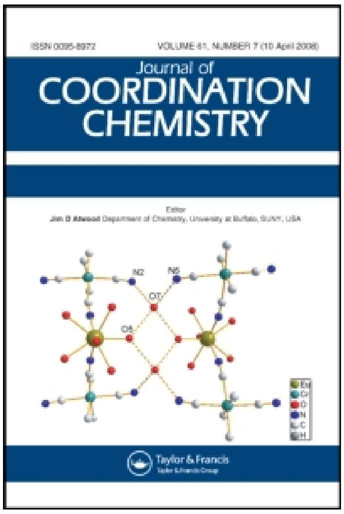

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Synthesis and crystal structure of a three-dimensional 3d-4f heterometallic supramolecular complex {Eu(DMF)$_4$(H$_2$O)$_2$Cr(CN)$_6$·;H$_2$O}<b><i>n</i>

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Synthesis and crystal structure of a three-dimensional 3d-4f heterometallic supramolecular complex $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6 \cdot H_2O\}_n$

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A lanthanide-transition heterometallic supramolecular complex $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6 \cdot H_2O\}_n$ (**1**) has been synthesized based on the reaction of $K_3[Cr(CN)_6]$, *N*,*N*-dimethylformamide (DMF) and $Eu(NO_3)_3 \cdot 6H_2O$. **1** crystallizes in the monoclinic space group $P2(1)/c$ with $a = 13.130(6)$ Å, $b = 12.923(7)$ Å, $c = 19.184(9)$ Å and $Z = 4$. In **1** each Eu(III) is eight-coordinate with six oxygen atoms from four DMF molecules and two H_2O molecules and two nitrogen atoms from two *cis*-bridging CN ligands to form a distorted dodecahedron. **1** has a three-dimensional network created by the incorporation of coordinative linkage, three inter-molecular and an intrachain hydrogen bond.

Keywords: Heterometallic supramolecular complex; Three-dimensional; Hydrogen bonds

1. Introduction

Self-assembled supramolecular architectures have fascinating structures with potential applications in catalysis, host-guest chemistry, molecule-based magnets, optical materials, ion-exchange and gas absorption [1–4]. Considerable effort has been devoted to cyano-bridged lanthanide-transition metal supramolecular complexes because of interesting structures and possibilities for preparation of various materials, such as orthoferrites, electroceramic and chemical sensor materials, fluorescent materials and magnetic materials [5–11]. A series of cyano-bridged supramolecular complexes based on reaction of polycyanometallates(III) (Fe, Co, Cr, Mn) and 4f metal ions have been reported [12–19]. In self-assembled supramolecular compounds, hydrogen bonding interactions between moieties in the supramolecular system are well-developed methods for increasing structural dimensionality [20–22]. Here we report a three-dimensional lanthanide-transition heterometallic supramolecular complex created by the incorporation of coordinative linkage and different hydrogen bonds.

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2. Experimental

2.1. *Materials and synthesis*

For the preparation of **1**, an aqueous solution (25 mL) of $K_3[Cr(CN)_6]$ (32.5 mg, 0.1 mmol) was added dropwise under stirring to a DMF solution (15 mL) of $Eu(NO_3)_3 \cdot 6H_2O$ (89.2 mg, 0.20 mmol). After the mixed solution was stirred for two hours, the mixed solution was filtered. By slow evaporation of the mixed solvent for several days in the dark, light yellow crystals suitable for X-ray crystallography were obtained. Anal. Calcd for $C_{18}H_{34}Cr\ EuN_{10}O_7$: C, 30.57; H, 4.81; N, 19.81%. Found: C, 30.28; H, 4.62; N, 19.58%.

2.2. *Physical measurements*

C, H, N elemental analyses were carried out using a Perkin–Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR–408 infrared spectrophotometer in the 4000–600 cm^{-1} region. All reagents were commercially available and used as received. Variable-temperature magnetic susceptibilities were measured on a LDJ 9600 vibrating-sample magnetometer in the temperature range 90–300 K.

2.3. *X-ray crystallography*

Data collection was performed on Bruker Smart 1000 area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$) at 293(2) K. Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods, successive Fourier difference syntheses (SHELX-97) and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [23]. Hydrogen atoms were generated geometrically and refined isotropically.

Crystal data for 1: $C_{18}H_{34}CrEuN_{10}O_7$, M = 706.51, Monoclinic, *P*2(1)/c, $a = 13.130(6)$, $b = 12.923(7)$, $c = 19.184(9)$ Å, $\beta = 109.636(8)^\circ$, $Z = 4$, $D_c = 1.531\ g\ cm^{-3}$, $V = 2846.4(16)$ Å^3, $\mu = 2.431\ mm^{-1}$, $F(000) = 1420$, crystal dimensions $0.40 \times 0.25 \times 0.20\ mm^3$, 5414 unique reflections, 4700 observations ($I > 2.00\sigma(I)$), final $R_1 = 0.0351$, $wR_2 = 0.0832$, GOF = 1.046, largest difference peak and hole: 0.886 and -0.706 e Å^{-3}.

3. Results and discussion

3.1. *Description of the structure of complex 1*

Figure 1 shows the atom labelling scheme of **1** viewed along the crystallographic *c* axis. **1** exhibits a cyano-bridged one-dimensional zigzag chain $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6\}$ with an alternation of Eu(III) and Cr(III) units linked by cyanide bridges in *cis* geometry with respect to Cr(III). The Eu atom is eight coordinate with six oxygens from four DMF molecules and two H_2O molecules as well as two nitrogens from two *cis*-bridging CN ligands. The Eu(III) lies in a distorted dodecahedral environment.

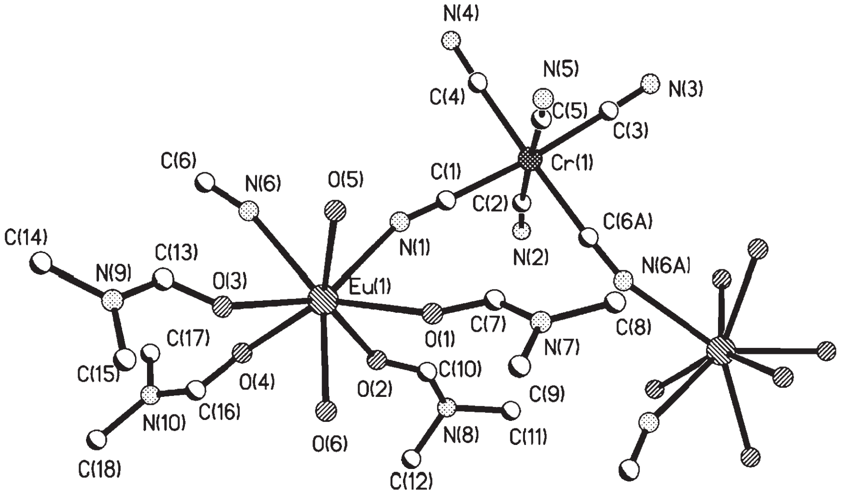

Figure 1. The atom labelling scheme of **1**.

The bond distances are Eu(1)–N(1) = 2.517(5) Å, Eu(1)–N(6) = 2.538 (5) Å, Eu(1)–O(1) = 2.367(4) Å, Eu(1)–O(4) = 2.401(5) Å, Eu(1)–O(5) = 2.428(4) Å and Eu(1)–O(6) = 2.369 (4) Å. The O–Eu–O bond angles range from 71.06(16)° to 145.98(16)°. The O–Eu–N bond angles range from 78.17(15)° to 82.21(17)°. The N(1)–Eu(1)–N(6) bond angle is 75.15(15)°. The bond angle for the bridging CN and Eu (C(1)–N(1)–Eu(1) and C(6)–N(6)–Eu(1)) are 159.8(4) and 162.4(4)°, respectively. The geometry of $Cr(CN)_6^{3-}$ is approximately octahedral with Cr–C bond lengths from 2.057(6) to 2.090(5) Å. The two cyano-bridged ligands in **1** lead to distortion of C1–Cr1–C6 (94.7(2)°). The Cr–C–N bond angle ranges from 171.8(5) to 178.8(6)°. The C–N bond distances range from 1.128(7) to 1.152(8) Å. There are three different inter-molecular and an intrachain hydrogen bonds. Figure 2 shows the hydrogen-bonded networks. In each one-dimensional zigzag complex chain $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6\}$, one of two coordinated water molecules and two *cis*-terminal CN groups from two different μ_2-bridging $[Cr(CN)_6]^{3-}$ groups connect to an uncoordinated water molecule through O $\cdots$ N and O $\cdots$ O inter-molecular hydrogen bonds (figure 2a). Each uncoordinated water molecule acts as a μ_4-bridge. Two uncoordinated and two coordinated water molecules from two different chains form a planar tetramer water clusters $(H_2O)_4$. For the water clusters, the O(5) $\cdots$ O(7) distance is 2.801 Å. The bond angles of O(5) $\cdots$ O(7) $\cdots$ O(5)′ and O(7) $\cdots$ O(5) $\cdots$ O(7)′ are 82° and 97°, respectively. The O(5) $\cdots$ O(7) $\cdots$ O(5)′ $\cdots$ O(7)′ torsion angle is 0°. The N(2) $\cdots$ O(7) distance is 2.876 Å. The N(2) $\cdots$ O(7) $\cdots$ N(2)′ and O(5) $\cdots$ O(7) $\cdots$ N(2) are 100° and 109°, respectively. In each one-dimensional zigzag chain $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6\}$, another coordinated water molecule of each Eu(III) atom connects to two nitrile nitrogen atoms through inter-molecular and intrachain O $\cdots$ N hydrogen bonds (figure 2b). The intrachain N(4) $\cdots$ O(6) distance is 2.758 Å and inter-molecular N(3) $\cdots$ O(6)″ is 2.776 Å. The N(4) $\cdots$ O(6) $\cdots$ N(3)″ bond angle is 104°. Each one-dimensional zigzag chain connects to two others through O $\cdots$ N and O $\cdots$ O inter-molecular hydrogen bonds, resulting in a hydrogen-bonded 3D network. Figure 3 shows a 2D packing diagram viewed along

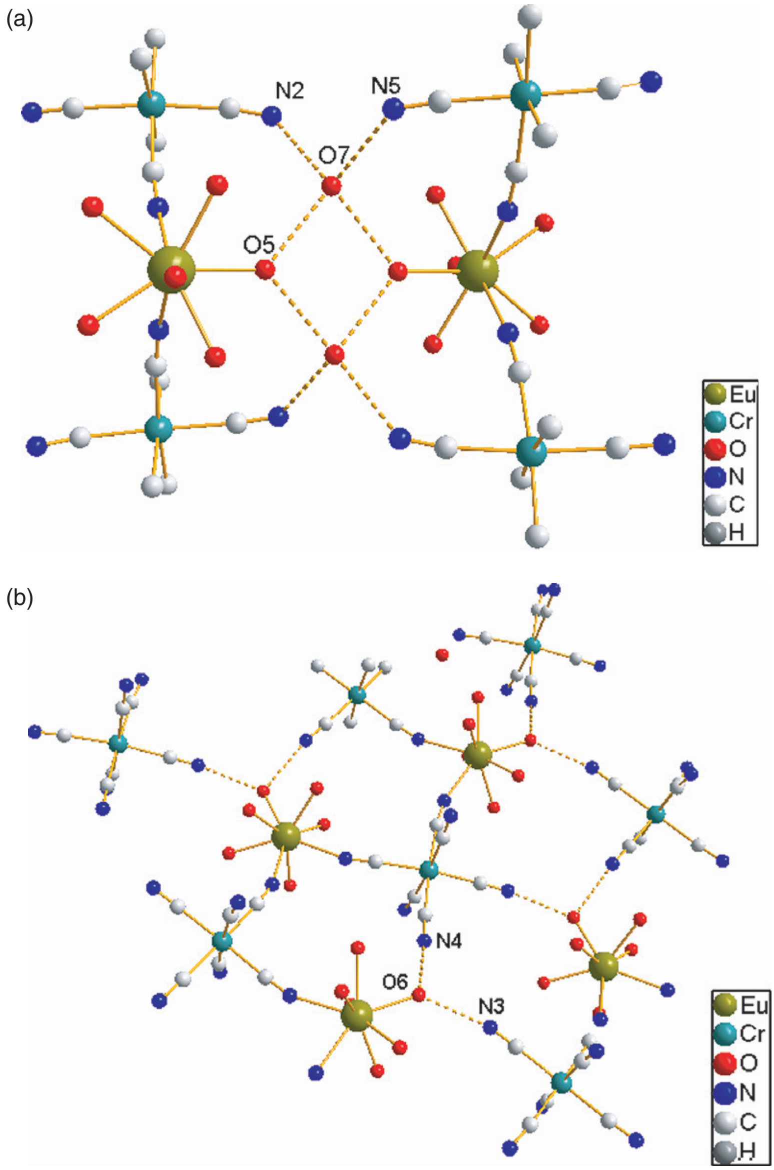

Figure 2. (a) Hydrogen-bonded interaction between the uncoordinated water molecules and the zigzag complex chain $\{Eu(DMF)_4(H_2O)_2Cr(CN)_6\}$. (b) The hydrogen bonds between the coordinated water molecules and terminal nitrile nitrogen atoms.

the crystallographic *c* axis and the 3D packing diagram of **1** viewed along the crystallographic *a* axis.

3.2. *Spectroscopic properties*

At room temperature, the solid state infrared spectrum of **1** has two ν_{CN} bands at 2156(s) and 2123(m) cm^{-1}, indicating two types of cyanide. The lower frequency

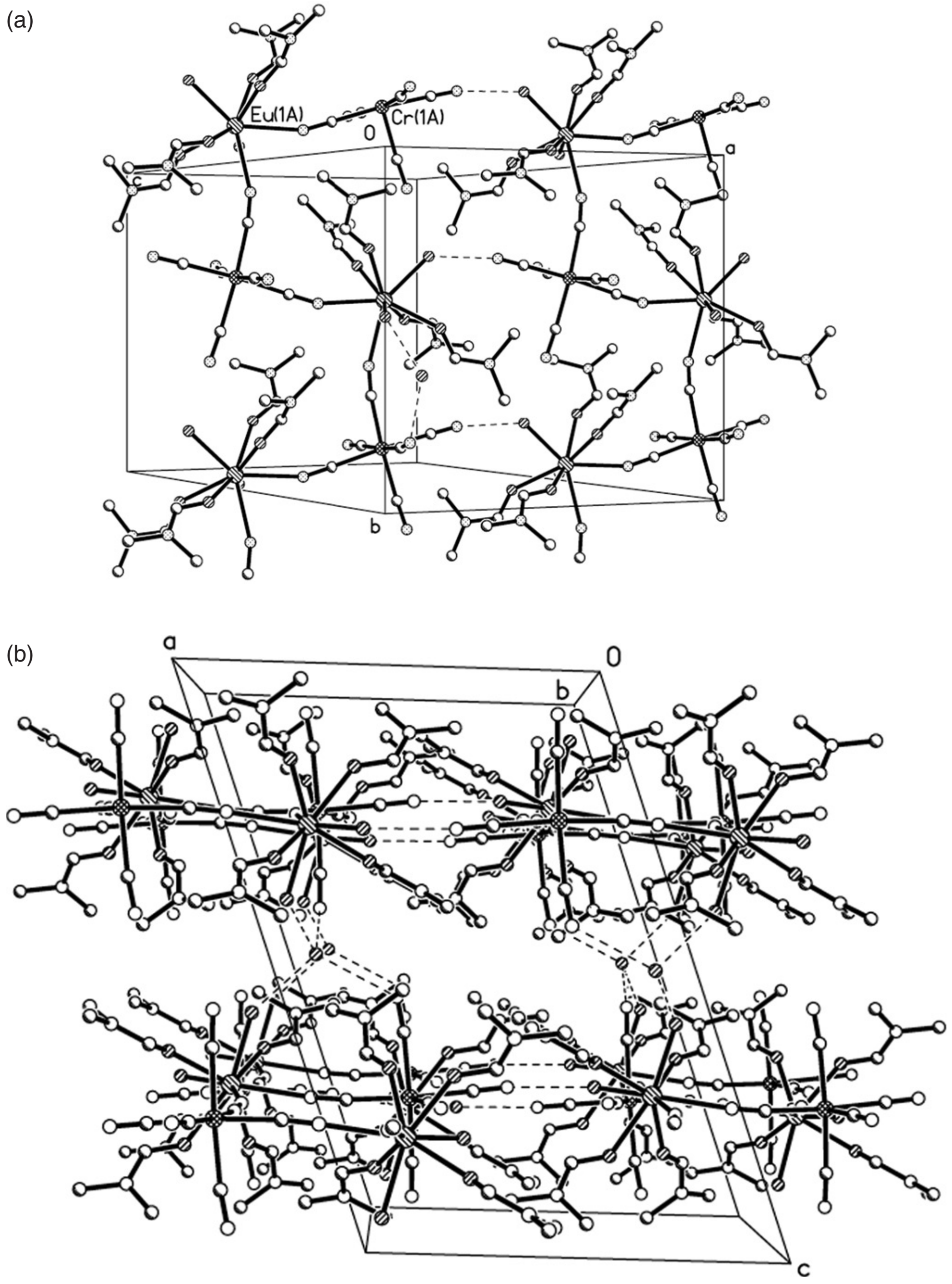

Figure 3. (a) The 2D packing diagram of **1** viewed along the crystallographic *c* axis. (b) The 3D packing diagram of **1** viewed along the crystallographic *a* axis. Hydrogen atoms and carbon and nitrogen atoms of DMF molecules are omitted for clarity.

band can be ascribed to nonbridging cyanide and the higher frequency to bridging cyanide [24].

3.3. *Magnetic properties*

The magnetic behavior of **1** is shown in figure 4. The observed μ_{eff} value is $4.85\,\mu_{\mathrm{B}}$ at 300 K, inconsistent with the calculated value of $3.87\,\mu_{\mathrm{B}}$ for one Cr(III) ($S = 3/2$) and one independent Eu(III) assuming that only the ground state $^7F_0$ of the Eu(III) ion is thermally populated. The disagreement is ascribed to the presence of thermally populated excited states as is well known for Eu(III) complexes [25]. Upon cooling, the μ_{eff} value decreases monotonically, due to the progressive depopulation of excited levels ($J = 1 - 6$) of Eu(III), crystal field effect and the exchange coupling between the Eu(III) and Cr(III) ions. The radially contracted nature of the valence orbitals in the crystal field experienced by Eu(III) ion is small in relation to the spin-orbit coupling λ. Thus, to a first approximation the magnetic susceptibility of Eu(III) can be described by the free-ion approximation equation (1) [26].

$$\chi_{\mathrm{Eu(III)}} = \frac{N\beta^2}{3KTx}\left[\frac{A}{B}\right]$$

$$\begin{aligned} A = 24 &+ (27x/2 - 3/2)\mathrm{e}^{-x} + (135x/2 - 5/2)\mathrm{e}^{-3x} + (189x - 7/2)\mathrm{e}^{-6x} \\ &+ (405x - 9/2)\mathrm{e}^{-10x} + (1485x/2 - 11/2)\mathrm{e}^{-15x} + (2457/x - 13/2)\mathrm{e}^{-21x} \end{aligned}$$

$$B = 1 + 3\mathrm{e}^{-x} + 5\mathrm{e}^{-3x} + 7\mathrm{e}^{-6x} + 9\mathrm{e}^{-10x} + 11\mathrm{e}^{-15x} + 13\mathrm{e}^{-21x}$$

$$x = \frac{\lambda}{KT} \tag{1}$$

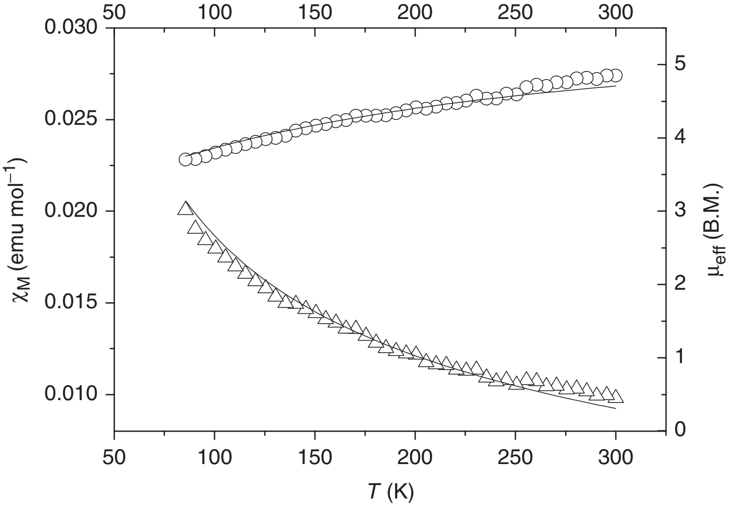

Figure 4. μ_{eff} *vs.* T plots for **1**.

and the magnetic susceptibility of Cr(III) can be described with equation (2).

$$\chi_{\mathrm{Cr(III)}} = \frac{Ng^2\beta^2}{3\mathrm{KT}}\frac{3}{2}\left(\frac{3}{2}+1\right) \quad g = 2 \tag{2}$$

Thus the magnetic susceptibility of the complex can be treated as sum of the contributions of one Eu(III) and one Cr(III) (equation 3) [27].

$$\chi_{\mathrm{Tot}} = \chi_{\mathrm{Eu(III)}} + \chi_{\mathrm{Cr(III)}} \tag{3}$$

Taking into account the interaction between Cr(III) and Eu(III) ions, a correction can be made (equation 4).

$$\chi_{\mathrm{Tot}} = \frac{\chi_{\mathrm{Tot}}}{[1 - 2zJ'\chi_{\mathrm{Tot}}/Ng^2\beta^2]} \tag{4}$$

A good fit to experimental data is obtained for $\lambda = 416$, $g = 2$, $zJ' = -6$. The agreement factor R defined here as $\Sigma_{\mathrm{I}}(X_i^{\mathrm{obs}})^{-1}(X_i^{\mathrm{obs}} - X_i^{\mathrm{calcd}})^2$ is equal to approx 8.8×10^{-4}. The value of zJ' reveals antiferromagnetic interaction between the Cr(III) and Eu(III) ions.

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