(9C)···N(7) = 2.10(4), O(9)···N(7) = 2.967(4) Å, and N(10)–H(9D)–O(9) = 154(3)° and N(7)–H(9C)–O(9) = 160(4)°. These interactions lead to the formation of one-dimensional (1D) supramolecular arrangements in which the mean coordination planes of the tetranuclear units are practically orthogonal, yielding zigzag chains as shown in Figure 2. Intramolecular  $\pi$ – $\pi$  stacking interactions between a phenyl ring of a  $L^2CuNa$  entity and the six-membered ring involving the copper atom, the



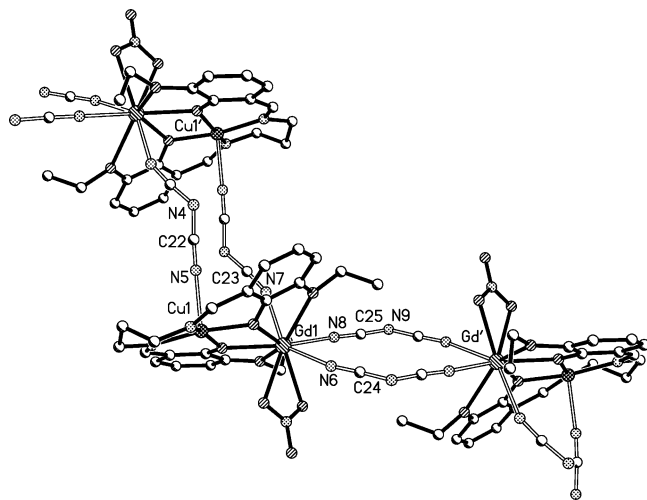
**Figure 3.** Structure of the asymmetric unit in complex **2** with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**, **2**, and **3**

[(L <sup>2</sup> CuNa(NCNCN)) <sub>2</sub> (H <sub>2</sub> O)] ( <b>1</b> )			
Cu(1)–O(1)	1.892(2)	Cu(1)–O(2)	1.892(2)
Cu(1)–N(1)	1.918(2)	Cu(1)–N(2)	1.939(2)
Na(1)–O(2)	2.332(2)	Na(1)–O(1)	2.335(2)
Na(1)–N(9)	2.415(3)	Na(1)–N(6)	2.441(3)
Na(1)–O(3)	2.703(2)	Na(1)–O(4)	2.707(2)
C(37)–N(6)	1.156(4)	N(5)–C(37)	1.295(4)
N(5)–C(38)	1.308(4)	C(38)–N(7)	1.136(4)
C(39)–N(9)	1.130(4)	N(8)–C(39)	1.299(4)
N(8)–C(40)	1.314(4)	C(40)–N(10)	1.136(4)
Na(1)–N(6)–Na(2)	98.29(10)	C(37)–N(5)–C(38)	122.4(3)
C(39)–N(8)–C(40)	118.8(3)		
[L <sup>1</sup> CuGd(NO <sub>3</sub> )(NCNCN) <sub>2</sub> ](CH <sub>3</sub> ) <sub>2</sub> CO] ( <b>2</b> )			
Gd(1)–O(1)	2.305(3)	Gd(1)–O(2)	2.358(3)
Gd(1)–N(8)	2.443(3)	Gd(1)–N(7)	2.489(4)
Gd(1)–O(5)	2.492(3)	Gd(1)–O(6)	2.500(3)
Gd(1)–O(3)	2.511(3)	Gd(1)–N(6)	2.518(3)
Gd(1)–O(4)	2.576(3)	Cu(1)–O(2)	1.966(3)
Cu(1)–O(1)	1.981(3)	Cu(1)–N(1)	1.980(3)
Cu(1)–N(5)	2.295(4)	Cu(1)–N(2)	1.993(3)
C(25)–N(9)–C(24)'	121.3(3)	C(22)–N(4)–C(23)'	121.5(3)
[L <sup>1</sup> CuGd(NO <sub>3</sub> ) <sub>3</sub> ](CH <sub>3</sub> ) <sub>2</sub> CO] ( <b>3</b> )			
Cu(1)–O(1)	1.947(2)	Cu(1)–O(2)	1.964(2)
Cu(1)–N(2)	1.971(2)	Cu(1)–N(1)	1.984(3)
Cu(1)–O(14)	2.427(3)	Gd(1)–O(2)	2.332(2)
Gd(1)–O(1)	2.333(2)	Gd(1)–O(9)	2.458(2)
Gd(1)–O(4)	2.493(2)	Gd(1)–O(12)	2.514(3)
Gd(1)–O(5)	2.509(3)	Gd(1)–O(6)	2.515(3)
Gd(1)–O(8)	2.536(3)	Gd(1)–O(3)	2.555(3)
Gd(1)–O(11)	2.556(2)		

nitrogen imine, and oxygen phenol atoms (Cu(1)–N(1)–C(7)–C(6)–C(1)–O(1)) of another  $L^2CuNa$  moiety are present. The centroid–centroid distance between these staggered aromatic rings is 3.495 Å.

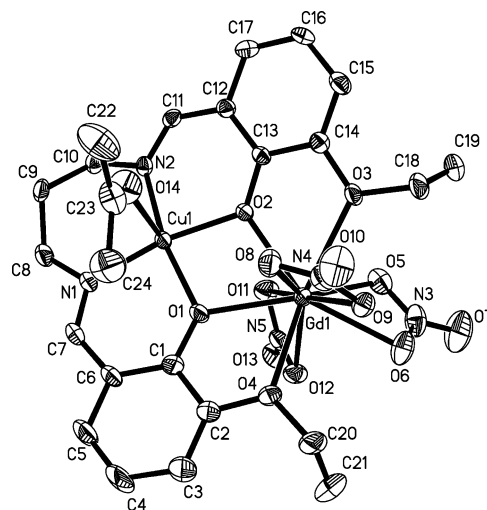
The asymmetric unit of complex **2**, along with the atom labeling scheme, is depicted in Figure 3, whereas the relevant interatomic bonds lengths are collected in Table 2. The copper and gadolinium ions are linked to the deprotonated compartmental ligand ( $L^1$ )<sup>2–</sup>, respectively, in the N<sub>2</sub>O<sub>2</sub> and



**Figure 4.** Fragment of the coordination polymer  $\{[L^1CuGd(NO_3)(NC-N-CN)_2](CH_3)_2CO\}_n$  (**2**).

$O_2O_2$  coordination sites. The Cu(OO)Gd core including two phenoxo oxygen atoms is essentially planar, with a dihedral angle between the Cu(1)O(1)O(2) and Gd(1)O(1)O(2) planes equal to  $3.3(2)^\circ$  and a related Cu(1)⋯Gd(1) separation of  $3.4811(9)$  Å. The copper ion is pentacoordinate to the  $N_2O_2$  donor set of  $(L^1)^{2-}$  in the basal plane, whereas the nitrogen atom of the  $N(CN)_2^-$  ligand is axially bonded. Cu(1) is displaced from the mean equatorial  $N_2O_2$  plane by  $0.209(2)$  Å toward the axially coordinated nitrogen atom. The coordination polyhedron of the nine-coordinate  $Gd^{III}$  cation may be described as a slightly distorted monocapped tetragonal antiprism formed by four oxygen atoms of the polydentate ligand  $(L^1)^{2-}$ , two oxygen atoms from a nitrate anion acting as an  $\eta^2$  chelating ligand, and three nitrogen atoms from dicyanamide ligands. All dicyanamide anions act as  $\mu_{1,5}$ -end-to-end bidentate-bridging ligands either between two gadolinium ions or between a copper and a gadolinium ion. These bridges are alternately arranged between the  $L^1CuGd$  entities, two Cu⋯Gd bridges following two Gd⋯Gd bridges, thus generating an extended zigzag coordination polymer formulated as  $\{[L^1CuGd(NO_3)(NC-N-CN)_2](CH_3)_2CO\}_n$  (**2**) (Figure 4). The  $L^1CuGd$  entities are separated by Gd(1)⋯Gd(1)' ( $8.197(3)$  Å) and Cu(1)⋯Cu(1)' ( $8.974(3)$  Å), distances much longer than the Cu(1)⋯Gd(1) intramolecular one ( $3.4811(9)$  Å).

The molecular structure of **3** is built from isolated dinuclear complex molecules of  $[L^1CuGd(NO_3)_3(CH_3)_2CO]$ . A perspective view of this compound with the corresponding labeling scheme is depicted in Figure 5. This structure is very similar to the dinuclear units of the polymeric compounds **1** and **2**, and to the analogous 3d–4f Schiff base complexes studied earlier.<sup>14</sup> In each bimetallic unit, the Cu<sup>II</sup> and Gd<sup>III</sup> atoms occupy the inner  $N_2O_2$  and  $O_2O_2$  sites, respectively. The two ions are doubly bridged to each other by two phenoxo oxygen atoms, with a Cu(1)⋯Gd(1) distance



**Figure 5.** Molecular structure of the complex **3** with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

of  $3.454(1)$  Å. The dihedral angle between the CuOO and OOGd planes is equal to  $11.1(3)^\circ$ . The ten-coordinate Gd cation is surrounded by four oxygen atoms belonging to the Schiff base and by three nitrate anions acting as bidentate  $\eta^2$  chelating ligands. The Cu<sup>II</sup> cation has a square-pyramidal (4 + 1) geometry, with the acetone oxygen atom in the apical position.

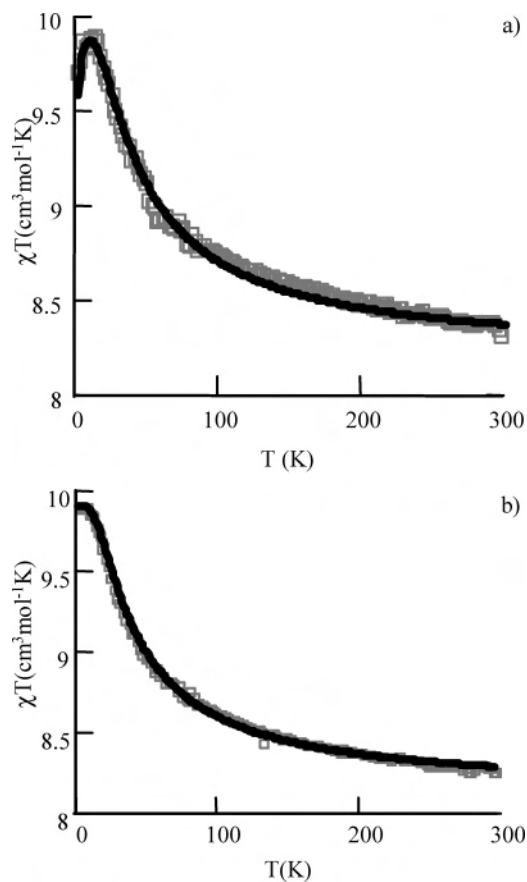
**Magnetic Properties.** The magnetic behavior of compound **2** is shown in Figure 6 in the form of the thermal variation of the  $\chi_M T$  product,  $\chi_M$  being the molar susceptibility corrected for diamagnetism. At 300 K, the  $\chi_M T$  product for **2** ( $8.37$  cm<sup>3</sup> mol<sup>-1</sup> K) corresponds to the value expected for uncoupled Cu<sup>II</sup> and Gd<sup>III</sup> metal ions. A decrease in the temperature induces a  $\chi_M T$  increase up to  $9.87$  cm<sup>3</sup> mol<sup>-1</sup> K at 10 K. This value compares well with that ( $10.0$  cm<sup>3</sup> mol<sup>-1</sup> K) expected for a  $S = 4$  spin state resulting from ferromagnetic coupling between Cu<sup>II</sup> ( $S = 1/2$ ) and Gd<sup>III</sup> ( $S = 7/2$ ) assuming  $g_{Cu} = g_{Gd} = 2$ . A quantitative analysis has been performed on the basis of an expression derived from the spin-only Hamiltonian  $H = -J_{Cu-Gd}S_{Cu}S_{Gd}$ . Taking into consideration the  $g$  values associated with the low-lying levels  $E(4) = 0$  ( $g_4 = (7g_{Gd} + g_{Cu})/8$ ) and  $E(3) = 4J(g_3 = (9g_{Gd} - g_{Cu})/8$ ),<sup>14,15a</sup> the following expression is obtained

$$\chi T = N\alpha + \frac{4N\beta^2 T}{k(T - \theta)} \frac{15g_4^2 + 7g_3^2 \exp\left(-\frac{4J}{kT}\right)}{9 + 7 \exp\left(-\frac{4J}{kT}\right)}$$

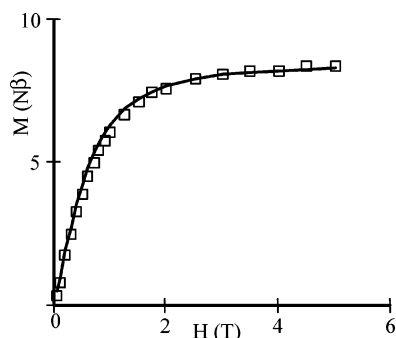
Least-squares fitting to the experimental data led to the following set of parameters for **2**:  $g_{Gd} = 1.99$ ,  $g_{Cu} = 2.03$ ,  $\theta = -0.08$  K,  $J = 8.50$  cm<sup>-1</sup>. For complex **3**, the following values are obtained:  $g_{Gd} = 1.98$ ,  $g_{Cu} = 2.06$ ,  $\theta = 0.0$  K,  $J = 8.63$  cm<sup>-1</sup>. The agreement factor,  $\sum(\chi T_{\text{calcd}} - \chi T_{\text{obs}})^2 / \sum(\chi T_{\text{obs}})^2$ , is equal to  $1.5 \times 10^{-5}$  and  $8 \times 10^{-6}$  for complexes

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(15) (a) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (b) Chiari, B.; Cinti, A.; David, L.; Ferraro, F.; Gatteschi, D.; Piovesana, O.; Zanazzi, P. F. *Inorg. Chem.* **1996**, *35*, 7413. (c) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343. (d) Drillon, M.; Coronado, E.; Beltran, D.; Georges, R. *Chem. Phys.* **1983**, *79*, 449.



**Figure 6.** Thermal dependence of  $\chi_M T$  for **2** (a) and **3** (b). The full lines correspond to the best fit to the experimental data.



**Figure 7.** Field dependence of the magnetization for **2**. The solid line corresponds to the Brillouin function for a  $S = 4$  spin-state.

**2** and **3**, respectively. The  $N\alpha$  parameter, which is very weak, has been omitted in our calculations.

Use of a magnetic model that takes into account the heterometallic Cu–Gd 1D chain in which the dimeric unit is assumed to act as an effective  $S_d$  classical spin system<sup>15b-d</sup> indicates that the magnetic interaction transmitted through dca ligands is negligible ( $j \approx -0.002 \text{ cm}^{-1}$ ). The experimental magnetization values measured at 2.0 K for **2** and **3** are correctly fitted by the Brillouin function for a  $S = 4$  spin state (Figure 7), thus confirming the ferromagnetic nature of the Cu<sup>II</sup>–Gd<sup>III</sup> interaction and the absence of intermolecular magnetic interactions between the dinuclear units of compound **2**.

In the tetranuclear complex **1**, including two magnetically active Cu<sup>II</sup> centers, the  $\chi_M T$  product is constant and equal to

$0.79 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  from 300 to 20 K, although a slight decrease is observed between 20 and 2 K, where  $\chi_M T$  equals  $0.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . This decrease is assumed to be the consequence of a weak antiferromagnetic interaction between the two copper centers. From the Bleaney–Bowers equation,<sup>16</sup> the following parameter values have been estimated,  $J = -0.6 \text{ cm}^{-1}$ ,  $g = 2.07$ ,  $R = 2 \times 10^{-4}$ . This weak antiferromagnetic coupling is more probably propagated through the  $\pi$ – $\pi$  interactions than through the Cu–O–Na–dca–Na–O–Cu pathway. The single EPR signal of complex **1** (X band) confirms that magnetic interactions operate between copper ions and its  $g = 2.07$  value agrees with the one ( $g = 2.09$ ) deduced from the magnetic data.

## Discussion

The main interest of this work resides in the structural determinations of novel dicyanamide complexes. First of all, a new coordination mode has been evidenced for the dca ligand, the  $\mu_{1,1}$  mode which has not been observed previously.<sup>1c</sup> Such a coordination mode implies different mesomeric forms as sketched hereafter (Scheme 2).

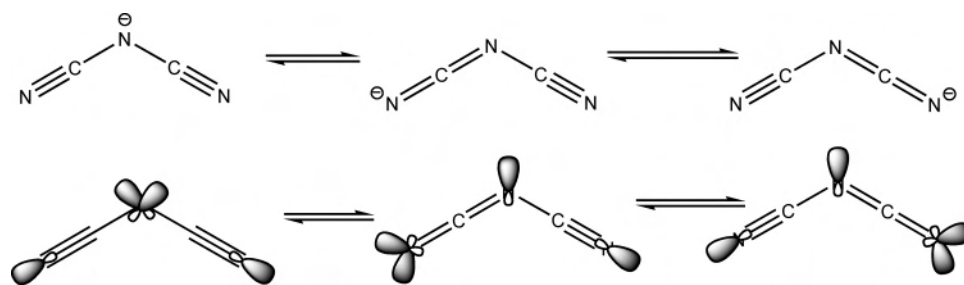
A closer look at the structural parameters shows a very slight increase of the C–N bonds and N–C–N angles for the terminal coordination (N(9)–C(39) = 1.130(4) Å, (N(9)–C(39)–N(8) = 173.2(4)°) compared to the  $\mu_{1,1}$  bridging one (N(6)–C(37) = 1.156(4) Å, N(6)–C(37)–N(5) = 175.0(3)°) for the dca anions in **1**. The Na(1)–N(6)–Na(2) angle is equal to 98.3(1)°, a value quite similar to those found for end-on azido bridges.<sup>17</sup> The noncoordinated nitrogen atoms of the two dca ligands are involved in hydrogen bonds with the coordinated water molecule, which results in infinite zigzag chains.

In complex **2**, the Cu–Gd entities are held together by two  $\mu_{1,5}$  dca bridges in such a way that each copper ion is linked to one dca ligand whereas each gadolinium ion is linked to three different dca ligands. A given unit is bridged to the next one by two  $\mu_{1,5}$  dca, linking a copper ion to the gadolinium one of the next unit and vice versa, thus inducing a head to tail arrangement of these dinuclear units. Each unit is also bridged to the previous one through two  $\mu_{1,5}$  dca ligands that involve two gadolinium ions, thus implying a face to face arrangement of these dinuclear units. The resulting polymer formulated as  $\{[\text{L}^1\text{CuGd}(\text{NO}_3)(\text{NC}-\text{N}-\text{CN})_2](\text{CH}_3)_2\text{CO}\}_n$  results from alternate pairs of Cu<sup>II</sup>–Gd<sup>III</sup> and Gd<sup>III</sup>–Gd<sup>III</sup> interactions through dca ligands, yielding again infinite zigzag chains. Only two dca ligands are involved in the coordination sphere of each gadolinium ion whereas a chelating nitrate anion is still involved in the gadolinium coordination sphere. This is most probably related to the use of gadolinium nitrate as starting material in the synthetic process. Indeed, we have previously shown that using gadolinium chloride yields a complex formulated as  $\text{LCuGd}(\text{NC}-\text{N}-\text{CN})_3$ , as demonstrated by analytical and FAB<sup>+</sup>

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Scheme 2



mass spectrometry results.<sup>18</sup> As expected from the structural determination of complex **2**, the magnetic properties of this zigzag chain are comparable with those of the heterodinuclear complex **3**. This means that the  $\mu_{1,5}$  dicyanamide bridge linking an axial position of a copper ion to the gadolinium ion of the next entity is not efficient in transmitting magnetic interaction between these two ions. Indeed, the magnetic orbital of the copper ion in a square pyramidal geometry is described by a  $d_{x^2-y^2}$  type orbital mainly located in the basal plane, leading to a very weak spin density in the axial position. This implies that, similarly, the two  $\mu_{1,5}$  dicyanamide bridges linking two gadolinium ions do not mediate magnetic interaction. Recently, the study of an infinite chain formulated  $[\text{Gd}(\text{dca})_3(2,2'\text{-bipy})_2(\text{H}_2\text{O})]_n$  in which the gadolinium ions are held together by  $\mu_{1,5}$  dicyanamide bridges has led to the same conclusion.<sup>20</sup>

### Conclusion

With its two different bridging modes, the dicyanamide ligand has allowed isolation and characterization of two heterodinuclear infinite chains by assembling heterodinuclear copper–gadolinium or copper–sodium units. The  $\text{Cu}^{\text{II}}$  and  $\text{Gd}^{\text{III}}$  or  $\text{Cu}^{\text{II}}$  and  $\text{Na}^{\text{I}}$  cations of these heterodinuclear units are held together by the two phenoxo bridges of the

compartmental ligand. In the Cu–Gd case (complex **2**), the dca ligands bridge in the  $\mu_{1,5}$  mode, alternately and by pairs, Cu to Gd and Gd to Gd. In the Cu–Na case (complex **1**), the bridging scheme is more complex. First, a dca ligand bridges two Cu–Na units in an original  $\mu_{1,1}$  mode observed for the first time. The resulting tetranuclear entities then interact through two hydrogen bonds established between the water molecule coordinated to one of the sodium ions and the free nitrogen atom of the two dca ligands. Unfortunately, none of these dca bridges is efficient in the transmission of a magnetic interaction. Finally, this report describes the structure of the first Cu–Gd complexes involving dca ligands, and the Cu–Na complex provides the first example of a unique end-on coordination of dca, quite similar to the end-on coordination of the azido ligand.

**Acknowledgment.** G.N. is grateful to NATO for support of this work through a postdoctoral grant. S.S. and G.N. acknowledge INTAS for financial support (Project 2000-00565).

**Supporting Information Available:** X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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