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

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The self-assembly reaction of $[Cr(CN)_6]^{3-}$, Ln^{3+}, and a chelated phen ligand resulted in the first examples of cyano-bridged 3d-4f helical chains $[Ln(phen)_3(H_2O)][Cr(CN)_6]\cdot 3H_2O$ [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 $[Ln(phen)_3(H_2O)][Cr(CN)_6]\cdot 3H_2O$ [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 $P\bar{1}$. 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 $Nd(phen)_3(H_2O)$ and $Cr(CN)_6$ fragments (Figure 1).
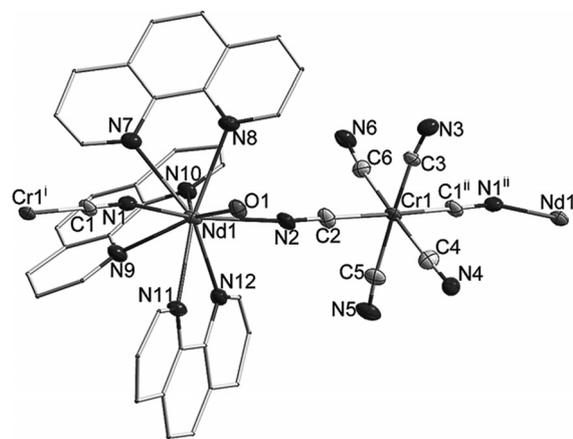

Figure 1. ORTEP diagram of compound **4** showing the 30% probability thermal motion ellipsoid. All hydrogen atoms and crystallized water molecules are omitted for clarity. Symmetry codes: (i) x + 1, y, z; (ii) x – 1, y, z.

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In the $[Nd(phen)_3(H_2O)]^{3+}$ fragment, each Nd^{III} 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 $[W(CN)_8]^{3-}$-based layers $Ln(H_2O)_5W$-$(CN)_8$ (Ln = Sm, Eu, Gd, Tb).[6] The coordination sphere around the Nd^{III} center is completed by six nitrogen atoms of three phen ligands, two nitrogen atoms of two μ_2-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 Nd^{III} 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 in our case is coordinated unusually by three 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 the early lanthanide ion has a larger radius and can hold more blocking ligands.[9]

Each Cr^{III} ion in the $[Cr(CN)_6]^{3-}$ moiety is coordinated by six cyanide groups, furnishing a distorted octahedral coordination, typical of this type of species.[10] The average Cr1–C and C–N distances are 2.012 and 1.194 Å, respectively. The Cr1–C–N bond angles are almost linear and range from 173.4(4) to 178.4(4)°, indicative of strong directional bonding involving the π orbitals of the metal center. As a result, each $Nd(phen)_3(H_2O)$ fragment links two adjacent $Cr(CN)_6$ moieties in a *trans* fashion, whereas each $Cr(CN)_6$ fragment connects two neighboring Nd^{III} ions with *trans*-cyanide bridges, generating achiral helical chains of $[Ln(phen)_3(H_2O)Cr(CN)_6]_n$ with a left-handed or right-handed helix decorated with phen ligands running along the *a* axis (Figure 2). To the best of our knowledge, cyano-bridged 4f-3d assemblies with helical chain structures have not been reported. There is one $[Nd(phen)_3(H_2O)]^{3+}$ unit and one $[Cr(CN)_6]^{3-}$ moiety in each helical cycle. The intrachain Cr1···Nd1 distance across the cyanide bridge is 5.737 Å, and the Nd1 and Cr1 atoms in a pitch form a scarce irregular pentagonal channel viewed along the screw axis (Figure S1, Supporting Information), different to the rhombus, rectangle, square, or ring observed in other helical chain compounds.[4,11] It should be noted that the presence of three phen ligands with dihedral angles of 31.01, 68.79, and 88.24° is responsible for the formation of the helical chain and also provides potential supramolecular recognition sites for π–π aromatic stacking interaction. In the crys-

tal lattice of compounds **1**–**4**, the crystallized water molecules are hydrogen-bonded to one coordinated water molecule and one non-bridging cyanide N atom and are adjacent to free water molecules. The interplay of intermolecular hydrogen bonds and π–π stacking interactions between phen ligands of neighboring chains provides additional stabilization of the crystal structure, giving a 3D supramolecular network. Furthermore, the crystal structure is porous – channels exist between the chain fragments when viewed from the *a* axis, and these channels contain guest water molecules.
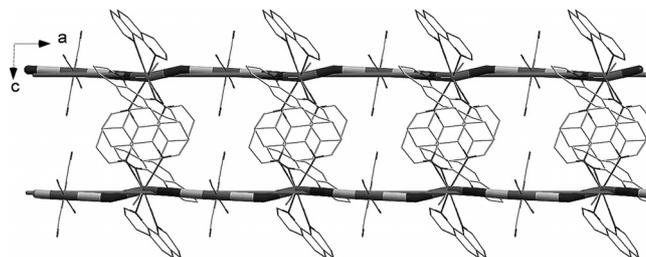

Figure 2. Perspective view of the left- (top) and right-handed (bottom) helical chains of compound **4**.

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 $\chi_M T$–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 $\chi_M T$ values [2.34 (for **2**) and 3.08 (for **4**) $cm^3 K mol^{-1}$] for both compounds are lower than the theoretical ones [2.78 (for **2**) and 3.61(for **4**) $cm^3 K mol^{-1}$] for the superposition of isolated Ln^{III} and Cr^{III} ions.[12] The $\chi_M T$ values decrease continuously by cooling the temperature, due to the depopulation of excited Stark sublevels,[13] reaching minimum values of 2.11 $cm^3 K mol^{-1}$ at 25 K and 2.73 $cm^3 K mol^{-1}$ at 30 K for compounds **2** and **4**, respectively. A continued decrease in the temperature leads to a sharp increase in $\chi_M T$, and the values of 3.20 (for **2**) and 7.33 (for **4**) $cm^3 K mol^{-1}$ were observed 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 2.0 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**) $N\mu_B$ at $H =$ 70 kOe. The magnetic behavior of both compounds indicated the presence of antiferromagnetic interactions between the Ln^{III} and Cr^{III} ions through the cyanide groups, which were also observed in other cyano-bridged $Ln^{III}Cr^{III}$ (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 $\chi_M T$ value of 3.21 $cm^3 K mol^{-1}$ at 300 K is lower than the expected one of 3.58 $cm^3 K mol^{-1}$ for isolated one Pr^{III} and
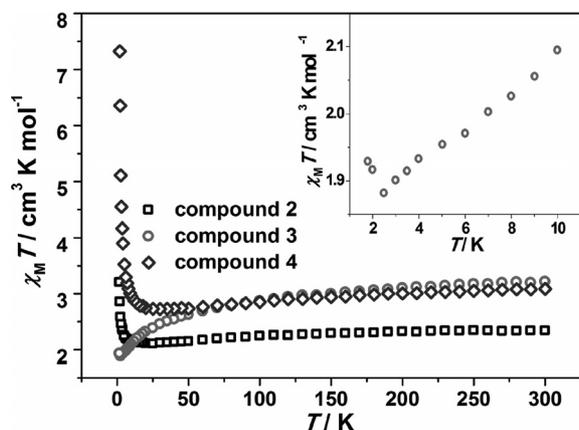
Figure 3. Temperature dependence of $\chi_M T$ for compounds **2**–**4**. Inset: Low temperatures for compound **3**.
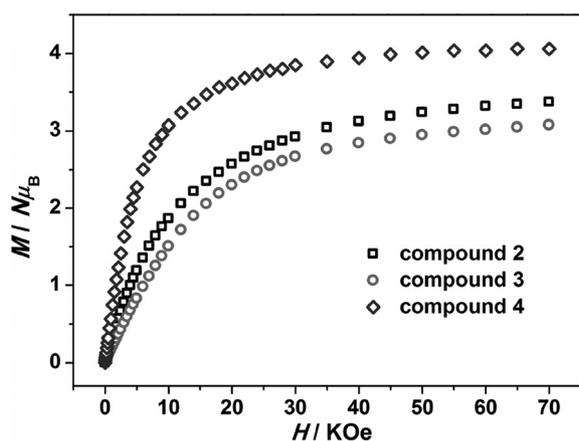

Figure 4. Field dependence of the magnetization performed at 2.0 K for compounds **2**–**4**.

one Cr^{III}.[12] However, the $\chi_M T$ value below 50 K decreased drastically to reach the minimum value of 1.88 cm³mol⁻¹ K at 2.5 K and increased slightly to 1.93 cm³ K mol⁻¹ at 1.8 K upon further cooling. The slight increase in $\chi_M T$ at low temperatures can be attributed to the Cr···Cr interaction through the diamagnetic Pr ion.[14] The experimental magnetization at 2.0 K increases monotonically and achieves a value of 3.07 at 70 kOe. Obviously, the exact magnetic characters cannot be concluded from these data.

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 magnetostructural 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 4000–400 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.[15]

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 $Ln(NO_3)_3$·6H₂O (0.10 mmol) and phen (0.30 mmol) into a water solution (15 mL) of $K_3[Cr(CN)_6]$·H₂O (0.10 mmol). After about two weeks, block-shaped colorless crystals suitable for single-crystal X-ray diffraction experiment were obtained. $C_{42}H_{32}CrLaN_{12}O_4$ (**1**, 959.69): calcd. C 52.56, H 3.36, N 17.51; found C 52.61, H 3.38, N 17.46. $C_{42}H_{32}CeCrN_{12}O_4$ (**2**, 960.91): calcd. C 52.50, H 3.36, N 17.49; found C 52.48, H 3.40, N 17.45. $C_{42}H_{32}CrN_{12}O_4Pr$ (**3**, 961.70): calcd. C 52.45, H 3.35, N 17.48; found C 52.42, H 3.39, N 17.49. $C_{42}H_{32}CrN_{12}NdO_4$ (**4**, 965.03): calcd. C 52.27, H 3.34, N 17.42; found C 52.30, H 3.35, N 17.45. IR (KBr): $\nu_{C\equiv N}$ = 2132 (for **1**), 2135 (for **2**), 2137 (for **3**), 2138 (for **4**) cm⁻¹.

Crystal Data for Compounds 1–4: $C_{42}H_{32}N_{12}O_4CrLa$ for compound **1**, M_r = 959.71, triclinic, space group $P\bar{1}$, a = 11.4830(13) Å, b = 13.3340(18) Å, c = 18.0490(12) Å, V = 2480.9(5) Å³, Z = 2, D_c = 1.285 g cm⁻³, R_1 (wR_2) = 0.0458 (0.1070) and S = 1.065 for 9377 reflections with $I > 2\sigma(I)$. $C_{42}H_{32}N_{12}O_4CrCe$ for compound **2**, M_r = 960.92, triclinic, space group $P\bar{1}$, a = 11.3530(17) Å, b = 13.2230(18) Å, c = 17.8240(11) Å, V = 2402.5(5) Å³, Z = 2, D_c = 1.328 g cm⁻³, R_1 (wR_2) = 0.0460 (0.1148) and S = 1.022 for 9299 reflections with $I > 2\sigma(I)$. $C_{42}H_{32}N_{12}O_4CrPr$ compound **3**, M_r = 961.71, triclinic, space group $P\bar{1}$, a = 11.3591(13) Å, b = 13.2282(14) Å, c = 17.9891(17) Å, V = 2424.8(4) Å³, Z = 2, D_c = 1.317 g cm⁻³, R_1 (wR_2) = 0.0533 (0.1307) and S = 1.020 for 9359 reflections with $I > 2\sigma(I)$. $C_{42}H_{32}N_{12}O_4CrNd$ for compound **4**, M_r = 965.04, triclinic, space group $P\bar{1}$, a = 11.2885(13) Å, b = 13.099(3) Å, c = 17.7188(15) Å, V = 2365.0(6) Å³, Z = 2, D_c = 1.355 g cm⁻³, R_1 (wR_2) = 0.0483 (0.1199) and S = 1.069 for 8999 reflections with $I > 2\sigma(I)$. CCDC-869683 (for **1**), -869684 (for **2**), -869682 (for **3**), and -869681 (for **4**) contain the supplementary 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.

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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