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Synthesis and Crystal Structure of $Mo_{6-x}Nb_xI_{11}$ ($x = 1–1.5$)

S. B. Artemkina[a, *], **N. G. Naumov**[a, b], **A. V. Virovets**[a], **and V. E. Fedorov**[a, b]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
pr. akad. Lavrent'eva 3, Novosibirsk, 630090 Russia
[b] *Novosibirsk National Research University, Novosibirsk, Russia*
**e-mail: artem@niic.nsc.ru*

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Abstract—A solid solution $Mo_{6-x}Nb_xI_{11}$ ($x = 1.1–1.5$) containing cluster cores $\{Mo_5NbI_8\}$ is obtained by the high-temperature reaction of molybdenum, niobium, and iodine (550°C, 70 h, quartz ampule). According to the X-ray diffraction data, heating at 800°C in a molybdenum container results in the decomposition of the solution to Mo_6I_{12} and Nb_6I_{11}. According to the X-ray structure analysis data, the compounds are isostructural to the high-spin modification Nb_6I_{11} (space group *Pccn*). The presence of Nb atoms in the structure changes the structural type from the layered (Mo_6I_{12}) to framework structure, noticeably increases the metal–metal distances (2.661–2.716 Å, average 2.695 Å) compared to the Mo_6 octahedron with the retention of the distance from the metal (M) to the μ_3-“capped” I atoms, and strongly elongates the M_6–I–M_6 bridges almost to the value observed in Nb_6I_{11}.

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Heterometallic octahedral clusters of transition metals attract attention of researchers due to the possibility of substantially affecting the electronic structures and properties of the clusters remaining in terms of one structural type. Nonisovalent substitution in the cluster core can change either the number of cluster valence electrons (VECs) or the charge of the cluster core. These regularities were well studied for the chalcogenide clusters. The substitution of molybdenum in the Chevrel phases for other metals $Mo_{6-x}M_xQ_8$ (M = Re, Q = S, Se, Te, $x = 4$; M = Ru, Q = Se, Te, $0 \le x \le 2$; M = Rh, Q = Te, $x = 0.5$, 1.33) [1–3] changes the number of VECs and physical properties. On the one hand, the Chevrel phases $Nb_xRu_{6-x}Te_8$ ($2.83 < x < 3.50$) with the VECs from 21.5 to 23.5 are metals in the temperature range from 4 to 290 K [4]. On the other hand, the substitution of the rhenium atoms in the cores $\{Re_6Q_8\}$ (Q = S, Se) for osmium in the high-temperature phases $Cs_3Re_5OsS_{11}$ [5] and $Re_4Os_2Se_8Cl_4$, $Cs_3Re_5OsSe_8Cl_6$, and $K_2[Re_3Os_3Se_8Cl_6][Re_4Os_2Se_7Cl_7]$ [6] results in a change in the cluster core charge, but the number of VECs remains unchanged and equal to 24.

Unlike the chalcogenide clusters, halide heterometallic clusters are studied to a lower extent. Only one example for nonisovalent substitution, $Ta_{6-x}Mo_xCl_{15}$, with the heterometallic core of the M_6X_{12} type [7] was known to the beginning of this work. Varying the ratio of the starting molybdenum and tantalum pentachlorides in the ampule synthesis, the authors [7] obtained cluster polymers Ta_5MoCl_{15} and $Ta_4Mo_2Cl_{16}$ with different compositions of the heterometallic cores, $\{Ta_5MoCl_{12}\}$ and $\{Ta_4Mo_2Cl_{12}\}$. After the dissolution of the prepared compounds, the authors [7] isolated salt of molecular complexes $[Ta_5MoCl_{18}]^{2-}$ (15 VECs), $[Ta_5MoCl_{18}]^{3-}$ (16 VECs), and $[Ta_4Mo_2Cl_{18}]^{2-}$ (16 VECs).

We have recently published the works on the chemistry of molecular heterometallic clusters molybdenum–niobium $[Mo_5NbI_8L_6]$ (L = H_2O, OH, CN, Cl) [8, 9]. These compounds were obtained by the reaction of “cutting out” of the cluster core $\{Mo_5NbI_8\}^{3+}$ from polymer $Mo_{6-x}Nb_xI_{11}$ ($x = 1.1–1.5$) followed by the substitution of the apical ligands.

In this work we report the synthesis, conditions of formation, and crystal structure of the solid solution $Mo_{6-x}Nb_xI_{11}$ ($x = 1–1.5$), which serves as the starting compound for syntheses of molecular complexes with the $\{Mo_5NbI_8\}$ core.

EXPERIMENTAL

Powder diffraction patterns were detected on a Philips PW 1830/1820/1710 diffractometer (CuK_α radiation, graphite monochromator, silicon plate as an external standard). An energy dispersive X-ray analysis (EDXA) of the content of metals and iodine was carried out using an EX23000BU energy dispersive analyzer with a JSN-6700F scanning electron microscope.

Synthesis of $Mo_{6-x}Nb_xI_{11}$ (I). Prior to loading into an ampule, a molybdenum powder was annealed in a hydrogen flow at 700°C for 1 h. Other reagents were

Table 1. Crystallographic characteristics and parameters of diffraction experiments for compounds $Mo_{6-x}Nb_xI_{11}$

Parameter	Value		
	I	**II** at 220 K	**II** at 110 K
Empirical formula	$Mo_{4.7}Nb_{1.3}I_{11}$	Mo_5NbI_{11}	Mo_5NbI_{11}
Crystal shape and color	Black octahedron	Black piece	Black piece
Crystal size, mm	0.09 × 0.07 × 0.06	0.06 × 0.04 × 0.04	0.06 × 0.04 × 0.04
Detection temperature, K	295	220	110
FW	1968.53	1968.51	1968.51
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pccn*	*Pccn*	*Pccn*
a, Å	15.3216(4)	15.2873(14)	15.2588(10)
b, Å	11.0950(2)	11.0571(10)	11.0364(9)
c, Å	13.1567(3)	13.1289(9)	13.0874(10)
V, Å^3; Z	2236.55(9); 4	2219.2(3); 4	2203.9(3); 4
ρ_{calcd}, g/cm	5.846	5.892	5.933
μ, mm^{-1}	18.522	18.522	18.650
T_{min}, T_{max}	0.770, 1	0.545, 1	0.078, 1
θ Range, deg	4.54–55.0	4.54–52.82	4.56–55.0
Diffractometer	Bruker X8 Apex CCD	Bruker X8 Apex CCD	Bruker X8 Apex CCD
Ranges of indices for h, k, l	$-19 < h < 19$, $-10 < k < 14$, $-17 < l < 17$	$-19 < h < 19$, $-13 < k < 10$, $-12 < l < 16$	$-19 < h < 14$, $-13 < k < 14$, $-8 < l < 17$
Measured/independent/observed reflections	19259/2569/2410	8934/2279/1607	9272/2312/1589
R_{int}	0.0269	0.0707	0.0707
Method for applying absorption correction	SADABS	SADABS	SADABS
Refined parameters	78	78	78
$R(F)$, $wR(F^2)$ for $F_{obs} > 4\sigma(F)$	$R_1 = 0.0197$, $wR_2 = 0.0432$	$R_1 = 0.0366$, $wR_2 = 0.0734$	$R_1 = 0.0426$, $wR_2 = 0.0860$
$R(F)$, $wR(F^2)$ for all data	$R_1 = 0.0218$, $wR_2 = 0.0438$	$R_1 = 0.0710$, $wR_2 = 0.0852$	$R_1 = 0.0802$, $wR_2 = 0.0999$
Goodness-of-fit for all data	1.235	1.087	1.031
Residual electron density (min/max), e Å^{-3}	–1.213/0.889	–2.618/1.815	–3.946/2.774

used without preliminary treatment. A mixture of elemental substances, namely, molybdenum (0.835 g, 8.70 mmol), niobium (0.404 g, 4.35 mmol), and iodine (2.995 g, 11.8 mmol), was placed in a 17-mL quartz ampule. The ampule was pumped under dynamic vacuum under cooling with liquid nitrogen and sealed. The high-temperature synthesis was carried out according to the following scheme: heating to 550°C for 11 h, keeping at 550°C for 70 h, and cooling to ambient temperature for 12 h. The ampule was opened, and the content (dark gray powder with metallic luster) was heated under dynamic vauum at 200°C to remove volatiles. The elemental analysis (EDXA) results for crystals **I** correspond to the composition $Mo_{4.7}Nb_{1.3}I_{11}$.

The powder diffraction patterns of the samples contain reflections of $Mo_{6-x}Nb_xI_{11}$, which are consistent with the calculation on the basis of the single-crystal data, and unidentified reflections.

The crystals as black shining blocks or octahedra for single-crystal X-ray structure analysis were isolated from a mixture of products obtained by the same procedure at the temperatures 650 (**I**) and 700°C (**II**).

X-ray structure analysis. The crystallographic data and details of X-ray structure experiments for single crystals of compounds **I** and **II** are presented in Table 1. The reflection sets for crystal **II** were measured at two temperatures to answer the question about the possible low-temperature phase transition induced by spin crossover. The crystal structure of compound **I** was solved by a direct method. The model found for compound **I** was used to refine structure **II**. Since the Mo and Nb atoms are indiscernible in scattering ability, the positions of three independent metal atoms were modeled by the superposition of the Mo and Nb atoms in the ratio dictated by the assumed composition of the compound. Based on the EDXA data, the composition $Mo_{4.7}Nb_{1.3}I_{11}$ was accepted for structure **I**, which gave the ratio 0.21667 Nb/0.78333 Mo in each position. No chemical analysis was made for crystal **II**, but the composition Mo_5NbI_{11} (0.16667 Nb/0.8333 Mo) was accepted on the basis of the chemical data and similarity of the unit cell parameters (see below). Structures **I** and **II** were refined by full-matrix least squares for F^2 in the anisotropic approximation using the SHELXTL program package [10–12]. The coordinates of atoms and other parameters for structures **I** and **II** were deposited with the Inorganic Crystal Structure Database (ICSD) (CSD nos. 425085 (**I**), 425086 (**II** at 110 K), and 425087 (**II** at 220 K); crysdata@fiz-karlsruhe.de) and are available from the authors.

RESULTS AND DISCUSSION

A solid solution of $Mo_{6-x}Nb_xI_{11}$ is formed as the main phase in the ampule synthesis from a stoichiometric mixture of molybdenum, niobium, and iodine (4 : 2 : 5.5) at 550°C. The solid solution $Mo_{6-x}Nb_xI_{11}$ was placed in a molybdenum container, and the latter was in a quartz ampule. The ampule was evacuated, sealed, and heated at 800°C for two weeks. The powder diffraction pattern detected for the obtained product showed reflections attributed to polymer Nb_6I_{11} and Mo_6I_{12} and the absence of the starting heterometallic iodide. Thus, the decomposition of $Mo_{6-x}Nb_xI_{11}$ affords earlier known lower molybdenum and niobium iodides. It is most likely that heterometallic iodide $Mo_{6-x}Nb_xI_{11}$ is a metastable phase. It is seen that $Mo_{6-x}Nb_xI_{11}$ evolves molecular iodine on storage. Attempts to obtain single-phase samples by increasing the temperature and/or time of the synthesis were unsuccessful. For example, an increase in the synthesis temperature to 650 and 700°C resulted in the interaction of the reaction mixture and reaction products with the material of the ampule (quartz) and in the formation of new admixture phases. A new compound, $[Nb_4OI_8][Mo_6I_{14}]_{2\infty}$ [13] containing a new square niobium cluster $\{Nb_4(\mu_4\text{-}O)I_8\}$, was also obtained.

Heterometallic iodides $Mo_{6-x}Nb_xI_{11}$ (compounds **I** and **II**) are isostructural to the high-temperature high-spin phase Nb_6I_{11} existing above 274 K, whose structure was solved by Simon and coauthors in the orthorhombic space group *Pccn* [14, 15]. Crystalline homometallic iodide Nb_6I_{11} undergoes spin crossover at 274 K [14] with a change in the spin state from quartet to doublet accompanied by the second-order phase transition. The space group changes from *Pccn* (high-spin form) to $P2_1cn$ (low-spin form), which is easily determined from the reflection intensities ($0kl$), $l = 2n + 1$ [14, 15]. None of 347 reflections of this type is observed in compound **II** at $T = 110$ K, and the average value of I/σ for them is only 0.4. Thus, we observed no spin crossover.

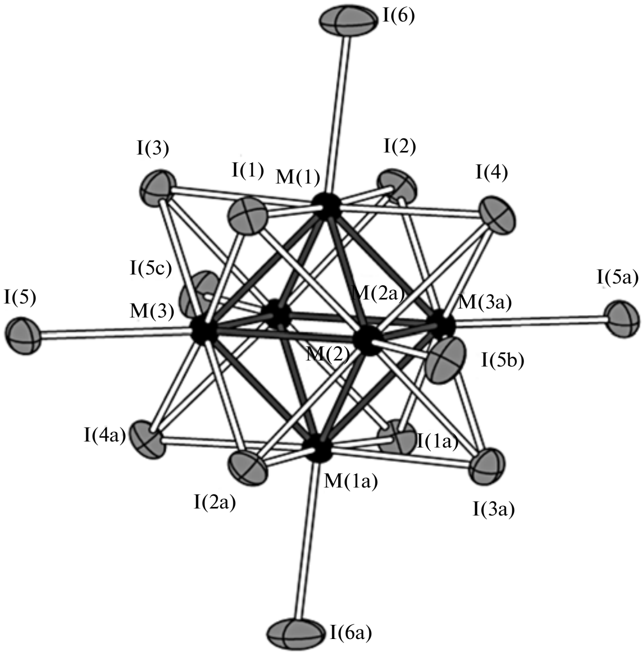

Fig. 1. Structure of the cluster core $\{Mo_{6-x}Nb_xI_8\}$ in thermal ellipsoids (80%). The atomic coordinates were multiplied by the following symmetry procedures: $1 - x$, $2 - y$, $2 - z$.

The asymmetric unit in the structure is presented by three metal atoms (Mo, Nb) and six iodine atoms. The cluster core (Figs. 1 and 2) (its mass center is at the inversion center) has a structure typical of clusters of the $\{M_6(\mu_3\text{-}X)_8\}$ type: an octahedron of six metal atoms is coordinated by eight ligands (μ_3-I usually designated as I^i) at the sides of the octahedron. Other iodine atoms (μ_2-I usually designated as I^a) bind the cluster cores into a three-dimensional framework with the **rob** topology (according to the accepted terminology [16]). Thus, the structural formula of $Mo_{6-x}Nb_xI_{11}$ can be written as $Mo_{6-x}Nb_xI^i_8I^a_{6/2}$.

The compositions of compounds **I** and **II** are likely similar. The EDXA data give $Mo_{4.7}Nb_{1.3}I_{11}$ for crystal **I**. The lattice parameters for compound **I** at ambient temperature differ noticeably (especially parameter c, by ~0.40 Å) from those found for Nb_6I_{11} ($a = 15.310(2)$, $b = 11.300(2)$, $c = 13.556(4)$ Å in the chosen axial system, $V = 2345.2(9)$ Å^3 [15]). Crystal **II** has the composition similar to Mo_5NbI_{11}. Its parameters were measured at two temperatures. The linear approximation to ambient temperature gives the values $a \approx 15.306$, $b \approx 11.071$, $c \approx 13.156$ Å, $V \approx$

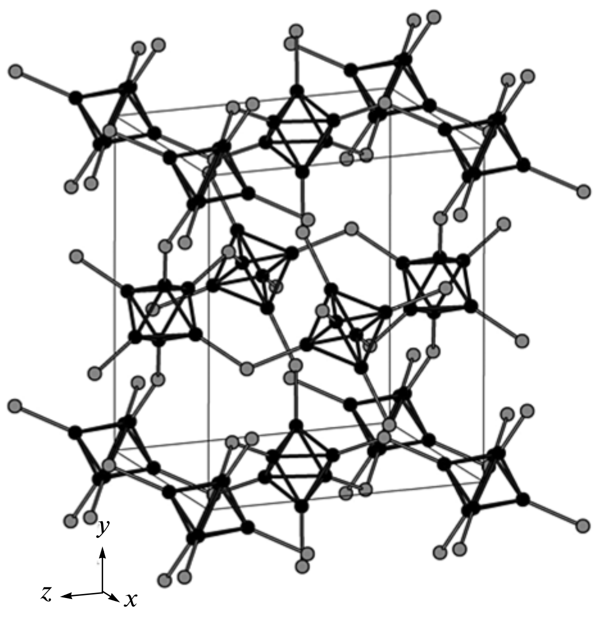

Fig. 2. Fragment of the framework within the unit cell. Internal ligands of the cluster cores (iodine atoms) are omitted for clarity.

2229.4 Å^3, which coincide with those found for compound **I** within 0.024 Å.

Thus, the introduction of one to two molybdenum atoms into the structure jumpwise changes the structural type from MoI_2 (Mo_6I_{12}) to Nb_6I_{11}. To reveal the reason, let us consider the number of VECs in Mo_6I_{12}, Nb_6I_{11}, and $Mo_{6-x}Nb_xI_{11}$. The cluster polymer Nb_6I_{11} has 19 VECs and can sorb molecular hydrogen due to the electron-deficient character of the cluster core [17]. On the one hand, in the HNb_6I_{11} formed the hydrogen atom is inbuilt into the center of the $\{Nb_6I_8\}$ cluster core, which increases the number of VECs by one electron (up to 20 VECs). On the other hand, the number of VECs in Mo_6I_{12} is 24. This “magic” number is characteristic of stable six-membered clusters [18]; i.e., this cluster is electron-precise. Two of six I^a atoms are terminal, which results in the layered structure $Mo_6I_8I^a_2I^a_{4/2}$. The replacement of one molybdenum atom by the niobium atom should decrease the number of VECs; however, the transformation of the terminal iodine atoms into bridging atoms with the change in the structural type again results in the electron-precise cluster $\{Mo_5NbI_8\}$ with 24 VECs.

The solid solution $Mo_{6-x}Nb_xI_{11}$ also contains paramagnetic 23-electron $\{Mo_4Nb_2I_8\}$. The electron spin resonance (ESR) spectrum of $Mo_{6-x}Nb_xI_{11}$ gives a broad signal corresponding to one unpaired electron. Taking into account that clusters are characterized by broad signals in the ESR spectra, we may assume that the solid solution $Mo_{6-x}Nb_xI_{11}$ contains the 23-electron cluster core $\{Mo_4Nb_2I_8\}$.

The existence of $\{Mo_5NbI_8\}$ is confirmed by the reaction products of core “excising” and further formation of a series of molecular complexes with the known crystal structures [8, 9]. No paramagnetic complexes with the $\{Mo_4Nb_2I_8\}$ core were isolated as individual compounds so far.

The bond lengths in the structures of several cluster polymer iodides are listed in Table 2. The average metal–metal bond lengths in $Mo_{6-x}Nb_xI_{11}$ (2.693–2.697 Å) lie in the range of average M–M values in homometallic MoI_2 (2.672 Å) and Nb_6I_{11} (2.850 Å in the high-spin form and 2.853 Å in the low-spin form). The M–I^a bond length is similar to that for M=Nb. On the contrary, the M–I^i bond length is close to that for M=Mo. In other words, the introduction of only one to two Nb atoms noticeably “loosens” the cluster core, elongating the metal–metal distances (compared to the Mo_6 octahedron) with the retention of distances from M to μ_3-“capped” I atoms and strongly elongating the iodide intercluster bridges: almost to the value observed in Nb_6I_{11}. Evidently, the latter is directly

Table 2. Selected bond lengths (min–max (average)) in the crystal structures of polymer molybdenum and niobium iodides

Formula	VECs	M–M, Å	M–I^i, Å	M–I^a, Å	Literature
$Mo_{4.7}Nb_{1.3}I_{11}$	23/24	2.6673(6)–2.7165(6) (2.697)	2.7598(5)–2.8199(5) (2.789)	2.9130(5)–2.9544(5) (2.931)	This work
Mo_5NbI_{11} 220 K	24	2.6642(16)–2.7121(16) (2.697)	2.7547(15)–2.8145(14) (2.784)	2.9070(15)–2.9507(15) (2.924)	This work
Mo_5NbI_{11} 110 K	24	2.6611(19)–2.7145(19) (2.693)	2.7516(17)–2.8104(16) (2.781)	2.8990(17)–2.9448(17) (2.918)	This work
Nb_6I_{11} low-spin form ($T = 110$ K)	19	2.676(4)–2.982(4) (2.853)	2.808(3)–2.901(3) (2.864)	2.901(3)–2.960(3) (2.921)	[14]
Nb_6I_{11} high-spin form ($T = 298$ K)	19	2.743(3)–2.917(3) (2.850)	2.834(3)–2.903(3) (2.867)	2.899(2)–2.958(3) (2.926)	[14]
MoI_2	24	2.670(4)–2.676(5) (2.672)	2.764(3)–2.778(3) (2.772)	2.805(5)–2.893(5) (2.862)	[19]

related to the change in the structural type from the layered to framework type.

The dependence of the bond length on the temperature of crystal analysis is observed for these heterometallic polymers: the average bonds are shortened with the temperature decrease (Table 2).

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