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A Luminescent and Magnetic Cyano-Bridged Tb^{3+}–Mo^{5+} Coordination Polymer: toward Multifunctional Materials

Elena Chelebaeva,[†] Joulia Larionova,*,[†] Yannick Guari,[†] Rute A. Sá Ferreira,[‡] Luis D. Carlos,*,[‡] Filipe A. Almeida Paz,[§] Alexander Trifonov,[||] and Christian Guérin[†]

Institut Charles Gerhardt Montpellier, UMR 5253, Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Place E. Bataillon, 34095 Montpellier cedex 5, France, Departamentos de Física e Quimica and CICECO, Universidade de Aveiro, 3810 -193 Aveiro, Portugal, and G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Science, Tropinina 49, GSP-44S, 603950, Nizhny Novgorod, Russia

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A new cyano-bridged coordination polymer network $Tb(H_2O)_5[Mo(CN)_8]$ was obtained and characterized. This compound has a two-dimensional layered structure and presents luminescence along with a magnetic transition at low temperature.

The design and study of multifunctional materials have attracted a great deal of attention due to their fundamental interesting qualities and their potential applications.[1] Among these, research aimed at molecule-based magnets presenting besides magnetism another property, such as optical activity,[2] nonlinear optical property,[3] porosity,[4] or conductivity,[5] has increased in recent years. Analogous efforts regarding multifunctional molecule-based materials combining magnetism and luminescence have been comparatively few in number,[6,7] and not many molecule-based networks truly present the coexistence of a magnetic ordering with luminescence properties.[7]

One of the promising ways to achieve multifunctional luminescent molecule-based magnets is to design multidimensional networks in which luminescent lanthanide ions are associated with transition-metal ions.[8] However, the f−f transitions of lanthanides are spin- and parity-forbidden,[9] and to exploit the luminescent properties, the lanthanide−transition-metal ions couple as well as the bridging ligand should be carefully chosen to prevent the quenching of the lanthanide luminescence by an energy transfer process. In this connection, cyanometalates of 4d metal ions seem to be interesting building blocks for the design of multidimensional luminescent magnetic networks in association with lanthanide ions. It should be outlined that numerous one-,[8,10] two-,[8,11] and three-dimensional[8,12] cyano-bridged molecule-based magnets based on the association of 4f−*n*d ($n = 3-5$) ions have been reported in the last 30 years due to their original architectures and interesting magnetic properties. However, to the best of our knowledge, the luminescent properties of these compounds have never been investigated except for the preliminary study of A. Vogler and H. Kunkely on a heavy atom effect of $Gd[M(CN)_6]$ ($M = Cr, Co$), inducing the appearance of phosphorescence under ambient conditions.[13] In this Communication, we report the first study of the luminescent properties of a new two-dimensional cyano-bridged molecule-based magnet $Tb(H_2O)_5[Mo(CN)_8]$.

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* To whom correspondence should be addressed. E-mail: joulia.larionova@univ-montp2.fr. (J.L.), lcarlos@fis.ua.pt (L.D.C.). Fax: (33) 467143852 (J.L.), (351) 424965 (L.D.C.).

[†] Université Montpellier II.

[‡] Departamento de Física and CICECO, Universidade de Aveiro.

[§] Departamento de Quimica and CICECO, Universidade de Aveiro.

[||] G. A. Razuvaev Institute.

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The slow diffusion of ether (1.5 mL) to a 4.7×10^{-4} M (2 mL) solution of $[(N(C_4H_9)_4]_4[Mo(CN)_8]\cdot 2H_2O$[14] and 6.0×10^{-4} M (1.5 mL) of $[Tb(H_2O)_5](NO_3)_3$ in acetonitrile leads to the formation of a highly crystalline compound[15] whose crystal structure was ultimately elucidated by using single-crystal X-ray diffraction. The infrared spectrum of this compound exhibits two sharp bands at 2181 (w) and 2136 (s) cm^{-1}, which are attributed to the ν(CN) stretching modes. The presence of several CN stretches reveals the presence of both bridging and terminal cyano ligands. The single-crystal X-ray crystallographic study shows that this compound has a two-dimensional crystal structure determined in the tetragonal *P*4/*nmm* space group.[16] It contains two crystallographically independent metallic centers, Mo(1) and Tb(1), both located in special crystallographic positions. Mo(1) appears in the crystal structure coordinated to eight cyanides, with the $\{MoC_8\}$ coordination geometry resembling a slightly distorted dodecahedron, which is in good agreement with the structural features reported for similar compounds (Figure 1S, Supporting Information).[11b,17] While half of the coordinated cyanide groups are terminal, exhibiting statistical disorder for the uncoordinated nitrogen atom, the other half is bidentate, establishing physical links (μ_2-CN) with neighboring Tb^{3+} centers. The coordination sphere of the Tb^{3+} centers is composed of four cyanide groups plus five water molecules, $\{TbN_4O_5\}$, describing a slightly distorted tricapped trigonal prism. The intermetallic connectivity through the μ_2-cyanide bridges leads to the formation of neutral two-dimensional $_\infty{}^2[Tb(H_2O)_5Mo(CN)_8]$ corrugated layers placed in the *ab* crystallographic plane (Figure 1). The shortest interlayer distance between $Mo^{5+}-Mo^{5+}$ or between $Tb^{3+}-Tb^{3+}$ ions is equal to 7.1961(9) Å. Connections between layers are assured by relatively strong O−H⋯N hydrogen bonds connecting the O(1W) coordinated molecules from one layer to the unidentate C(2)−N(2) cyanide groups of another layer with $d_{O\cdots N}$ of 2.617(1) Å.

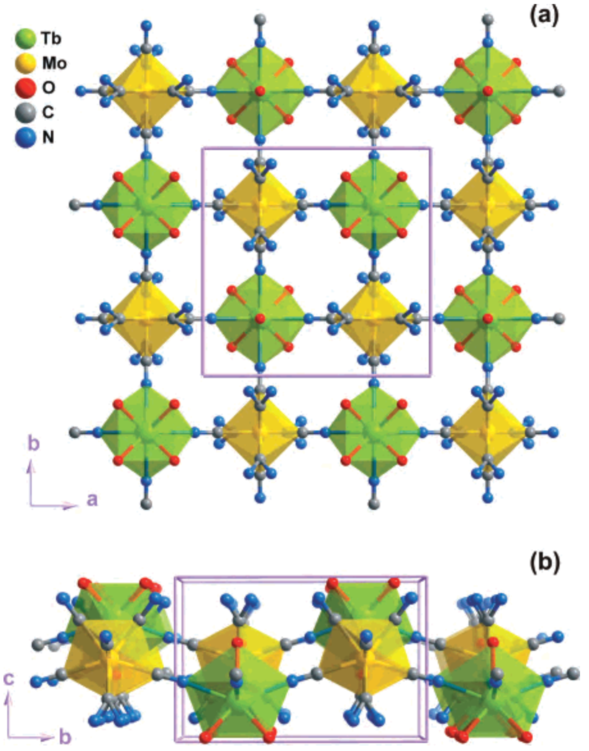

Figure 1. Schematic representation of the crystal packing of $Tb(H_2O)_5$-$[Mo(CN)_8]$ viewed in perspective along the (a) [001] and (b) [010] crystallographic directions.

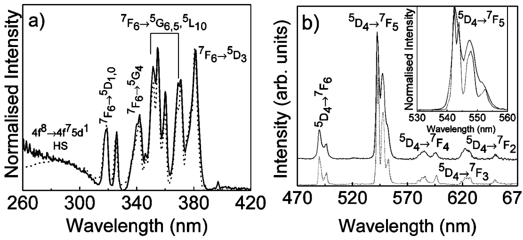

Figure 2. (a) Room-temperature (solid line) and 14 K (dotted line) excitation spectra monitored around 544 nm and (b) room-temperature (solid line) and 14 K (dotted line) emission spectra excited at 380 nm. The inset shows a magnification of the $^5D_4 \rightarrow {}^7F_5$ transition.

The $Tb(H_2O)_5[Mo(CN)_8]$ compound shows luminescence in the solid state at low and room temperature.[18] Figure 2a shows its excitation spectra monitored within the $^5D_4 \rightarrow {}^7F_5$ transition, in the 14−300 K temperature range. These spectra

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(15) Anal. Calcd for $C_8H_{10}MoN_8O_5Tb$: C, 17.35; N, 20.25; Mo, 17.35; Tb, 28.75. Found: C, 17.61; N, 20.49; Mo, 17.01; Tb, 28.45.

(16) Crystal data for $Tb(H_2O)_5[Mo(CN)_8]$: $C_8H_{10}MoN_8O_5Tb$, $M = 553.10$, tetragonal, space group *P*4/*nmm*, $Z = 2$, $a = 10.8912(2)$ Å, $c = 7.1961(2)$ Å, $V = 853.59(3)$ Å^3, μ(Mo K_α) = 4.878 mm^{-1}, $D_c = 2.152$ g cm^{-3}. Independent reflections, 580 ($R_{int} = 0.0305$). Final R1 = 0.0208 [$I > 2\sigma(I)$] and wR2 = 0.0560 (all data). Data completeness to θ = 27.48°, 99.5%. CCDC 660990.

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(18) The photoluminescence spectra were recorded between 14 K and room temperature on a Fluorolog-3 model FL3-2T with a double excitation spectrometer and a single emission spectrometer (TRIAX 320) coupled to a R928 photomultiplier, using the front face acquisition mode. The excitation source was a 450 W xenon lamp. The lifetime measurements were acquired between 14 K and room temperature with the setup described for the luminescence spectra using a pulsed Xe−Hg lamp (6 μs pulse at half width and 20−30 μs tail).

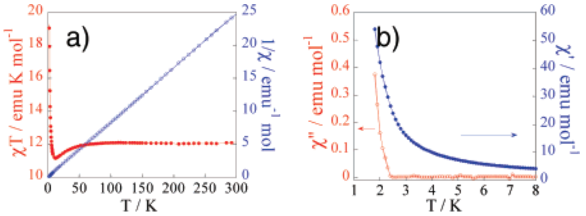

Figure 3. (a) Temperature dependence of the χT product and $1/\chi$ performed with an applied field of 1000 Oe and (b) temperature dependence of in-phase, χ', and out-of-phase, χ'', components of the ac susceptibility at 1 Hz.

do not depend on the temperature and display a series of sharp lines, ascribed to the intra-4f^8 transitions between the $^7F_6$ and the $^5G_{4-6}$, $^5L_{10}$, and $^5D_{0,1,3}$ levels, and a low-intensity band in the 250−310 nm region attributed to the spin-forbidden (high-spin, HS) interconfigurational f−d transition.[19] Figure 2b compares the emission spectra of the $Tb(H_2O)_5[Mo(CN)_8]$ compound at 14 K and room temperature under direct intra-4f^8 excitation (380 nm, $^5L_{10}$). Both spectra display the typical $^5D_4 \rightarrow {}^7F_{6-2}$ Tb^{3+} intra-4f^8 lines. The low-temperature spectrum is more structured than the room temperature one, with a higher number of Stark components observed, in particular for the $^5D_4 \rightarrow {}^7F_5$ transition (inset of Figure 2b). The high full width at half maximum value of the intra-4f^8 lines (~40 cm^{-1}) reflects a broad distribution of closely equivalent Tb^{3+} local environments, in good agreement with the X-ray diffraction results.

The $^5D_4$ lifetime values were estimated between 14 and 300 K by monitoring the emission decay curves within the $^5D_4 \rightarrow {}^7F_5$ transition (544 nm) under direct intra-4f^8 excitation ($^5D_3$, 380 nm) and via the HS interconfigurational f−d band (290 nm) (Figure 2S, Supporting Information). Both emission decay curves are well modeled using a single-exponential function, with the observation that the lifetime values estimated for direct intra-4f^8 excitation are higher than those observed under 290 nm excitation wavelength (1.313 ± 0.014 ms and 1.183 ± 0.020 ms, respectively). The complex displays small lifetime dependence with temperature, being 1.120 ± 0.009 ms at 14 K and excited at 380 nm.

The magnetic properties of $Tb(H_2O)_5[Mo(CN)_8]$ were determined by using a supercondconducting quantum interference device (SQUID) magnetometer working in the 1.8−350 K temperature range and with applied fields of up to 5 T.[20] The temperature dependences of the χT product and $1/\chi$ performed for $Tb(H_2O)_5[Mo(CN)_8]$ with an applied field of 1000 Oe are shown in Figure 3a. At 2 K, the χT value of 19.04 emu K mol^{-1} decreases rapidly as the temperature increases, reaches the minimum value (11.14 emu K mol^{-1}) at 12 K and then increasing to 12.12 emu K mol^{-1} at 300 K. This later value corresponds to the calculated values for one noninteracting Tb^{3+} ion (11.75 emu K mol^{-1}) and one noninteracting Mo^{5+} (0.37 emu K mol^{-1}) ion.[21] The presence of the minimum on this curve may be attributed to the depopulation of the Stark levels of the terbium $^7F_6$ ground state. Above 50 K, the temperature dependence of $1/\chi$ may be fitted with the Curie−Weiss law, $1/\chi_M = (T - \Theta)/C$, with the Curie constant of 12.06 emu K mol^{-1} and the Weiss constant of 0.27 K suggesting predominant ferromagnetic interactions. The field dependence of the magnetization performed at 1.8 K shows the value of the saturation magnetization of 5.9 μ_B at 50 kOe expected for ferromagnetic interactions between Tb^{3+} and Mo^{5+} ions (6 μ_B) if we assume a spin of $S = {}^1/_2$ with $g = 2$ for molybdenum ion and an effective spin of $S = {}^1/_2$ with $g_{||} = 10$ and $g_{\perp} = 0$ for terbium ion (Figure 3S, Supporting Information).[10a] The presence of ferromagnetic $Tb^{3+}-Mo^{5+}$ interactions through the cyano bridge is in agreement with the previously reported cyano-bridged one-dimensional compound.[10a] The temperature dependences of the alternating current (ac) susceptibility, its in-phase, χ' (absorptive), and out-of-phase, χ'' (dispersive), components performed in zero applied direct current (dc) field for the frequency of 1 Hz, show that both χ' and χ'' responses increase dramatically above 3.0 and 2.3 K, respectively (Figure 3b). The temperature dependences of χ' and χ'' responses are not frequency dependent, suggesting the presence of a magnetic ordering below 2.3 K. However, the exact nature of this magnetic transition may not be properly determined from these measurements.

To summarize, we have obtained a new two-dimensional cyano-bridged coordination polymer based on luminescent lanthanide ions Tb^{3+} and the $[Mo(CN)_8]^{5-}$ building block. This compound displays the typical emission lines ascribed to the intra-4f^8 transitions between the first excited state and the ground multiplet ($^5D_4 \rightarrow {}^7F_{6-2}$). The study of its magnetic properties reveals the presence of ferromagnetic interactions between Tb^{3+} and Mo^{5+} ions inducing the appearance of a magnetic transition below 2.3 K. The work on the investigation of the luminescent and magnetic properties at low temperature of cyano-bridged molecule-based magnets based on the association of 4f−*n*d (*n* = 4, 5) ions is currently in progress.

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Supporting Information Available: Crystallographic data; emission decay curves; field-dependence magnetization. This material is available free of charge via the Internet at http://pubs.acs.org.

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