Synthesis, structure, luminescence and magnetic properties of the coordination polymer $\{[Eu(H_2O)_5][Mo(CN)_8]\}_\infty$ containing bridging cyanide ligands

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The reaction of $[Eu(H_2O)_6](NO_3)_3$ and $[N(C_4H_9)_4]_3[Mo(CN)_8]\cdot 2H_2O$ afforded a new two-dimensional coordination polymer $\{[Eu(H_2O)_5[Mo(CN)_8]\}_\infty$ (**1**) in which the europium and molybdenum atoms are bound through the bridging CN groups. The luminescence and magnetic properties of complex **1** were studied in a wide temperature range.

Key words: lanthanides, coordination polymers, polycyanometallates, luminescence, magnetism.

In recent years, one-, two-, and three-dimensional coordination polymers based on transition metals containing bridging cyanide ligands have attracted attention of researchers as promising objects for the creation of new polyfunctional materials.[1] One of important directions is the production of molecular magnets possessing magnetic, luminescence, nonlinear-optical, *etc.* properties. Coordination polymers based on lanthanides and possessing simultaneously magnetic and luminescence properties are few in number.[2] It is known[3,4] that the f—f-transitions in lanthanide ions are forbidden by the selection rules and, therefore, the nature of the bridging ligand plays a decisive role in preventing luminescence quenching during the energy transfer process. In this connection, cyanometallate anions are promising counterions for lanthanide cations. The Eu^{3+} ion was chosen because of its high quantum yield and long-lived emission, which is characteristic of its compounds, whereas the Mo^{5+} ion, unlike Fe^{3+}, does not quench luminescence during the energy transfer through the cyanide bridge.[5]

Results and Discussion

The reaction between equimolar amounts of $[Eu(H_2O)_6](NO_3)_3$ and $[N(C_4H_9)_4]_3[Mo(CN)_8]\cdot 2H_2O$ (see Ref. 2) was carried out in acetonitrile at room temperature. Slow diffusion of diethyl ether into the reaction mixture results in the formation of orange crystals of the $\{[Eu(H_2O)_5][Mo(CN)_8]\}_\infty$ complex (**1**) in 75% yield. The IR spectrum of complex **1** exhibits three narrow intense absorption bands at 2177, 2161, and 2128 cm^{-1} assigned to stretching vibrations of CN, indicating the presence of both bridging and terminal cyanide ligands. In addition, the bands at 3571, 3375, and 3195 cm^{-1} indicate that complex **1** contains coordinated water molecules. The X-ray diffraction study showed that complex **1** represents

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 466—469, February, 2010.

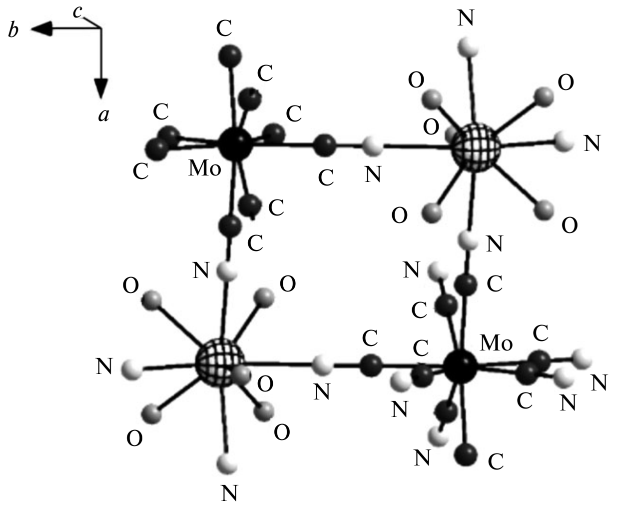

Fig. 1. Fragment of the polymer layer of complex **1**.

a 2D coordination polymer (Fig. 1). Selected bond lengths and bond angles for complex **1** are listed in Table 1, and X-ray data collection and refinement statistics are given in Table 2. The molybdenum atom in complex **1** coordinates eight cyanide ligands, four of which are terminal and four others are bridging ligands linking the Mo and Eu atoms in the μ_2 coordination mode. In addition, the europium atom coordinates five water molecules. The average Eu—N bond length is 2.502(14) Å. The binding of the metal centers through the μ_2-bridging cyanide ligands affords neutral two-dimensional corrugated layers lying in the crystallographic plane *ab* (see Fig. 1). The layers are linked *via* relatively strong hydrogen bonds between the water molecules, which lie in a single layer with the nitrogen atoms of the CN groups of another layer, and the O...N distances are 2.617(1) Å.

Table 1. Selected bond lengths (*d*) and bond angles (ω) for complex **1**

Parameter	Characteristics
Bond	*d*/Å
Eu(1)—O(1W)	2.523(17)
Eu(1)—O(2W)	2.428(12)
Eu(1)—N(1)	2.502(14)
Mo(1)—C(1)	2.140(15)
Mo(1)—C(2)	2.117(14)
Angle	ω/deg
O(2W)—Eu(1)—O(1W)	127.4(4)
O(2W)—Eu(1)—O(2W)	68.4(4)
O(2W)—Eu(1)—O(2W)	105.2(8)
O(2W)—Eu(1)—N(1)	137.66(18)
O(2W)—Eu(1)—N(1)	71.7(4)
N(1)—Eu(1)—O(1W)	69.5(3)
N(1)—Eu(1)—N(1)	138.9(6)
N(1)—Eu(1)—N(1)	82.9(2)
C(1)—Mo(1)—C(1)	95.1(2)
C(1)—Mo(1)—C(1)	145.1(7)
C(2)—Mo(1)—C(1)	144.7(6)
C(2)—Mo(1)—C(1)	76.2(3)
C(2)—Mo(1)—C(1)	70.1(6)
C(2)—Mo(1)—C(2)	129.3(5)
C(2)—Mo(1)—C(2)	74.6(9)

Table 2. Crystallographic data and X-ray diffraction data collection and refinement statistics for complex **1**

Parameter	Characteristics
Formula	$C_8H_{10}EuMoN_8O_5$
Molecular weight	546.14
Crystal system	Tetragonal
Space group	*P*4/*nmm*
a/Å	10.9601(4)
c/Å	7.1277(4)
V/Å^3	856.35(7)
*Z*2	
d_{calc}/g cm^{-3}	2.118
μ/mm^{-1}	4.395
θ Scan range/deg	3.72—25.34
Number of measured reflections	15477
Number of reflections with $I > 2\sigma(I)$	472 (R_{int} = 0.0305)
R_1 ($I > 2\sigma(I)$)	0.0462
wR_2 ($I > 2\sigma(I)$)	0.1200
R_1 (based on all data)	0.0463
wR_2 (based on all data)	0.1200
Residual electron density (max/min)/e • Å^{-3}	3.291/—1.710

The luminescence properties of complex **1** in the crystalline state were studied at 14 and 300 K. The luminescence excitation spectrum at 300 K contains broad low-intensity lines in the region of 250—310 nm and a series of narrow bands (360, 375, 383, 399, 395, 465, 525, 536 nm) attributed to the f—f-transitions ($4f^6$) in the Eu^{3+} cation (Fig. 2). As the temperature decreases to 14 K, the relative

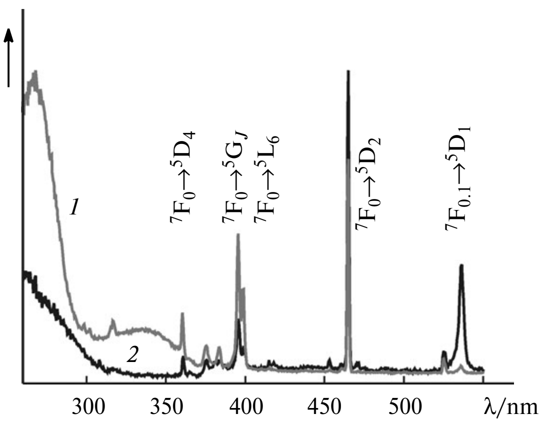

Fig. 2. Excitation spectra of complex **1** at 14 (*1*) and 300 K (*2*). The wavelength of detection is 617 nm.

band intensity at 250—310 nm increases and other broad associated bands appear in a region of 310—360 nm. The emission spectra of complex **1** at 300 K reflecting the f—f-transitions ($4f^6$) $^5D_0 \to {}^7F_J$ (J = 0—4), which are characteristic of the Eu^{3+} ions,[3,4] are shown in Fig. 3.

The lifetime of the $^5D_0$ level for the Eu^{3+} complex in the temperature range from 14 to 300 K was calculated by the curves of intensity change near the most intense line of the emission spectrum of complex **1** (λ_{lum} = 618 nm) at the exciting radiation wavelength 464 nm.

The quenching curves (see Fig. 3, inset) cannot be resolved using an exponential law but are well described by the two-exponential function for the lifetimes τ equal to 0.992±0.213 and 1.472±0.069 ms (14 K), 0.421±0.022 and 1.279±0.088 ms (300 K). A decrease in the lifetime with increasing temperature from 14 to 300 K is indicative of the existence of thermally activated nonradiative processes.

The magnetic processes of complex **1** were studied in the 1.8—350 K range. The temperature dependences of the magnetic susceptibility (χ) and the χT value measured at a field strength of 1000 Oe are shown in Fig. 4. At 300 K χT = 1.79 K mol^{-1} cm^{-3}, which is slightly lower than the value 1.875 K mol^{-1} cm^{-3} calculated for the non-interacting Eu^{3+} (1.500 K mol^{-1} cm^{-3}) and Mo^{5+} (0.375 K mol^{-1} cm^{-3}) ions. The χT value decreases gradually with the temperature decrease and reaches 0.007 K mol^{-1} cm^{-3} at 2 K. The magnetic susceptibility increases with the temperature decrease and has the maximum value at 2.4 K (see Fig. 4). At low temperature the europium ion is characterized by the population of only the ground nonmagnetic state $^7F_0$, whereas the excited states are populated at room temperature ($^7F_1$ and $^7F_2$). In this case, the magnetic susceptibility of an isolated europium ion becomes temperature-independent and, hence, the low-temperature magnetic behavior of complex **1** should be defined by exchange interactions only between the Mo^{5+} ions with the spin 1/2 through the Mo—CN——Eu—NC—Mo bridge.[6] The magnetic susceptibility at temperatures above 230 K is defined by the Curie—Weiss law due to the presence of populated excited states. However, more detailed calculations of magnetic interactions for the europium-based complexes are difficult.[7] The maximum observed in the temperature plot of the ac magnetic susceptibility indicates the antiferromagnetic exchange interactions. The real component of the magnetic susceptibility (χ´) has a frequency-independent peak at 2.33 K, whereas the imaginary component is equal to zero, which confirms the presence of antiferromagnetic interactions at low temperature (see Fig. 4, inset).

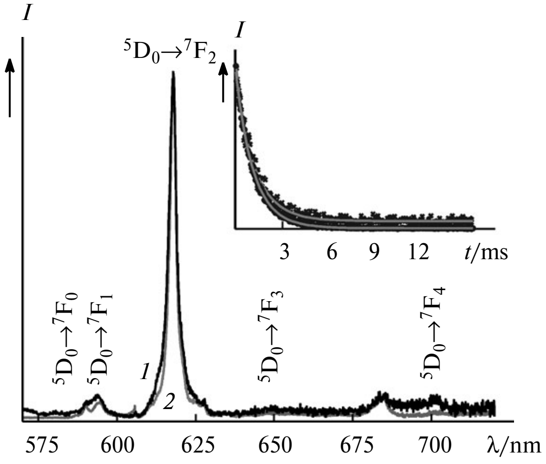

Fig. 3. Emission spectra of complex **1** at the exciting radiation wavelengths 284 (*1*) and 464 nm (*2*) at 300 K. Inset: the curves of changes in the emission intensity of complex **1** at 14 and 300 K (the solid line corresponds to the data of the best approximation to the exponential function (R > 0.999)).

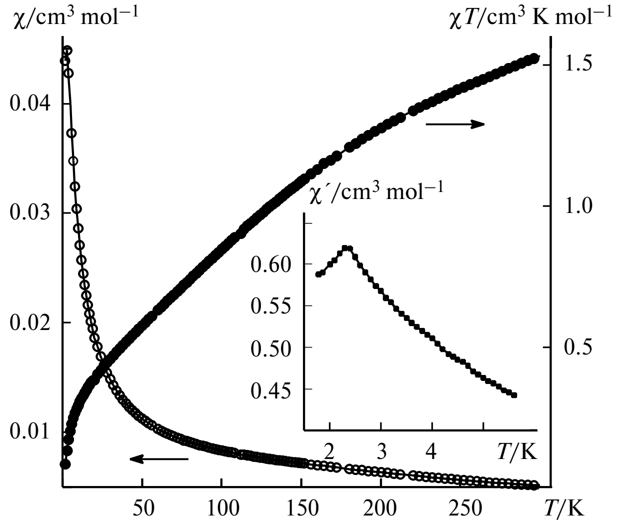

Fig. 4. Temperature dependences of the magnetic susceptibility (χ) and the χT value for complex **1** at a field strength of 1000 Oe. Inset: the temperature dependence of the real component of the ac magnetic susceptibility (χ´) at a frequency of 125 Hz.

In spite of interest in coordination polymers observed in recent years and the regular reports[8—12] on the synthesis and structural studies of the polycyanometallate complexes of lanthanides with different structures (two-dimensional coordination polymers, one-dimensional chains, molecular complexes), the europium derivatives remain unknown and there were no data on magnetic luminescent bifunctional materials. We synthesized the first representative of two-dimensional cyano-bridged coordination polymers consisting of the Eu^{3+} ions and $[Mo(CN)_8]^{5-}$ fragments and simultaneously possessing magnetic and luminescence properties. An analysis of the luminescence properties of compound **1** reveals the characteristic emission lines corresponding to the $4f^8$-transitions between the first excited state and the ground multiplet in the Eu^{3+} ions ($^5D_4 \to {}^7F_{6-2}$). The study of the magnetic properties of complex **1** indicates that at low temperatures the antiferromagnetic interactions occur between the Mo^{5+} ions through the Mo—CN—Eu—NC—Mo bridges.

Experimental

IR spectra were recorded on an Avatar 320 FT-IR spectrophotometer in KBr pellets in the range of 400—4000 cm^{-1}. Luminescence excitation and luminescence spectra at 14 and 300 K were detected on an instrument consisting of a Fluorolog-3 Model FL3—2T fluorimeter equipped with a TRIAX 320 double excitation and emission spectrometer, an R928 photomultiplier, and a receiver. Excitation sources were a xenon lamp (450 W) and a Xe—Hg pulse-discharge lamp (for measuring lifetimes). Magnetic measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer in the range 2—300 K. The diamagnetic contribution of ions was taken into account according to Pascal´s scheme in calculations of the paramagnetic component of the magnetic susceptibility of the complex.[13]

Complex $\{[Eu(H_2O)_5][Mo(CN)_8]\}_\infty$ (1). A solution of $[N(C_4H_9)_4]_3[Mo(CN)_8]\cdot 2H_2O$ (0.400 g, 0.49 mmol) in MeCN (2 mL) was added to a solution of $[Eu(H_2O)_6](NO_3)_3$ (0.217 g, 0.49 mmol) in MeCN (2 mL). Slow diffusion of diethyl ether into the reaction mixture resulted in yellow crystals of complex **1**. The yield was 0.200 g (75%). IR (KBr), ν/cm^{-1}: 3571 (OH); 3375 (OH); 3195 (OH); 2177 (C≡N); 2161 (C≡N); 2128 (C≡N). Found (%): C, 17.45; H, 1.58; Eu, 27.96; Mo, 17.02; N, 20.45. Calculated (%): C, 17.59; H, 1.85; Eu, 27.83; Mo, 17.57; N, 20.52.

X-ray diffraction study of complex 1. Experimental intensities at $T = 180(2)$ K were measured on a Bruker X8 Kappa APEX II Smart APEX automated diffractometer (graphite monochromator, Mo-Kα radiation, ω and φ scan modes). Selected crystallographic characteristics and the X-ray data collection and refinement statistics are given in Tables 1 and 2. The structure of complex **1** was solved by the Patterson method and refined by least squares based on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were revealed from difference Fourier maps and refined isotropically. All calculations were performed using the SHELXTL-97 program package.[14,15] An absorption correction was applied using the SADABS program.[16]

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Received January 19, 2009;
in revised form September 9, 2009