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Unique seven-node rare-earth octacyanomolybdate(IV) three-dimensional molecular frameworks: $\{[Er(H_2O)_5(Er(H_2O)_4)_3][Mo(CN)_8]_3 \cdot 11H_2O\}_n$ and $\{[Eu(H_2O)_5(Eu(H_2O)_4)_3][Mo(CN)_8]_3 \cdot 11H_2O\}_n$

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ABSTRACT

The crystal structure analyses of $\{[Er(H_2O)_5(Er(H_2O)_4)_3][Mo(CN)_8]_3 \cdot 11H_2O\}_n$ (**1**) and $\{[Eu(H_2O)_5(Eu(H_2O)_4)_3][Mo(CN)_8]_3 \cdot 11H_2O\}_n$ (**2**), show that they are not only new neutral three-dimensional rare-earth octacyanomolybdate(IV) molecular frameworks, but that they also belong to an unknown structure type having seven different nodes. To the best of our knowledge this is different to any other known molybdenum(IV) octacyanide complexes published to date. Both compounds crystallize in the triclinic system, space group *P-1*, and are isostructural and isotypic. The coordination polyhedra of the molybdenum atoms in the three different $[Mo(CN)_8]^{4-}$ anions are trigonal prisms, with two additional atoms. A new bridging mode for octacyanometallates is also observed with five of the eight cyanide groups involved in bridging either three or four rare-earth atoms, while the three remaining cyanide groups are terminal and are involved in hydrogen bonding. The four rare-earth atoms in **1** and **2** have different coordination polyhedra in the form of trigonal prisms with two additional atoms. The three-dimensional structures are made up of infinite two-dimensional slabs linked by one of the rare-earth metal atoms. In both compounds, apart from the 17 coordinated water molecules, there are 11 lattice water molecules of crystallization present in the cavities of the three-dimensional frameworks. The 28 water molecules and the terminal CN^- groups are involved in an extensive O–H···O and O–H···N hydrogen bonding network.

1. Introduction

Transition metal cyanide complexes, containing rare-earth metal cations in the outer shell, have been investigated in the past due to their interesting magnetic, optical and absorption properties. The crystal structures of several rare-earth hexacyanide complexes, for example $LnFe(CN)_6$, $Ln_4[Fe(CN)_6]_3$ [1], $KLnFe(CN)_6 \cdot nH_2O$ [2], $KLnRu(CN)_6 \cdot nH_2O$ [3], $Ln_4[T(CN)_6]_3 \cdot nH_2O$ (T = Fe, Ru) [4], $LnFe(CN)_6 \cdot nH_2O$ [5], and $LnCo(CN)_6 \cdot nH_2O$ [6], have been reported. Two series of rare-earth octacyanometallate-based complexes, $Ln(H_2O)_5[W(CN)_8]$ [Ln = La, Pr, Nd, Eu, Gd] and $Ln(H_2O)_4[W(CN)_8]$ [Ln = Ho, Er, Tm, Lu], have also been synthesized and characterized structurally [7].

The subject of octacyanides in polynuclear molecular materials has been reviewed recently by Sieklucka et al. [8]. The authors show that there are many examples of 0D, 1D and 2D $[M^{IV}(CN)_8]^{4-}$ and $[M^{V}(CN)_8]^{3-}$ complexes, involving essentially M = W, Mo, Nb, and first-row transition metals, such as manganese, iron, cobalt, nickel and copper. There are relatively few inorganic 3D bimetallic cyanide-bridged systems. Most of them involve the $[W^{IV}(CN)_8]^{4-}$ anion and first row transition metal dications. There are two main types found; one where four of the cyanide groups are bridging [9,10] and the other where all eight cyanide groups are bridging [11–14]. Complexes involving $[Mo^{IV}(CN)_8]^{4-}$ and lanthanide ions, such as, $KYMo(CN)_8 \cdot 7H_2O$ [15], $KLaMo(CN)_8 \cdot 7H_2O$ [16], $KSmMo(CN)_8 \cdot 7H_2O$ [17], and $KYbMo(CN)_8 \cdot 7H_2O$ [18], all require a K^+ ion to neutralize the charges, and in general form 1D, or 2D polymers. Three-dimensional networks involving just $[M^{IV}(CN)_8]^{4-}$ and lanthanide ions are rare. To the best of our knowledge the first such structure reported, $[\{Nd^{III}(CH_3OH)Mo^{IV}(CN)_8\}_3]^3 \cdot [Nd^{III}(H_2O)_8]^{3+} \cdot 8CH_3OH$, was unexpectedly obtained from the reaction of

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$[Mo^{V}(CN)_8]^{3-}$ and Nd^{III}, and contains guest molecules of methanol and the cation $[Nd^{III}(H_2O)_8]^{3+}$ [19]. In this complex four of the cyanide ligands bridge to neighboring Nd^{III} ions in the 3D framework, while the four remaining cyanide groups are terminal.

A search of the Cambridge Structural Database [20] revealed the presence of four polymeric complexes involving $[Mo^{IV}(CN)_8]^{4-}$ and lanthanide ions Er and Eu, but which also include an organic ligand or a solvent molecule coordinated to the lanthanide ion [21–24].

The synthesis and IR-spectroscopy of some rare-earth metal octacyanomolybdates (IV), described originally by the formula $Ln_4[Mo(CN)_8]_3\cdot nH_2O$ (Ln = Sc, Y, La–Lu, except Pu and Pr, $n = 4–15$), were first reported many years ago [25]. However, to the best of our knowledge, the X-ray study of their solid-state structures has never been investigated. Herein, we report on the synthesis and the crystal structures of the erbium and europium octacyanomolybdate (IV) complexes, whose composition was found to be $\{[Er(H_2O)_5(Er(H_2O)_4)_3][Mo(CN)_8]_3\cdot 11H_2O\}_n$ (**1**) and $\{[Eu(H_2O)_5(Eu(H_2O)_4)_3][Mo(CN)_8]_3\cdot 11H_2O\}_n$ (**2**).

2. Experimental

2.1. Syntheses

$K_4[Mo(CN)_8]\cdot 2H_2O$ was prepared by a method similar to that described more recently by Wang et al. [10], and then transformed into $H_4[Mo(CN)_8]\cdot 6H_2O$ by the same method as described by Xu et al. [2]. Erbium and europium carbonate were obtained by dissolving the oxide in nitric acid followed by the addition of 15–17% $(NH_4)_2CO_3$ solution with continued stirring. The precipitate obtained was filtered off and treated with carbonic gas for 4–5 h. The resulting suspension of the rare-earth carbonate was washed with water and dried in air. Compounds **1** and **2** were prepared by the reaction of octacyanomolybdate(IV) acid, $H_4[Mo(CN)_8]\cdot 6H_2O$, with erbium and europium carbonate [25]. The reactions lead to the formation of orange-yellow precipitates. These were filtered, rinsed with water and dried in air. Solutions of the original polycrystalline samples in a small quantity of water were prepared and left in the dark for several months. It was only possible to produce good quality single crystals of the complexes, where Ln = Eu and Er (**1** and **2**). The chemical content of the crystals of complexes (**1**) and (**2**) revealed the presence of a total of 28 water molecules. This is more than for the original previously reported complexes which were thought to contain a maximum of 15 water molecules [25].

2.2. Characterization

Infrared spectra were obtained from sample powders mixed with mineral oil on a UR-10 IR spectrometer over a range 400–4000 cm^{-1}.

2.3. X-ray crystallography

The intensity data for a yellow plate-like crystal of (**1**) and a yellow rod-like crystal of (**2**) were collected at 173 K on a Stoe IPDS II diffractometer [26] with Mo $K\alpha$ radiation (graphite monochromator). The structures were solved by direct methods using the program SHELXS-97 [27] and refined using the program SHELXL-97 [27]. Not all the hydrogen atoms of the water molecules could be located in difference Fourier maps. Therefore, some of them were included in calculated positions [28,29]. The non-coordinating water molecules were refined as rigid groups with distance O–H = 0.87 Å and angle H–O–H = 109.5°. The coordinating water molecules (with the same geometry as the non-coordinating ones) were placed to form a regular tetrahedron (O–M,H,H) and the rotation angle around the M–O bond was refined. The low occupancy disordered water molecules were refined without the H atoms, but the H atoms were added to the reported formula (atoms O29 in both **1** and **2**). Several water molecules which are involved in competing hydrogen bonding were refined to form a hydrogen bond and then fixed in that position (waters O17, O18, O19, O27 in **1**; waters O26 and O28 in **2**). The reported hydrogen bonds are within the D–A distance of 3.1 Å with a minimum D–H–A angle of 120° (Supplementary material: Table S1 and Figure S1). They were all refined with $U_{iso}(H) = 1.5U_{eq}(O)$. All the non-hydrogen atoms were refined anisotropically, using the full-matrix least-squares method on F^2. Due to the irregular shape of the crystal numerical absorption corrections could not be applied, hence semi-empirical absorption corrections (multi-scan) were applied using the MULscanABS routine in PLATON [30]. Further crystallographic data and refinement details for compounds (**1**) and (**2**) are given in the Table 1. Selected bond distances for compound (**1**) are given in Table 2. Further geometrical details are available in the archived CIF's.

3. Results and discussion

As compounds **1** and **2** are isostructural and isotypic only the spectral and structural features of compound **1** will be described.

3.1. Infrared (IR) spectra

In the IR spectra of compound **1** the absorption bands at 2105/2120, 2130/2140 and 2150/2180 cm^{-1} are assigned to the bridging and non-bridging ν(CN) bands of the CN^- groups. The splitting of these bands may be attributed to the fact that the three $[Mo(CN)_8]^-$ polyhedra in the structure are different. The ν(MoC) band was

Table 1
Crystal data and structure refinement details for compounds **1** and **2**.

	1	2
Formula	$C_{24}H_{34}Er_4Mo_3N_{24}$ $O_{17}\cdot 11(H_2O)$	$C_{24}H_{34}Eu_4Mo_3N_{24}$ $O_{17}\cdot 11(H_2O)$
M	2085.79	2024.59
Wavelength/Å	0.71073	0.71073
Temperature/K	173	173
Crystal system	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
a, Å	9.1937(4)	9.2319(5)
b, Å	15.6911(7)	15.7997(10)
c, Å	22.7865(10)	23.0451(13)
α, deg	93.397(4)	93.464(5)
β, deg	100.618(3)	100.594(4)
γ, deg	97.434(3)	97.100(5)
V/Å^3	3192.1(2)	3266.8(3)
Z	2	2
D_c/Mg m^{-3}	2.17	2.06
μ(Mo-Kα)/mm^{-1}	5.86	4.43
Absorption T_{min}/T_{max}	0.528/1.000	0.377/1.000
F(000)	1980	1940
Crystal size/mm	0.30 × 0.19 x 0.10	0.45 × 0.29 x 0.16
θ Limits/°	1.66–29.3	1.30–25.7
Measured reflections	42,766	36,169
Unique reflections, R_{int}	17,164, 0.089	12,294, 0.152
Observed reflections $[I > 2\sigma(I)]$	11,917	8572
Goodness of fit on F^2	1.00	1.00
$R_1(F)$, $[I > 2\sigma(I)]$[a]	0.065	0.075
wR_2 (F^2), $[I > 2\sigma(I)]$[b]	0.150	0.184
$R_1(F)$, [all data][a]	0.101	0.106
wR_2 (F^2), [all data][b]	0.168	0.202
Residual density $\Delta\rho_{max}$/ $\Delta\rho_{min}$ e Å^{-3}	3.57/−4.32 near Er atoms	3.03/−3.29 near Eu atoms

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.