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REGULARITIES IN THE CRYSTAL STRUCTURES OF HETEROCATIONIC OCTACYANOMETALLATES(IV) MOLYBDENUM AND TUNGSTEN

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Abstract. A review of the crystal structures of octacyanomolybdates(IV) and octacyanotungstates(IV) of $\{[K(H_2O)][Ln(H_2O)_4][M(CN)_8] \cdot 2H_2O\}_n$ ($M^{4+} = Mo$ and $Ln^{3+} = Y, La, Sm, Gd, Yb$, $M^{4+} = W$ and $Ln^{3+} = Tb, Dy, Ho, Er, Lu$) composition has been done. These compounds have 3D-structures and contain infinite chains $-C \equiv N - M - N \equiv C - Ln -$, which extend in three dimensions, unlike $CeH_3O[W(CN)_8] \cdot 6H_2O$, which has 2D-structure. The coordination polyhedra $[M(CN)_8]^{4-}$ ($M^{4+} = Mo, W$) is different (dodecahedron, square antiprism, bicapped trigonal prism), depending on the nature of the rare-earth elements. The composition and form of the coordination polyhedra of the atoms of rare-earth elements (square antiprism, monocapped tetragonal antiprism, tricapped trigonal prism) are also different. All complexes are polymeric compounds and differ in structure from octacyanomethylates(IV) d-elements and octacyanomethylates(V) f-elements.

Keywords: rare-earth element, octacyanomolybdate(IV), octacyanotungstate(IV), crystal structure.

1. Introduction

During last years cyano-bridged metal assemblies are intensively studied due to their interesting magnetic, optical, sorption, and catalytic properties. Majority of the metal assemblies, based on the interaction of $[M(CN)_8]^{4-/3-}$ ($M^{4+/5+} = Mo, W$) with rare-earth ions, can adopt different structure in the crystalline state, such as zero- (0D), one- (1D), two- (2D), or three- (3D) dimensional polymeric structure [1]. Coordination polyhedra $[M(CN)_8]^{4-/3-}$ ($M^{4+/5+} = Mo, W$) can adopt different spatial configurations: square antiprism (D_{4h}),

dodecahedron (D_{2d}), bicapped trigonal prism (C_{2v}), depending on their chemical environment such as the outsphere cations. Formation of the cyano-bridged heterometallic coordination networks by the “self-assembly” principle in which the formation of coordination bonds $M'-NC-M$ occurs between 3d- or 4f-elements and multidimensional blocks of the octacyanomethylates *via* weak intermolecular forces (hydrogen bonds, π - π interactions, electrostatic interactions), extending the coordination geometry to the infinite architecture of different dimensions and topology [2]. In cyanide precursors, which are octacyanomethylates $[M(CN)_8]^{4-/3-}$ ($M^{4+/5+} = Mo, W$), one can expect during the formation of complexes a significant influence on one another diffuse orbitals of 4d- (Mo) and 5d- (W) ions and the corresponding orbitals of 3d- and 4f-ions [1]. The ligand CN^- provides good electronic contact between the ions of d- and f-elements and is favorable for the appearance of various interesting crystalline structures. The aim of the present work is to summarize and discuss the results of the crystal structures studies of some heterocation octacyanomethylates(IV) of molybdenum and tungsten with potassium and rare-earth ions.

2. Experimental

The synthesis of cyano complexes of molybdenum and tungsten, investigation of their crystal structures were reported in works [3-10]. The series of $\{[K(H_2O)][Ln(H_2O)_4][M(CN)_8] \cdot 2H_2O\}_n$ ($M^{4+} = Mo$ and $Ln^{3+} = Y, La, Sm, Gd, Yb$, $M^{4+} = W$ and $Ln^{3+} = Tb, Dy, Ho, Er, Lu$) were prepared by mixing $H_4[Mo(CN)_8]$ or $H_4[W(CN)_8]$ with lanthanide carbonates or chlorides in

the aqueous solution. The solutions were stored in dark at room temperature after their mixing. In general, yellow-orange well-shaped crystals, suitable for single-crystal diffraction, were formed after several days or months.

X-ray single-crystal diffraction measurements were carried out on a Stoe Image Plate Diffraction System using a graphite-monochromated Mo $K\alpha$ radiation.

3. Results and Discussion

Description of the crystal structures of heterocation octacyanomethylates(IV) of molybdenum and tungsten with potassium and rare-earth ions studied by us are given in Table. Crystal structures of the complexes with a rare-earth element of the cerium subgroup, $\text{KLa}[\text{Mo}(\text{CN})_8] \cdot 7\text{H}_2\text{O}$, $\text{KSm}[\text{Mo}(\text{CN})_8] \cdot 7\text{H}_2\text{O}$ and $\text{CeH}_3\text{O}[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$, significantly differ from each other and form the structures of octacyanocomplexes formed by ions of f -elements of the yttrium subgroup, as follows from the obtained data. These complexes belong to different space groups and have different chemical compositions. The similarity of the structures of these complexes is that the polyhedron $[\text{M}(\text{CN})_8]^{4-}$ ($M = \text{Mo}, \text{W}$) has the form of square antiprism with different degree of deformation. The composition and structure of coordination polyhedra of rare-earth ions are different: $[\text{LaN}_4(\text{OH}_2)_5]$ has the form of monocapped tetragonal antiprism of *cis*- and *trans*-location of oxygen and nitrogen atoms, $[\text{SmN}_4(\text{OH}_2)_5]$ – tricapped trigonal prism (tetragonal antiprism with one centered edge) and $[\text{CeN}_5(\text{OH}_2)_4]$ – tricapped trigonal prism of different compositions. The distances Mo–C and C \equiv N in octacyanomolybdates(IV) are close to each other, but differ from the distances W–C and C \equiv N in $\text{CeH}_3\text{O}[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ and other octacyanotungstates. The new synthesized heterocation octacyanomolybdates(IV) and octacyanotungstates(IV) of rare-earth ions of the yttrium subgroup are isostructural and belong to the structural type $\text{KTb}[\text{W}(\text{CN})_8] \cdot 7\text{H}_2\text{O}$. As for the rare-earth elements of the cerium subgroup the formation of octacyanomolybdates(IV) and octacyanotungstates(IV) complexes with their own, individual crystal structures is observed, one can conclude that a decisive influence on the crystal structure of this type of complexes have the rare-earth ions, but not atoms of potassium, molybdenum or tungsten. The size of the atoms of rare-earth elements and their electronic configuration have decisive influence on the structure of

heterocation octacyanomethylates(IV) of molybdenum and tungsten. In particular, isostructural complexes with Gd, Tb, Dy, Ho, Er, Yb, and Lu can be explained by the completely filled $4f^7$ -subshell of the atoms of rare-earth elements of yttrium subgroup, while for the atoms of rare-earth elements of the cerium subgroup $4f^7$ -subshell is filled up to Eu atom. However, Mo and W atoms also affect the structure of the complexes, as exemplified by complexes of lanthanum, which obviously have different crystal structures. For octacyanotungstates(IV) of rare-earth elements of the yttrium subgroup during the transition from terbium to lutetium the unit-cell volume decreases due to the lanthanide compression (Fig. 1), as well as for three known octacyanomolybdates(IV) of rare-earth elements.

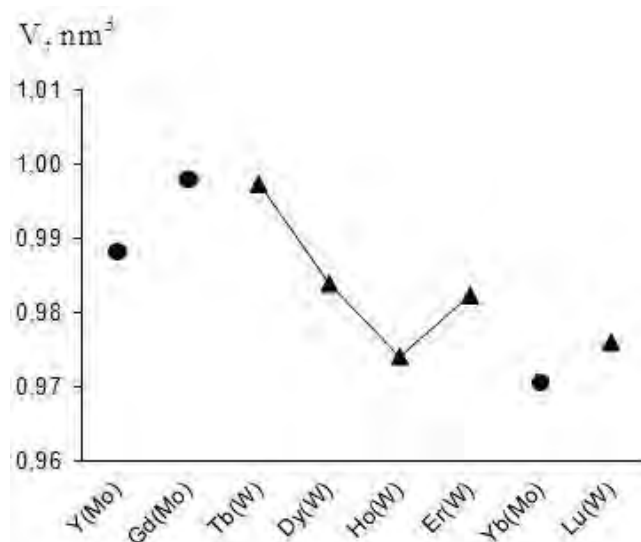


Fig. 1. Reduction of the unit-cell volume for isostructural complexes with $\text{KTb}[\text{W}(\text{CN})_8] \cdot 7\text{H}_2\text{O}$ -type structure

The structure of isostructural compounds of $\text{KTb}[\text{W}(\text{CN})_8] \cdot 7\text{H}_2\text{O}$ type significantly differs from that of $\text{CeH}_3\text{O}[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$, despite the fact that both structures belong to the same space group. They are distinguished by the presence of potassium ions in them, as well as different forms of coordination polyhedrons lanthanide ions. Thus, cerium ions have the environment $[\text{CeN}_5(\text{OH}_2)_4]$ as tricapped trigonal prism, while the rare earth ions in the isostructural compounds with the environment $[\text{LnN}_4(\text{OH}_2)_4]$ (where $\text{Ln}^{3+} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}, \text{Lu}$) are a tetragonal antiprism. The compounds differ by the cell size and shape parameters of coordination polyhedra $[\text{W}(\text{CN})_8]^{4-}$.

Table

Characteristics of heterocationic octacyanomolybdate(IV) and octacyanotungstate(IV) with potassium and f-elements

Compound	SG	V , nm ³	a , nm α , degree	b , nm β , degree	c , nm γ , degree	Composition, coordination polyhedron structure and interatomic distances, nm
1	2	3	4	5	6	7
KY[Mo(CN) ₈]-7H ₂ O, Single crystal (173 K) [3]	<i>P</i> -1	0.98823	0.76371 80.782	0.92569 87.644	1.449761 77.645	[Mo(CN) ₈]- dodecahedron Mo-C=0.2142-0.2172; C≡N=0.1145-0.1151. [YN ₄ (OH ₂) ₄]- square antiprism
Powder (298 K) [4]		0.99259	0.766334 80.632	0.92471 87.799	1.45356 77.584	Y-N=0.2413-0.2467; Y-O=0.2322-0.2411. [KN ₄ (OH ₂) ₃]- distorted trigonal prism K-N=0.2822-0.3000; K-O=0.2834-0.2985.
KLal[Mo(CN) ₈]-7H ₂ O, Single crystal (173 K) [5]	<i>P</i> 2 ₁ / <i>c</i>	2.10122	0.87451	2.52761 117.059	1.06744	[Mo(CN) ₈]- tetragonal antiprism Mo-C=0.2151-0.2167; C≡N=0.1147-0.1157. [LaN ₄ (OH ₂) ₅]- monocapped tetragonal antiprism. La-N=0.2622-0.2644; La-O=0.25216-0.26070. [KN ₄ (OH ₂) ₄]- distorted monocapped trigonal prism K-N=0.2781-0.3057; K-O=0.2757-0.2923.
KSm[Mo(CN) ₈]-7H ₂ O, Single crystal (173 K) [6]	<i>Pbcm</i>	2.1152	1.1718	1.22798	1.46993	[Mo(CN) ₈]- tetragonal antiprism. Mo-C=0.2142-0.2164; C≡N=0.1138-0.1157. [SmN ₄ (OH ₂) ₅]- tricapped trigonal prism Sm-N=0.2532-0.2591; Sm-O=0.2442-0.2497 [KN ₄ (OH ₂) ₃]- distorted monocapped trigonal prism K-N=0.2897-0.2989; K-O=0.2918-0.2958.
KGd[Mo(CN) ₈]-7H ₂ O, Powder (293 K) [4]	<i>P</i> -1	0.99897	0.76988 80.334	0.92549 87.710	1.45621 77.598	[Mo(CN) ₈]- dodecahedron [GdN ₄ (OH ₂) ₄]- square antiprism
KYb[Mo(CN) ₈]-7H ₂ O, Single crystal (173 K) [7]	<i>P</i> -1	0.9706	0.75737 80.674	0.92250 87.567	1.4421 77.513	[Mo(CN) ₈]- distorted trigonal prism with two added atoms Mo-C=0.2138-0.2171; C≡N=0.1138-0.1171. [YbN ₄ (OH ₂) ₄]- tetragonal antiprism. Yb-N=0.2374-0.2422; Yb-O=0.2281-0.2379. [KN ₄ (OH ₂) ₃]- distorted trigonal prism. K-N=0.2803-0.3090; K-O=0.2831-0.2965.
H ₃ OCe(H ₂ O) ₄ [W(CN) ₈]-2H ₂ O, Single crystal (298 K) [8]	<i>P</i> -1	0.886	1.0845 67.52	1.0112 83.10	0.8950 78.11	[W(CN) ₈]- tetragonal antiprism. W-C=0.212-0.220; C≡N=0.110-0.122. [CeN ₅ (OH ₂) ₄]- tricapped trigonal prism Ce-N=0.258-0.263; Ce-O=0.254-0.259.

Table (continued)

1	2	3	4	5	6	7
KTb[W(CN) ₈]·7H ₂ O, Single crystal (173 K) [9]	P-1	0.99727	0.76713 80.506	0.92686 87.580	1.45523 77.751	[W(CN) ₈]- tetragonal antiprism. W-C=0.2141-0.2176; C≡N=0.1150-0.1165; [TbN ₄ (OH ₂) ₄]-, tetragonal antiprism. Tb-N=0.2447-0.2500; Tb-O=0.2369-0.2461. [KN ₃ (OH ₂) ₂]- monocapped trigonal prism K-N=0.2812-0.3278; K-O=0.2836-0.2993.
KDy[W(CN) ₈]·7H ₂ O, Single crystal (173 K) [10]	P-1	0.98386	0.76284 80.673	0.92435 87.561	1.44778 77.603	[W(CN) ₈]- distorted tetragonal antiprism. W-C=0.2133-0.2177; C≡N=0.1143-0.1161. [DyN ₄ (OH ₂) ₄]- tetragonal antiprism. Dy-N=0.2413-0.2468; Dy-O=0.2332-0.2426. [KN ₃ (OH ₂) ₂]- distorted monocapped trigonal prism K-N=0.2807-0.3283; K-O=0.2825-0.2990.
KHo[W(CN) ₈]·7H ₂ O, Single crystal (173 K) [3] Powder (298 K) [4]	P-1	0.97412	0.75887 80.709	0.92232 87.525	1.44479 77.457	[W(CN) ₈]- dodecahedron W-C=0.2138-0.2187; C≡N=0.1123-0.1170. [HoN ₄ (OH ₂) ₄]-, tetragonal antiprism. Ho-N=0.2370-0.2434; Ho-O=0.2292-0.2395. [KN ₃ (OH ₂) ₂]- distorted monocapped trigonal prism K-N=0.2796-0.2993; K-O=0.2813-0.2981.
KEr[W(CN) ₈]·7H ₂ O, Single crystal (173 K) [3] Powder (298 K) [4]	P-1	0.99727	0.76713 80.506	0.92686 87.580	1.45523 77.751	[W(CN) ₈]- dodecahedron W-C=0.2143-0.2318; C≡N=0.1152-0.1171. [ErN ₄ (OH ₂) ₄]- tetragonal antiprism. Er-N=0.2393-0.2449; Er-O=0.2320-0.2409. [KN ₃ (OH ₂) ₂]- distorted monocapped trigonal prism K-N=0.2797-0.2997; K-O=0.2820-0.2975.
KLu[W(CN) ₈]·7H ₂ O, Powder (298 K) [4]	P-1	0.97604	0.76075 80.670	0.91968 87.630	1.44847 77.435	[W(CN) ₈]- dodecahedron [LuN ₄ (OH ₂) ₄]- tetragonal antiprism. [KN ₃ (OH ₂) ₂]- distorted monocapped trigonal prism

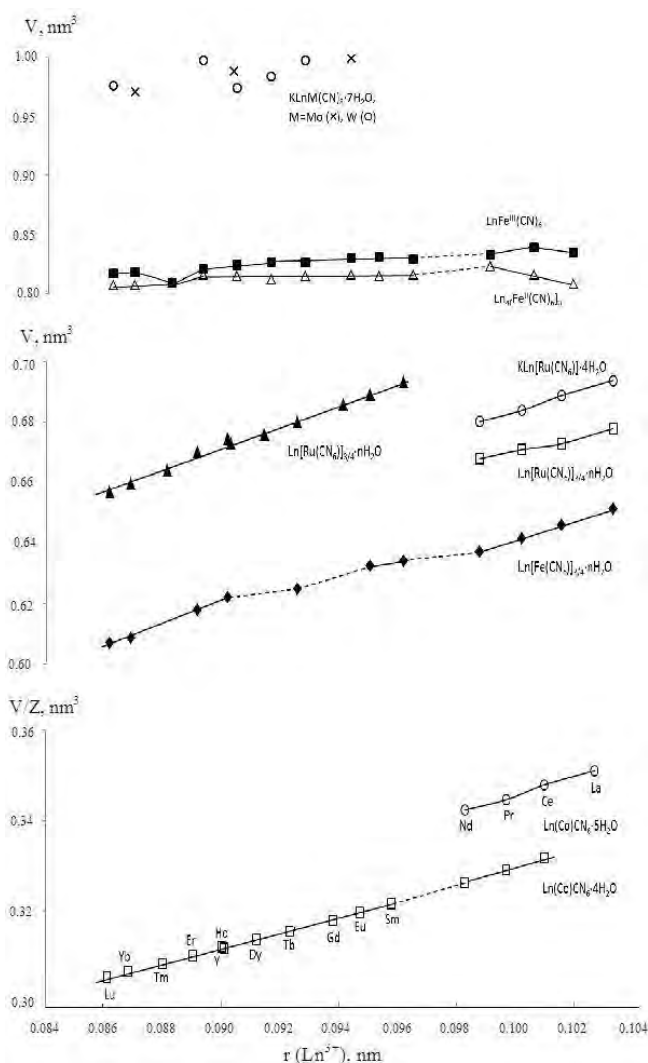


Fig. 2. Changing the V/Z or V in the ranks of complexes depending on the radii of rare-earth elements

In all investigated complexes some of cyano-groups are end-groups, and some ones are bridged that leads to the formation of coordination polymers $\{[K(H_2O)][Ln(H_2O)_4][M(CN)_8] \cdot 2H_2O\}_n$ ($M^{4+} = Mo$ and $Ln^{3+} = Y, La, Sm, Gd, Yb$, $M^{4+} = W$ and $Ln^{3+} = Tb, Dy, Ho, Er, Lu$), which have 3D-structure and form infinite chains $-Ln-N \equiv C-M-C \equiv N-$, which are distributed in three dimensions, unlike $CeH_3O[W(CN)_8] \cdot 6H_2O$, which has 2D-structure.

Comparison of the crystal structure of the investigated heterocations octacyanomolybdates(IV) and octacyanotungstates(IV) with potassium and f -elements with the structure of cyanide complexes five valent tungsten $-[Sm(H_2O)_5][W(CN)_8]$ [2], $[Gd(DMF)_6][W(CN)_8]$ [11], $Ln(H_2O)_5[M(CN)_8]$ ($Ln^{3+} = Eu, Tb, Sm, Gd$; $M^{5+} = Mo, W$) [12] shows that the crystal structure of complexes varies depending on the oxidation degree of the central atom.

Thus, the complex $[Sm(H_2O)_5][W(CN)_8]$ belongs to a tetragonal symmetry. Ion samarium in the complex is surrounded by four nitrogen ions of cyanogroups and five oxygen ions of water molecules on the monocapped square antiprism tops. Coordination polyhedron of tungsten ion is a square antiprism. 2D-Structure of the $[Sm(H_2O)_5][W(CN)_8]$ complex consists of $-Sm-C \equiv N-W-N \equiv C-$ layers which are connected by hydrogen bonds.

The isotopic compounds $Ln(H_2O)_5[M(CN)_8]$ ($Ln^{3+} = Eu, Tb, Sm, Gd$; $M^{5+} = Mo, W$) are crystallized in tetragonal symmetry and belong to the space group $P4/nmm$, forming two-dimensional structure.

Monoclinic complex $[Gd(DMF)_6][W(CN)_8]$ has 1D-structure. Coordination polyhedron of tungsten ion is asquare antiprism, gadolinium – distorted square antiprism $[GdN_2O_6]$ (oxygen atoms – DMF molecules). It was found that investigated octacyanometallates(IV) of molybden and tungsten with potassium and rare earth ions differ significantly from cyano-bridged bimetallic complexes $\{[M_2(H_2O)_4Mo(CN)_8] \cdot 4H_2O\}_n$ ($M^{2+} = Mn, Co$), which contain d -elements in the outer sphere and have 3D-structure. In these compounds each polyhedron $[Mo(CN)_8]^{4-}$ is connected by eight cyanide ligands with M^{2+} ions. The cyanide end-groups in these complexes are absent [13].

Crystal structures of cyanide complexes with f -elements are more widely investigated for the following compounds: $LnCo(CN)_6 \cdot nH_2O$ [14], $Ln[T(CN)_6]_{3/4} \cdot nH_2O$ ($T = Fe, Ru$) [15], $Ln_4[Fe(CN)_6]_3$ [16], $KLnFe(CN)_6 \cdot 3H_2O$ [17] and $KLnRu(CN)_6 \cdot 4H_2O$ [18]. It was established that these complexes exist both as medium and heterocations (mixed) salts and have crystal structures of various types.

Fig. 2 shows the change in V/Z or V in the ranks of these complexes depending on Shenon radii of rare-earth elements, taken from work [14].

For the comparison, the same Fig. 2 presents the dependence of the unit cells volume on the radii of rare earth elements for the studied compounds. In the ranks of all isostructural compounds it is observed almost linear increase of the unit cell volume with increasing ion radius of the rare earth elements.

4. Conclusions

The crystal structures of octacyanometallates(IV) of the general composition $\{[K(H_2O)][Ln(H_2O)_4][M(CN)_8] \cdot 2H_2O\}_n$ ($M^{4+} = Mo, Ln^{3+} = Y, La, Sm, Gd, Yb$; $M^{4+} = W, Ln^{3+} = Tb, Dy, Ho, Er, Lu$) were discussed for the first time. The nature of rare earth elements affects their structure, the degree of f -electron shells filling and the nature of metal complexing agents.

Depending on the nature of rare-earth elements the form of coordination polyhedra $[M(CN)_8]^{4-}$ ($M = Mo, W$) can be different (dodecahedron, tetragonal antiprism, bicapped trigonal prism). The composition and structure of coordination polyhedra of rare earth elements atoms (square antiprism, monocapped tetragonal antiprism, tricapped trigonal prism) are also different. All complexes are polymeric compounds and differ in structure from octacyanometallates(IV) d -elements and octacyanometallates(V) f -elements.

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ОСОБЛИВОСТІ КРИСТАЛІЧНИХ СТРУКТУР ГЕТЕРОКАТІОННИХ ОКТАЦІАНІДОМЕТАЛАТІВ МОЛІБДЕНУ ТА ВОЛЬФРАМУ

Анотація. Зроблено огляд кристалічних структур октаціанідомолібдатів(IV) та октаціанідовольфраматів(IV) складу $\{[K(H_2O)][Ln(H_2O)_4][M(CN)_8] \cdot 2nH_2O\}_n$ ($M^{4+} = Mo, Ln^{3+} = Y, La, Sm, Gd, Yb$; $M^{4+} = W, Ln^{3+} = Tb, Dy, Ho, Er, Lu$). Ці сполуки мають 3D-структуру і утворюють нескінченні ланцюги $-C \equiv N - M - N \equiv C - Ln -$, які поширюються в трьох вимірах, на відміну від $CeH_3O[W(CN)_8] \cdot 6H_2O$, що має 2D-структуру. Встановлено, що в залежності від природи рідкісноземельних елементів форма координаційних поліедрів $[M(CN)_8]^{4-}$ ($M = Mo, W$) є різною (додєкаедр, тетрагональна антипризма, двошаркова тригональна призма). Різними є склад і будова координаційних поліедрів атомів рідкісноземельних елементів (квадратна антипризма, одношаркова тетрагональна антипризма, тришаркова тригональна призма). Комплекси є полімерними сполуками та відрізняються за структурою від октаціанідометалатів(IV) d -елементів та октаціанідометалатів(V) f -елементів.

Ключові слова: рідкісноземельний елемент, октаціанідомолібдат(IV), октаціанідовольфрамат(IV), кристалічна структура.