

Synthesis and Structure of 1-D Heterometallic Thiocyanato-Bridged Cu^{II}Gd^{III} Polymers with Ferromagnetic Properties

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Reaction of the tetracoordinate CuL_A and CuL_B complexes with Gd(NCS)₃ leads to two unique one-dimensional {Cu–Gd}_n thiocyanato-bridged (I) and hydrogen-bonded (II) polymers, depending on the periphery of the L_A and L_B ligands, with ferromagnetic properties.

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Introduction

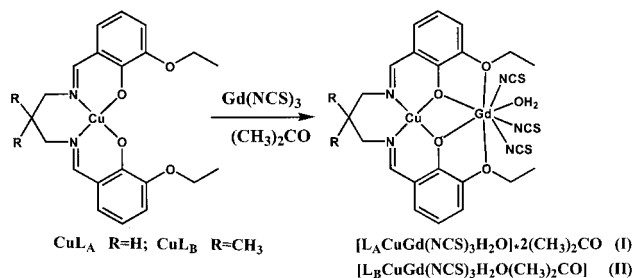
The synthesis and the design of solid-state architectures with ferromagnetic ordering is one of the major challenges in magnetochemistry.^[1–4] The controlled assembly of these structural units in the solid state is determined by a number of factors: (i) coordination bonding,^[5] (ii) versatile hydrogen-bonding interaction^[6] (iii) π - π -stacking^[7] and (iv) electrostatic interactions.^[8] Thiocyanates with orbitals oriented in various directions have been used to build up coordination networks for two different reasons. On the one hand, they can furnish directional conformation to structures, owing to linear coordination modes as well as π - π overlapping interactions;^[9] on the other hand, they can provide different super-exchange pathways, transmitting magnetic interactions between paramagnetic metal centres, owing to the diversity of their bonding modes.^[10]

We have previously shown that ferromagnetic interactions are predominant in Cu–Gd complexes.^[11] The linking of these units through intermolecular ferromagnetic interactions could yield high-spin species. So far, only tetranuclear entities have been obtained.^[12,13] In the present study, we report on the synthesis, crystal structure and magnetic properties of one heterometallic coordination polymer and one hydrogen-bonded polymer, which are based on the Cu^{II}-Gd^{III} core, on thiocyanate ligands and on water molecules.

Results and Discussion

The reaction of 3-ethoxysalicylaldehyde and propylenediamine or 2,2-dimethylpropylenediamine in methanol (2:1

molar ratio), followed by addition of CuOAc₂·H₂O, yielded the “compartmental complex ligands” CuL_A·H₂O and CuL_B·H₂O.^[14] These complexes possess a convenient O₂-O₂ metal-binding site, made of two phenoxide and two ethoxy oxygen atoms, which are able to accommodate 4f ions. Heterometallic Cu^{II}-Gd^{III} complexes were synthesized by reaction of the “compartmental complex ligands” CuL_A and CuL_B with Gd(NCS)₃ in acetone. Gd(NCS)₃ was prepared by metathesis with equimolar, warm solutions of Gd(NO₃)₃/6H₂O and KNCS in acetone (see Scheme 1).



Scheme 1

The IR spectra of the two complexes are nearly identical. The C=N stretching vibrations are observed at 1603 and 1610 cm^{−1}. Very strong bands (2076, 2054 cm^{−1}) corresponding to coordinated thiocyanate anions are observed for **I** and **II**. The splitting indicates the different structural functions of the thiocyanate ligands.^[15]

The structures of **I** and **II** were studied by X-ray diffraction methods at 180 K.^[16] The structure of complex **I** is shown in Figure 1 (top). Cu^{II} is bound to two imino nitrogen and to two phenoxide oxygen atoms of the deprotonated L_A ligand. The Cu^{II} and Gd^{III} centres are bridged by two phenoxide oxygens, with a Cu–Gd distance of 3.460(1) Å. The copper-atom deviation from the least-squares N₂O₂ plane, formed by the four coordinating

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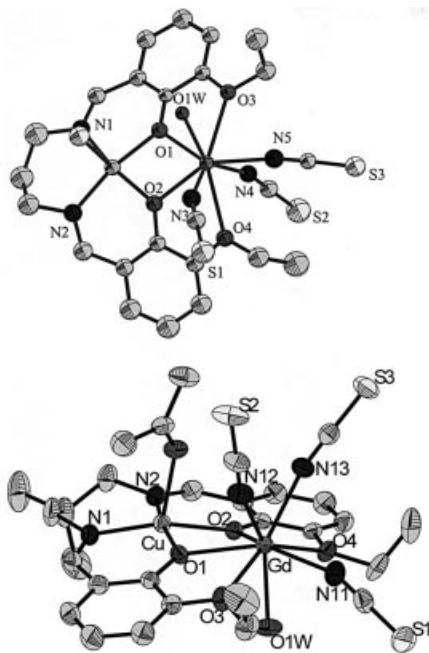


Figure 1. Views of the $\{\text{LCuGd}(\text{NCS})_3\text{H}_2\text{O}\}$ units, **I** (top) and **II** (bottom); hydrogen atoms and solvent molecules are omitted for clarity

atoms, is $-0.135(2)$ Å. The axial site is occupied by the sulfur atom of an NCS group, belonging to a neighbouring molecule ($\text{Cu}-\text{S} = 2.744(2)$ Å]. The Gd^{III} centre is eight-coordinate, with three nitrogen atoms from the thiocyanate ligands, four oxygen atoms from the "compartmental complex ligand" CuL_A , and one from a water molecule. The CuO_2Gd segment is not planar: the dihedral angle between the CuO1O2 and GdO1O2 planes is equal to $17.1(2)^\circ$. The

molecules form zigzag chains through $\text{Cu}(\text{SCN})\text{Gd}'$ bridges (see Figure 2). It is worth mentioning the π - π stacking interactions at $3.65(8)$, between two neighbouring chains.

The structure of **II** consists of $\text{L}_B\text{Cu}^{\text{II}}\text{Gd}^{\text{III}}$ binuclear units (see Figure 1, bottom), in which the metal ions are doubly bridged by the phenoxide oxygen atoms. Acetone occupies the apical position in the copper-coordination sphere, with a $\text{Cu}-\text{O}$ bond length of $2.293(2)$ Å. As in **I**, the copper(II) ion is situated in the inner N_2O_2 site of the Schiff-base ligand, L_B^{2-} . The Cu atom is displaced from this equatorial plane towards the apical position by $0.14(1)$ Å. The $\text{Cu}-\text{Gd}$ distance is $3.454(1)$ Å and the dihedral angle between the GdO1O2 and CuO1O2 planes is $19.18(4)^\circ$. The Gd atom in **II** is again eight-coordinate ($\text{N}_3\text{O}_4\text{O}_w$). The supramolecular arrangement of the heteronuclear unit $\{\text{L}_B\text{CuGd}(\text{NCS})_3\text{H}_2\text{O}\}$ is realised with hydrogen bonds that connect the coordinated water molecule to two sulfur atoms of thiocyanate ligands belonging to neighbouring molecules [$\text{O1}_w \cdots \text{S2} = 3.197(3)$; $\text{O1}_w \cdots \text{S3} = 3.292(3)$ Å (see Figure 3)].

The magnetic behaviour of **I** is shown in Figure 4 (top), as the thermal variation of the $\chi_M T$ product; χ_M is the molar susceptibility corrected for diamagnetism. At 300 K, $\chi_M T$ for **I** is equal to $8.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which corresponds to the value expected for two uncoupled metal ions. Lowering the temperature causes $\chi_M T$ to increase to $9.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 7 K. This value compares well with that of $9.85 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, expected for an $S = 4$ spin state, resulting from ferromagnetic coupling between Cu^{II} ($S = 1/2$) and Gd^{III} ($S = 7/2$) and assuming that $g_{\text{Cu}} = g_{\text{Gd}} = 2$.

A quantitative analysis for **I** was performed employing an expression derived from the spin-only Hamiltonian $H = -J_1 S_{\text{Cu}} S_{\text{Gd}}$. Taking into consideration the g values associated with the low-lying levels $E(4) = 0$ [$g_4 = (7g_{\text{Gd}} + g_{\text{Cu}})/$

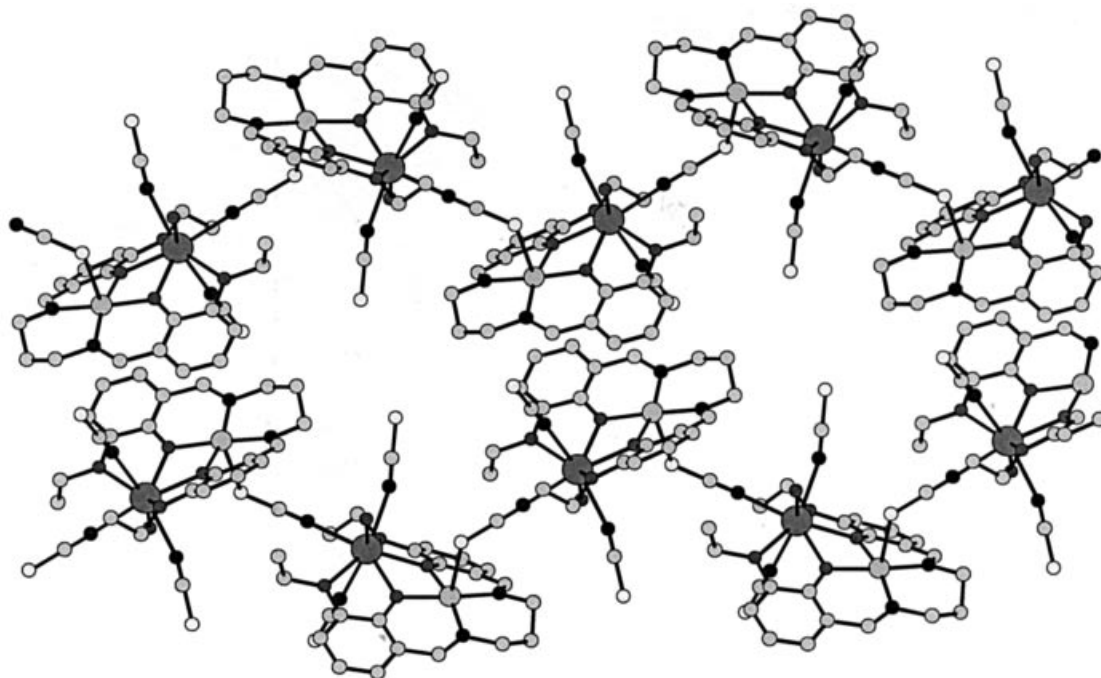
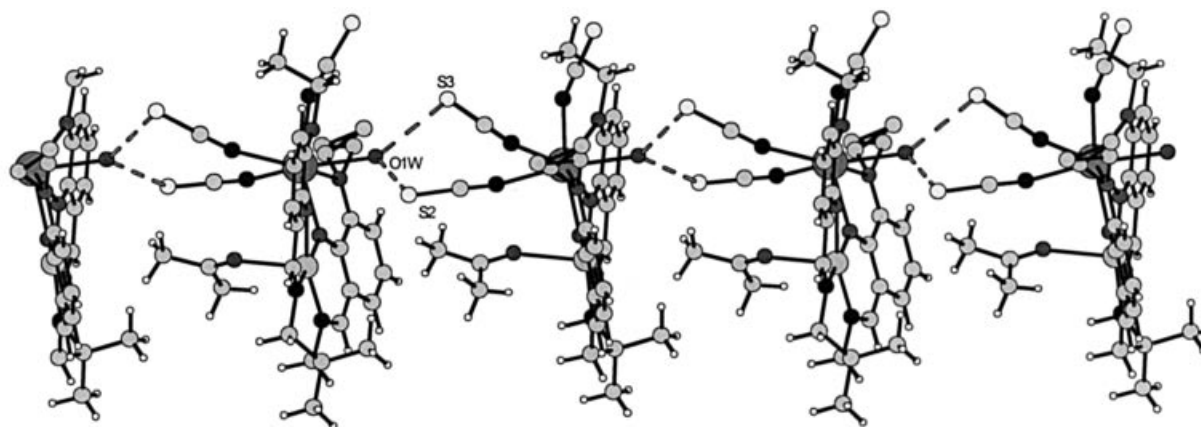
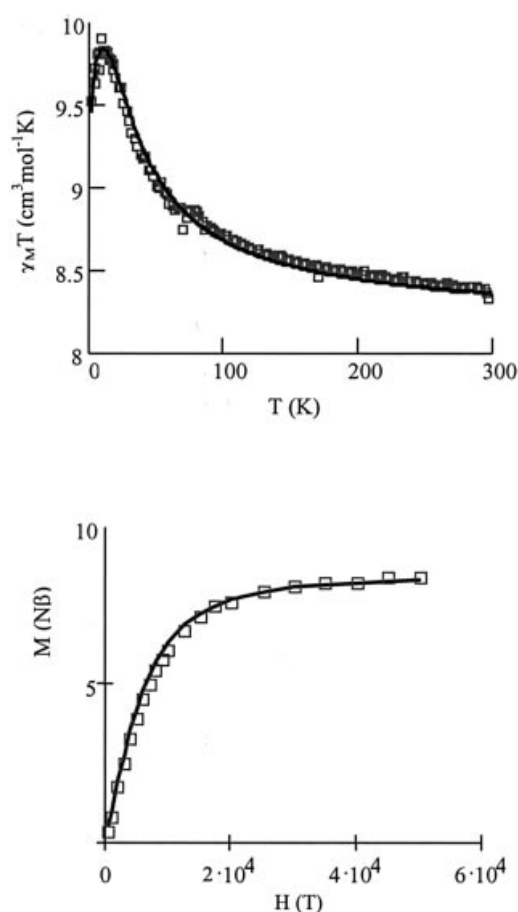


Figure 2. Stack of the polymeric **I** molecules; hydrogen atoms and solvent molecules are omitted for clarity

Figure 3. A portion of the hydrogen-bonded chain in **II**Figure 4. Magnetic behaviour of complex **I** between 2 and 300 K ($\chi_M T$ vs. T plot) and at 0.1 T (top), the solid line corresponds to the best fit; field dependence of the magnetization for compound **II** at 2 K (bottom), the solid line corresponds to the $S = 4$ ground state

8] and $E(3) = 4J_1 [g_3 = (9g_{Gd} - g_{Cu})/8]$,^[17] the following expression [Equation (1)] is obtained:

$$\chi_d T = \frac{4N\beta^2 T}{\kappa(T - \theta)} \cdot \frac{15g_4^2 + 7g_3^2 \cdot \exp(-\frac{4J_1}{kT})}{9 + 7 \cdot \exp(-\frac{4J_1}{kT})} \quad (1)$$

Least-squares fitting of the experimental data led to the following set of parameters: $g_{Gd} = 1.99$, $g_{Cu} = 2.04$, $J_1 = 9.20 \text{ cm}^{-1}$, $\theta = -0.11$ for **I** and $g_{Gd} = 1.99$, $g_{Cu} = 2.02$, $J_1 = 5.5 \text{ cm}^{-1}$, $\theta = -0.14$ for **II**. The agreement factors R [$R = \Sigma(\chi T_{calc} - \chi T_{obs})^2 / \Sigma(\chi T_{obs})^2$] are equal to 2×10^{-5} and 3×10^{-5} , respectively. From these values, it is clear that, from a magnetic point of view, these chain complexes behave as single dinuclear units.

For a better estimation of the magnetic interaction in the heterometallic Cu–Gd 1D chain, **I**, we adopted the model previously developed in the literature, in which the dimeric unit is assumed to act as an effective S_d classical-spin system.^[18]

$$S_d = \frac{-1 + \sqrt{1 + 4\left(\chi_d T / 0.1251 \bar{g}^2\right)}}{2} \quad (2)$$

The ladder chain can then be treated as a linkage of dimers and its contribution, χ_{chain} , to the total magnetic susceptibility, χ , according to Fisher's model^[19] using the Drillon function,^[20] is determined by Equation (3).

$$\chi_{chain} = \frac{Ng^2\beta^2 S_d(S_d + 1)}{3k_B T} \cdot \frac{1+u}{1-u} \quad (3)$$

$$u = \coth \left[\frac{2J_2 S_d(S_d + 1)}{k_B T} \right] - \frac{kT}{2J_2 S_d(S_d + 1)}$$

where J_2 is the inter-dimer coupling constant. Least-squares fitting of the experimental data for **I** leads to a J_2 value of -0.003 cm^{-1} . A similar result can be obtained for **II**. This very weak J_2 value confirms, as expected, that the dinuclear model can be retained to study the magnetic behaviour of these chain complexes. Indeed, the copper magnetic orbital is of the $d_{x^2-y^2}$ type while the interaction with

the gadolinium ion occurs via the axially coordinated SCN⁻ ligand, in a region of very low spin density. The experimental values of magnetization for **I** and **II**, measured at 2.0 K, are correctly fitted by the Brillouin function for an $S = 4$ spin state, which confirms the ferromagnetic nature of the Cu–Gd interaction and the dinuclear character of these polymers (see Figure 4, bottom).

In conclusion, we have shown that heterobimetallic chains are obtained by using thiocyanate ligands. Depending on the ligand coordinating the Cu and Gd ions, the arrangement of the dinuclear units furnishes chains involving either Gd–Gd bridges through hydrogen bonding (**II**) or Cu–Gd bridges through NCS binding (**I**). These types of binding could be responsible for weak antiferromagnetic interactions in the present complexes, **I** and **II**. Nevertheless, from a supramolecular point of view, we have demonstrated that a change at the periphery of the ligand complex can drastically change the assembling mode of the heterodinuclear complexes.

Experimental Section

All starting materials and solvents were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse. Magnetic susceptibility data were collected on powdered samples of a SQUID-based sample magnetometer on a Quantum Design model MPMS instrument. All data were corrected for diamagnetism of the ligands, estimated from Pascal's constants.^[21]

[L_ACuGd(NCS)₃H₂O]·2(CH₃)₂CO (I**):** CuL_A·H₂O (0.5 mmol), dissolved in acetone (50 mL), was added slowly to an acetone solution (20 mL) of Gd(NCS)₃ (0.5 mmol) under vigorous stirring. After partial evaporation of the solvent, blue-green crystals were formed. They were separated by filtration, washed with cold acetone and air dried. C₃₀H₃₈CuGdN₅O₅S₃ (897.62): calcd. C 40.14, H 4.27, N 7.80; found C 40.42, H 4.41, N 7.85.

[L_BCuGd(NCS)₃H₂O(CH₃)₂CO] (II**):** prepared following a similar procedure. C₂₉H₃₆CuGdN₅O₆S₃ (867.60): calcd. C 40.15, H 4.18, N 8.07; found C 40.95, H 4.23, N 8.11.

Acknowledgments

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- [16] Crystal data for **I**: C₃₀H₃₈CuGdN₅O₅S₃ $M_r = 897.62$ monoclinic; $P2_1/n$; $Z = 4$; $a = 13.347(5)$, $b = 15.344(5)$, $c = 17.930(5)$ Å; $\beta = 93.316(5)^\circ$; $V = 3666(2)$ Å³; $T = 180(2)$ K; 20945 reflections measured; 5252 independent ($R_{int} = 0.0561$); final residuals $R_1 = 0.0435$ [with $I > 2\sigma(I)$], $wR_2 = 0.0697$ (all data). Crystal data for **II**: C₂₉H₃₆CuGdN₅O₆S₃ $M_r = 867.60$ orthorhombic; P_{cab} ; $Z = 8$; $a = 16.8845(10)$, $b = 19.5134(13)$, $c = 21.6665(18)$ Å; $V = 7138.5(9)$ Å³; $T = 180(2)$ K; 54516 reflections measured; 6968 independent ($R_{int} = 0.0447$), final residuals $R_1 = 0.0319$, [with $I > 2\sigma(I)$], $wR_2 = 0.0748$ (all data). Structure solution and refinement were performed using the SHELXS-97 and SHELX97 programs, respectively. CCDC-220473 for **I** and -220474 for **II** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. See also <http://www.rsc.org/suppdata/cc/b3/bf> for crystallographic data in CIF or other electronic format.
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