Cyano-Bridged 4f-3d Assemblies with Achiral Helical Chains: Syntheses, Structures, and Magnetic Properties

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The self-assembly reaction of [Cr(CN)6]3–, Ln3+, and a chelated phen ligand resulted in the first examples of cyano-bridged 3d-4f helical chains [Ln(phen)3(H2O)][Cr(CN)6]·3H2O [Ln = La (1), Ce (2), Pr (3) and Nd (4)], in which the lanthanide center was coordinated unusually by three molecules of a bidentate ligand. The magnetic properties of compounds 2–4 were also investigated.

Introduction

In recent years, the design and elaboration of molecule-based magnets have received much attention.[1] Considering the rather large anisotropic magnetic moments inherent to the lanthanide(III) ions, these materials comprising paramagnetic 4f ions and polycyanometalates, for example, [M(CN)6]3– (M = Cr, Fe, Co) and [M(CN)8]3– (M = Mo, W), deserve special attention and have exhibited intriguing structural features and particularly fascinating magnetic features.[2]

However, it is still a rather challenging task to synthesize 4f-3d/4d/5d materials with specific topologies and therefore magnetic properties due to the liability of lanthanide ions and because of the absence of design strategies for such systems. In this regard, recent studies have indicated that the presence of aromatic bi- or tridentate ligands was crucial to block coordination sites on metal ions, hence restricting the growth of the structure to finite dimensions rather than extended networks.[3] We have successfully applied this building strategy to the preparation of several octacyanometalate(V)-based helical chains, in which the steric hindrance of the chelated bidentate ligands affected obviously the spatial orientation of the helical strands.[4] As part of a detailed study of cyano-bridged assemblies,[5] the above success inspired us to design 3d-4f magnetic systems with low dimensionalities, especially helical chains, by using magnetic hexacyanometalates as building blocks to react with lanthanide ions in the presence of bidentate organic ligands. This communication is devoted to the syntheses, crystal structures, and magnetic properties of the first cyano-bridged 3d-4f bimetallic compounds with a helical chain structure [Ln(phen)3(H2O)][Cr(CN)6]·3H2O [Ln = La (1), Ce (2), Pr (3), and Nd (4)].

Results and Discussion

Single-crystal X-ray diffraction analyses revealed that compounds 1–4 are isomorphous and crystallize in the triclinic space group $P1$. Here, only the structure of compound 4 is described in detail as an example, which is formed by chains of cyano-bridged alternating arrays of Nd(phen)3(H2O) and Cr(CN)6 fragments (Figure 1).

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In the [Nd(phen)₃(H₂O)]²⁺ fragment, each Nd³⁺ ion exhibits a nine-coordinate tricapped trigonal prism (the capping positions are occupied by O₁, N₇, and N₁₂ atoms), in agreement with the coordination geometry of lanthanide ions observed in [W(CN)₆]³⁻-based layers Ln(H₂O)₃W(CN)₆ (Ln = Sm, Eu, Gd, Tb).[6] The coordination sphere around the Nd³⁺ center is completed by six nitrogen atoms of three phen ligands, two nitrogen atoms of two μ₂-bridging cyanide groups, and one oxygen atom of the coordinated water molecule. The Nd₁–N distances to the nitrogen atoms of the phen ligands fall in the range 2.571–2.698 Å and the Nd₁–O bond length is 2.541(3) Å. The average Ln1–N bond lengths slightly decrease from compounds 1 to 4 due to the effect of lanthanide contraction.[7] Two bridging cyanides linked to the central Nd³⁺ ion deviate significantly from linearity with bond angles of 164.4(3)° for Nd₁–N₁–C₁ and 166.6(4)° for Nd₁–N₂–C₂, which can be attributed to the steric hindrance of the coordinated phen ligands and water molecule.

One interesting aspect of the structures for compounds 1–4 is the coordination environment of the lanthanide ion involved. The coordination sphere of the lanthanide ion in most cyano-bridged 4f-3d assemblies reported previously consists of one or two molecules of a bidentate blocking ligand (e.g., bpy).[8] It should be mentioned that the lanthanide ion has a larger radius and can hold more blocking molecules of a bidentate phen ligand acting as a capping group. This phenomenon has not been documented previously in such a system and may be rationalized by the fact that the early lanthanide ion in our case is coordinated unusually by three molecules of a bidentate blocking ligand acting as a capping group. The Nd₁ distance across the cyanide bridge is 7.37 Å, and the Nd₁ and Cr₁ atoms in a pitch form a scarce irregular pentagonal channel viewed along the a axis (Figure S1, Supporting Information). The experimental magnetization values decrease continuously by cooling the temperature to the depopulation of excited Stark sublevels,[13] reaching minimum values of 2.11 cm³ K mol⁻¹ at 25 K and 2.73 cm³ K mol⁻¹ at 30 K for compounds 2 and 4, respectively. A continued decrease in the temperature leads to a sharp increase in χ₂ MT values of 3.20 (for 2) and 7.33 (for 4) cm³ K mol⁻¹ at 1.8 K. These are typical characteristics of ferrimagnetic behaviors. However, the low-temperature magnetic measurements (zfc-fc) and susceptibility measurements (ac) for compound 4 indicated the absence of any magnetic ordering (Figures S2 and S3, Supporting Information). The experimental magnetization of compounds 2 and 4 at 2 K display a monotonic increase with an increasing value of the magnetic field and reach the values of 3.37 (for 2) and 4.06 (for 4) N₄H₉ at H = 70 kOe. The magnetic behavior of both compounds indicated the presence of antiferromagnetic interactions between the Ln³⁺ and Cr³⁺ ions through the cyanide groups, which were also observed in other cyano-bridged Ln³⁺Cr³⁺ (Ln = Ce, Nd) assemblies with ferrimagnetic character.[13]

The magnetic feature of compound 3 at high temperatures is similar to that of compounds 2 and 4. The χ₂ MT value of 3.21 cm³ K mol⁻¹ at 300 K is lower than the expected one of 3.58 cm³ K mol⁻¹ for isolated one Pr³⁺ and

Figure 2. Perspective view of the left- (top) and right-handed (bottom) helical chains of compound 4.

Magnetic susceptibility measurements for compounds 2–4 were performed on polycrystalline samples in an applied field of 1 kOe over the temperature range 1.8–300 K by using a SQUID magnetometer (Figures 3 and 4). The χ₂ MT–T curves for compounds 2 and 4 are similar, which can be characterized by a slight decrease as the temperature is decreased, followed by an abrupt increase at low temperatures. The room-temperature χ₂ MT values [2.34 (for 2) and 3.08 (for 4) cm³ K mol⁻¹] for both compounds are lower than the theoretical ones [2.78 (for 2) and 3.61 (for 4) cm³ K mol⁻¹] for the superposition of isolated Ln³⁺ and Cr³⁺ ions.[12] The χ₂ MT values decrease continuously by cooling the temperature, due to the depopulation of excited Stark sublevels,[13] reaching minimum values of 2.11 cm³ K mol⁻¹ at 25 K and 2.73 cm³ K mol⁻¹ at 30 K for compounds 2 and 4, respectively. A continued decrease in the temperature leads to a sharp increase in χ₂ MT values of 3.20 (for 2) and 7.33 (for 4) cm³ K mol⁻¹ at 1.8 K. These are typical characteristics of ferrimagnetic behaviors. However, the low-temperature magnetic measurements (zfc-fc) and susceptibility measurements (ac) for compound 4 indicated the absence of any magnetic ordering (Figures S2 and S3, Supporting Information). The experimental magnetization of compounds 2 and 4 at 2 K display a monotonic increase with an increasing value of the magnetic field and reach the values of 3.37 (for 2) and 4.06 (for 4) N₄H₉ at H = 70 kOe. The magnetic behavior of both compounds indicated the presence of antiferromagnetic interactions between the Ln³⁺ and Cr³⁺ ions through the cyanide groups, which were also observed in other cyano-bridged Ln³⁺Cr³⁺ (Ln = Ce, Nd) assemblies with ferrimagnetic character.[13]
Conclusions

In the present work, we described a convenient approach to construct the first cyano-bridged 3d-4f assemblies with helical chains. The flexibility of the coordination environment of the lanthanide ions and the importance of chelated bidentate ligands on the formation of low-dimensional assemblies, especially helical chains, have been witnessed again in our case. The novel system presented here opens a new perspective to the study of magnetostuctural correlations in cyano-bridged 3d-4f systems. Further work along this line is in progress in our laboratory.

Experimental Section

Physical Measurements: IR spectra were measured with a Nicolet FT 1703X spectrophotometer in the form of KBr pellets in the 400–400 cm⁻¹ region. All of the magnetization data were recorded with a Quantum Design MPMS-XL7 SQUID magnetometer. The molar magnetic susceptibilities were corrected for the diamagnetism estimated from Pascal's tables and for the sample holder by a previous calibration.[13]

Syntheses of [Ln(phen)₃(H₂O)][Cr(CN)₆]·3H₂O [Ln = La (1), Ce (2), Pr (3), and Nd (4)]: Single crystals of compounds 1–4 were prepared at room temperature in the dark by slow diffusion of an ethanol solution (3 mL) containing Ln(NO₃)₃·6H₂O (0.10 mmol) and phen (0.30 mmol) into a water solution (15 mL) of K₃[Cr(CN)₆]·H₂O (0.10 mmol). After about two weeks, block-shaped colorless crystals suitable for single-crystal X-ray diffraction experiment were obtained. C₄₂H₃₂CrN₁₂O₄La (1), C₄₂H₃₂CrN₁₂O₄Ce (2), C₄₂H₃₂CrN₁₂O₄Pr (3), and C₄₂H₃₂CrN₁₂O₄Nd (4) were prepared in this way.

Crystal Data for Compounds 1–4: C₄₂H₃₂CrN₁₂O₄La for compound 1, Mr = 959.71, triclinic, space group P1, a = 11.4830(13) Å, b = 13.3340(18) Å, c = 18.0490(12) Å, V = 2402.5(5) Å³, Z = 2, Dₐ = 1.285 g cm⁻³. C₄₂H₃₂CrN₁₂O₄Ce for compound 2, Mr = 960.92, triclinic, space group P1, a = 11.3530(17) Å, b = 13.2230(18) Å, c = 17.8240(11) Å, V = 2402.5(5) Å³, Z = 2, Dₐ = 1.328 g cm⁻³. C₄₂H₃₂CrN₁₂O₄Pr for compound 3, Mr = 961.70, triclinic, space group P1, a = 11.3591(13) Å, b = 13.2282(14) Å, c = 17.9891(17) Å, V = 2424.8(4) Å³, Z = 2, Dₐ = 1.317 g cm⁻³. C₄₂H₃₂CrN₁₂O₄Nd for compound 4, Mr = 965.03, triclinic, space group P1, a = 11.2885(13) Å, b = 13.0995(5) Å, c = 17.7188(15) Å, V = 2365.0(6) Å³, Z = 2, Dₐ = 1.353 g cm⁻³. χM/T values were obtained using the Quantum Design MPMS-XL7 SQUID magnetometer. The magnetic measurements were performed in the 2.0–300 K range with high magnetic fields up to 13 T. The magnetic susceptibilities were corrected for the diamagnetism of the lanthanide ions and the importance of chelated bidentate ligands on the formation of low-dimensional assemblies, especially helical chains, have been witnessed again in our case.

Supporting Information (see footnote on the first page of this article): Crystallographic diagram; ac and zfc-fc curves for compound 4.

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