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Crystal Structure of Lanthanum Potassium Octacyanomolybdate(IV) Nonahydrate

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Abstract—The crystal structure of $KLaMo(CN)_8 \cdot 9H_2O$ was determined from X-ray diffraction data. The crystals are monoclinic, space group $P2_1/c$, $a = 8.7451(4)$, $b = 25.2761(13)$, $c = 10.6744(5)$ Å, $\beta = 117.059(3)°$, $V = 2101.22(17)$ Å^3, $Z = 4$, $\rho(\text{calcd}) = 2.037$ g/cm^3, $R = 0.0242$, $wR_2 = 0.0500$ for 5656 independent reflections. The coordination polyhedra of the Mo, La, and K atoms are the tetragonal antiprism $[Mo(CN)_8]$, the monocapped tetragonal antiprism $[La(NC)_4(OH_2)_5]$, and the strongly distorted monocapped trigonal prism $[K(NC)_3(OH_2)_4]$, respectively. The La and K atoms are N-linked by seven bridging cyano groups to form double layers with two sandwiched uncoordinated water molecules and the sandwiched terminal CN group. The complex can be formulated as $\{[K(H_2O)_2][La(H_2O)_5][Mo(CN)_8]\}_n \cdot 2nH_2O$.

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Among octacyanotungsten(IV) and -molybdenum(IV) complexes with rare-earth metals, the crystal structures have been determined for $(H_3O)Ce(H_2O)_4[W(CN)_8] \cdot 2H_2O$ (**I**) [1], $\{[K(H_2O)][Tb(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$ (**II**) [2], $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$ (**III**) [3], $\{[K(H_2O)][Yb(H_2O)_4][Mo(CN)_8]\}_n \cdot 2nH_2O$ (**IV**) [4], $\{[K(H_2O)][Sm(H_2O)_5][Mo(CN)_8]\}_n \cdot 4nH_2O$ (**V**) [5]. Complexes **II–IV** relate to the same space group and are structurally similar, but they have somewhat different configurations of the coordination polyhedra of the central atoms and the rare-earth metals.

The goal of this study was to examine the crystal structure of lanthanum potassium octacyanomolybdate(IV) nonahydrate (**VI**).

EXPERIMENTAL

Complex **VI** was synthesized as described in [4]. Single crystals suitable for X-ray diffraction were growth by prolonged keeping of its solution in the dark.

X-ray diffraction analysis. An array of reflection intensities was collected at 173(2) K with a STOE IPDS diffractometer [6] (MoK_a radiation, graphite monochromator, ω scan mode for the range 0°–180° at φ = 0° and for the range 0°–100° at φ = 90°, scan step Δω = 2θ, frame exposure time 3 min, 2.29°–59.53°, d_{min}–d_{max} = 0.716–17.779 Å). The structure was solved by direct methods with the SHELXS program [7] and refined with the SHELXL-97 program [7]. The hydrogen atoms of water molecules were located from the difference electron-density map and refined for fixed O–H distances (0.88(2) Å) and for $U_{iso} = U_{equiv}$ of the corresponding O atom. The parameters of the H(8) atoms were fixed in the final refinement cycle. All the other atoms were refined anisotropically by the weighted full-matrix least-squares method on F^2. A semiempirical absorption correction was applied; the transmission factors T_{min}/T_{max} are 0.5055/0.7126. Crystallographic data for structure **VI** have been deposited with the Cambridge Crystallographic Data Collection (no. 723956; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). All drawings were made with the ATOM program [8].

The projection of structure **VI** onto the plane [010] is shown in Fig. 1. Crystallographic parameters and the data collection statistics for structure **VI** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

According to X-ray diffraction data, the crystal structure of complex **VI** consists of three structural units $[Mo(CN)_8]$, $[La(NC)_4(OH_2)_5]$, and $[K(NC)_3(OH_2)_4]$. The coordination polyhedra of the K, La, and Mo atoms in structure **VI** are shown in Fig. 2.

The molybdenum atom is surrounded by eight cyano groups making up a tetragonal antiprism. The

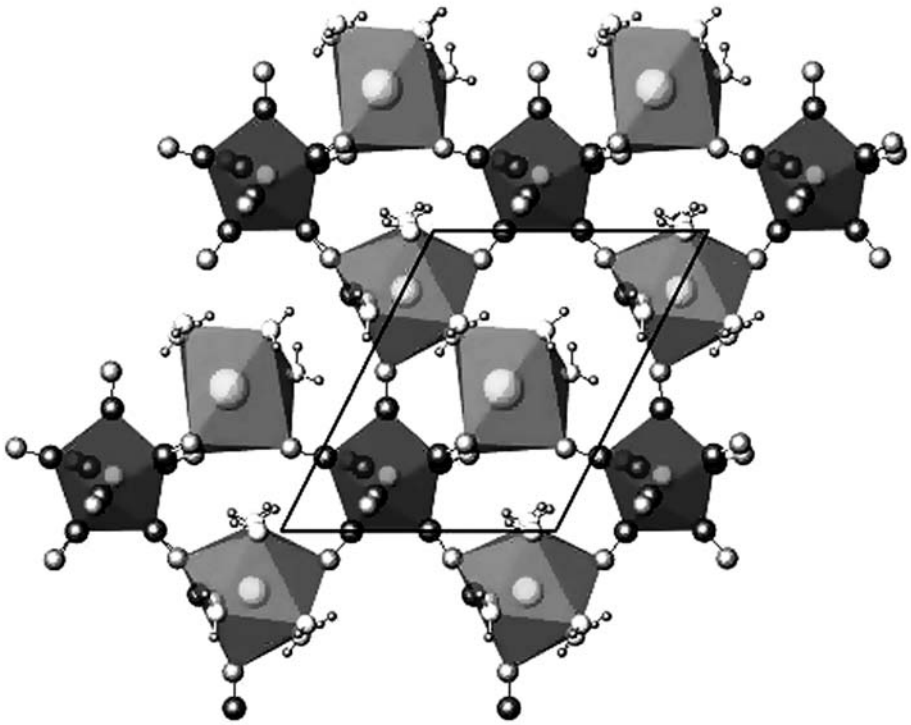

Fig. 1. Projection of the structure $\{[K(H_2O)_2][La(H_2O)_5][Mo(CN)_8]\}_n \cdot 2nH_2O$ onto the plane [010].

Fig. 2. Coordination polyhedra in the structure $\{[K(H_2O)_2][La(H_2O)_5][Mo(CN)_8]\}_n \cdot 2nH_2O$.

Mo–C distances range from 2.151(2) to 2.167(3) Å; the C≡N bond lengths vary from 1.147(3) to 1.157(3) Å. In the polyhedron $[Mo(CN)_8]$, the fragments Mo–C≡N are nearly linear (the angles MoCN are 175.20(18)°–179.1(2)°). The lanthanum atom is coordinated by four N atoms of the cyano groups and by five O atoms of the water molecules. The La–N and La–O distances are 2.622(2)–2.644(2) and 2.5216(15)–2.6070(17) Å. The coordination polyhedron of the La atom, $[La(NC)_4(OH_2)_5]$, can be described as a monocapped tetragonal antiprism with the square faces made up of two N atoms and two O atoms. Interestingly, the atoms of the same type are *trans* in one square face and *cis* in the other. Opposite to the latter face is an additional O atom (H_2O). The

Table 1. Crystallographic parameters and the data collection statistics for $KLaMo(CN)_8 \cdot 9H_2O$

Parameter	Value
Empirical formula	$C_8H_{14}KLaMoN_8O_7 \cdot 2H_2O$
M	644.25
Crystal color	Yellow
Crystal size (mm)	$0.12 \times 0.28 \times 0.40$
Crystal system	Monoclinic
Space group	$P2_1/c$
Lattice parameters:	
a, Å	8.7451(4)
b, Å	25.2761(13)
c, Å	10.6744(5)
β, deg	117.059(3)
V, Å^3	2101.22(17)
Z	4
ρ_{calcd}, g/cm^3	2.037
μ_{Mo}, mm^{-1}	2.856
θ, deg	1.61–29.67
Number of measured reflections	31289
Number of independent reflections	5656
Number of reflections with $I > 2\sigma(I)$	5202
Averaging factor	$R_{int} = 0.0312$
Number of parameters refined	295
R factors (for all reflections)	$R = 0.0242$, $wR = 0.0500$
R factors ($I > 2\sigma(I)$)	$R = 0.0209$, $wR = 0.0488$
GOOF	1.04
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.877/1.205

Table 2. Selected bond lengths and bond angles in $KLaMo(CN)_8 \cdot 9H_2O$

Bond	d, Å	Angle	ω, deg
Mo(1)–C(1)	2.151(2)	C(1)Mo(1)C(2)	78.35(8)
Mo(1)–C(2)	2.167(3)	C(1)Mo(1)C(3)	83.06(8)
Mo(1)–C(3)	2.153(2)	C(1)Mo(1)C(4)	142.08(9)
Mo(1)–C(4)	2.154(3)	C(1)Mo(1)C(5)	73.27(8)
Mo(1)–C(5)	2.159(3)	C(1)Mo(1)C(6)	71.59(9)
Mo(1)–C(6)	2.1505(19)	C(1)Mo(1)C(8)	144.97(10)
Mo(1)–C(7)	2.157(2)	C(1)Mo(1)C(7)	109.91(8)
Mo(1)–C(8)	2.1503(19)	C(2)Mo(1)C(3)	71.08(9)
La(1)–O(1)	2.5544 (18)	C(2)Mo(1)C(4)	119.78(9)
La(1)–O(2)	2.5216(15)	C(2)Mo(1)C(5)	75.86(9)
La(1)–O(3)	2.5396(18)	C(2)Mo(1)C(6)	139.20(8)
La(1)–O(4)	2.5881(17)	C(2)Mo(1)C(8)	74.78(9)
La(1)–O(5)	2.6070(17)	C(2)Mo(1)C(7)	142.49(9)
La(1)–N(1)	2.631(2)	C(3)Mo(1)C(4)	73.75(10)
La(1)–N(6)	2.644(2)	C(3)Mo(1)C(5)	142.50(10)
La(1)–N(7)	2.640(2)	C(3)Mo(1)C(6)	78.37(8)
La(1)–N(8)	2.622(2)	C(3)Mo(1)C(8)	108.47(8)
K(1)–O(1)	2.9232(18)	C(3)Mo(1)C(7)	144.66(10)
K(1)–O(5)	2.8741(18)	C(4)Mo(1)C(5)	140.38(9)
K(1)–O(7)	2.757(2)	C(4)Mo(1)C(6)	74.58(8)
K(1)–O(9)	2.785(3)	C(4)Mo(1)C(8)	72.18(9)
K(1)–N(2)	2.933(3)	C(4)Mo(1)C(7)	76.82(10)
K(1)–N(4)	2.781(3)	C(5)Mo(1)C(6)	119.07(8)
K(1)–N(5)	3.057(2)	C(5)Mo(1)C(8)	78.66(8)
N(1)–C(1)	1.147(3)	C(5)Mo(1)C(7)	72.17(10)
N(2)–C(2)	1.150(4)	C(6)Mo(1)C(8)	142.22(9)
N(3)–C(3)	1.154(3)	C(6)Mo(1)C(7)	75.27(8)
N(4)–C(4)	1.149(4)	C(7)Mo(1)C(8)	80.11(8)
N(5)–C(5)	1.157(3)		
N(6)–C(6)	1.151(3)		
N(7)–C(7)	1.149(3)		
N(8)–C(8)	1.155(3)		

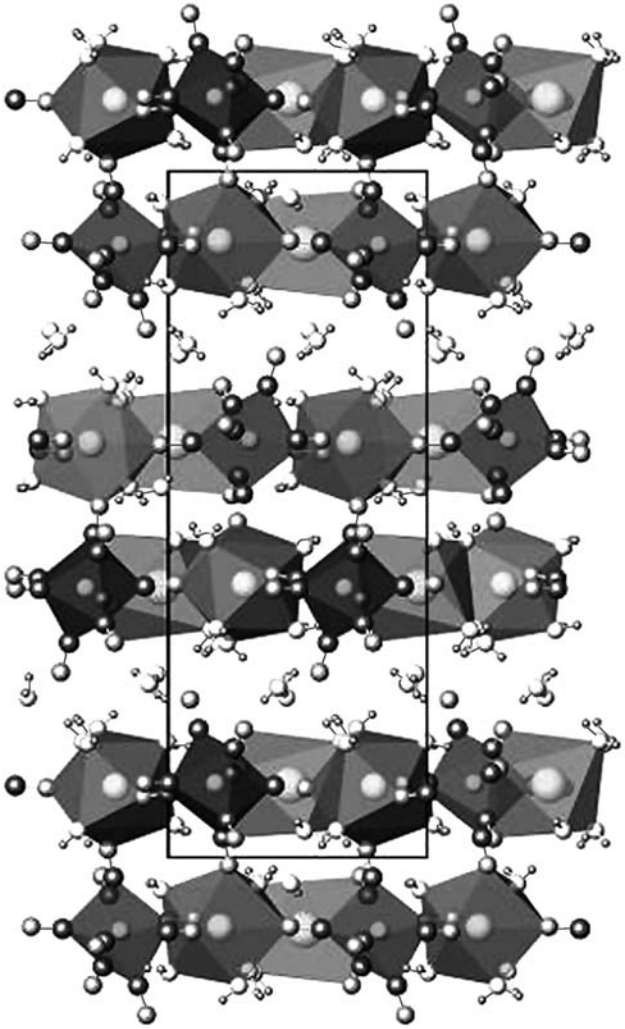

Fig. 3. Projection of the structure $\{[K(H_2O)_2][La(H_2O)_5][Mo(CN)_8]\}_n \cdot 2nH_2O$ onto the plane [100].

potassium atom is surrounded by three N atoms of the cyano groups and by four O atoms of the water molecules, which form the strongly distorted monocapped trigonal prism $[K(NC)_3(OH_2)_4]$.

Thus, each anion $[Mo(CN)_8]^{4-}$ is N-linked by three bridging cyano ligands with La cations in one layer and by one cyano ligand with a La cation in an adjacent layer to form double layers. Other three CN groups are coordinated by two K ions. Only one cyano group in the anion $[Mo(CN)_8]^{4-}$ acts as a terminal ligand. Structure **VI** consists of double layers of the coordination polyhedra of the Mo, La, and K atoms. The uncoordinated water molecules O(6) and O(8) and the terminal cyano group are sandwiched between layers (Fig. 3). The layers are hydrogen-bonded; coordinated and uncoordinated water molecules are also linked by hydrogen bonds with the terminal cyano groups of the anion $[Mo(CN)_8]^{4-}$ (Table 3). The O atoms of uncoordinated water molecules are hydrogen-bonded to the H atoms of coordinated water molecules and to cyano groups. This gives rise to a two-dimensional structure formulated as $\{[K(H_2O)_2][La(H_2O)_5][Mo(CN)_8]\}_n \cdot 2nH_2O$.

A comparison of the crystallographic data for complexes **I–VI** revealed that their crystals are not isostructural and belong to different space groups and that the coordination polyhedra of all the metal atoms are somewhat different. Such structural differences between lanthanide octacyanotungstates(IV) and octacyanomolybdates(IV) suggest the influence of the electronic config-

Table 3. Geometrical parameters of the hydrogen bonds in $KLaMo(CN)_8 \cdot 9H_2O$

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(1)–H(1*B*)···N(3)	0.87(3)	1.97(2)	2.837(3)	169(4)
O(2)–H(2*A*)···N(4)	0.86	2.18	3.030(3)	169
O(3)–H(3*A*)···O(6)	0.85(3)	1.90(3)	2.753(3)	179(5)
O(3)–H(3*B*)···O(8)	0.86(2)	1.95(2)	2.811(3)	174(3)
O(4)–H(4*A*)···N(5)	0.84(3)	2.24(3)	2.962(3)	145(3)
O(4)–H(4*B*)···O(4)	0.80(3)	2.58(2)	2.975(3)	112(2)
O(5)–H(4*A*)···O(7)	0.86(3)	1.95(3)	2.793(2)	168(3)
O(5)–H(5*B*)···N(5)	0.86(3)	2.03(3)	2.878(3)	169(3)
O(6)–H(6*A*)···N(2)	0.86(4)	2.03(4)	2.884(4)	167(4)
O(7)–H(7*A*)···N(8)	0.86(3)	2.48(3)	3.286(3)	156(3)
O(7)–H(7*B*)···N(5)	0.86(2)	2.51(3)	3.084(3)	126(3)
O(8)–H(8*A*)···N(3)	0.97	2.13	2.901(4)	135
O(8)–H(8*B*)···O(2)	0.86	1.89	2.735(3)	168
O(9)–H(9*A*)···N(1)	0.86(5)	2.56(5)	3.350(4)	154(4)
O(9)–H(9*B*)···O(6)	0.87(4)	2.31(5)	3.074(4)	148(5)

uration and the size of the rare-earth element on the structures of the complexes studied.

REFERENCES

1. Saramaga, I.V., Davydov, V.N., Semenyshyn, D.I., and Dovgei, V.V., *Ukr. Khim. Zh.*, 2001, vol. 67, no. 5, p. 14.
2. Stoeckli-Evans, H., Typilo, I., Semenyshyn, D., et al., *Pol. J. Chem.*, 2007, vol. 81, p. 2031.
3. Sereda, O.A., Stoeckli-Evans, G., Typilo, I.V, et al., *Koord. Khim.*, 2009, vol. 35, no 1, p. 17 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 35, no. 1, p. 15].
4. Sereda, O.A., Stoeckli-Evans, G., Typilo, I.V., et al., *Ukr. Khim. Zh.*, 2008, vol. 74, no. 8, p. 78.
5. Typilo, I., Sereda, O., Semenyshyn, D., et al., *Pol. J. Chem*, 2009, vol. 83, p. 339.
6. *Stoe IPDS Software.* Stoe & Cie GmbH, Darmstadt (Germany), 2006.
7. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
8. Dowty, E. and Atoms, A. *Computer Program for Displaying Atomic Structures*, Kingsport (TN), 1999.