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Tosylate Cluster Complexes $(Bu_4N)_2[M_6I_8(O_3SC_6H_4CH_3)_6]$ (M = Mo, W)

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Abstract—The reaction of $(Bu_4N)_2[M_6I_{14}]$ with silver *p*-toluenesulfonate (tosylate) $AgO_3SC_6H_4CH_3$ affords iodide cluster complexes $(Bu_4N)_2[M_6I_8(Pts)_6]$ (M = Mo (**I**), W (**II**); Pts is tosylate anion $CH_3C_6H_4SO_3$). According to the X-ray diffraction data (CIF file CCDC no. 1027969), the molybdenum atoms in $(Bu_4N)_2[Mo_6I_8(Pts)_6] \cdot 2Et_2O \cdot 2MeCN$ (**I′**) are coordinated via the monodentate mode by the tosylate ligands. The ^1H NMR and mass spectrometry data show that in donor solvents the complexes undergo solvolysis followed by the substitution of the tosylate ligands by the solvent molecules, which is accompanied by changes in the electrochemical properties, as shown by the cyclic voltammetry data.

Keywords: clusters, molybdenum, tungsten, iodides, *p*-toluenesulfonates, crystal structure, solvolysis

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INTRODUCTION

The octahedral halide cluster complexes $[\{M_6(\mu_3\text{-}X)\}_8L_6]$ (M = Mo, W; X = Cl, Br, I; L is organic or inorganic ligand; the braces and symbol μ are not always indicated further) are characterized by interesting photophysical properties [1, 2]. The molybdenum chloride and bromide clusters are most studied. It has been shown rather recently that the iodide clusters, which dropped out of sight for a long time, have record-breaking photophysical characteristics among the whole family of octahedral clusters of transition metals with 24 cluster skeletal electrons [3–12]. The octahedral tungsten clusters are studied to a much lower extent than the molybdenum clusters, whereas the tungsten iodide clusters remain almost unstudied. In addition to the expected similarity in the photophysical properties, the tungsten iodide clusters evoke interest due to the relative stability of the paramagnetic 23-electron state (the potential of the $[W_6I_{14}]^{2-}/[W_6I_{14}]^{-}$ pair in acetonitrile is only 0.57 V vs. standard calomel electrode [13]) and a unique combination of 14 heavy atoms in the $\{W_6I_8\}^{4+}$ cluster core providing a high factor of X-ray scattering on these atoms. Owing to this fact, similar cluster complexes are promising X-ray contrast substances [14].

Salts $[W_6I_{14}]^{2-}$ are used as the starting compounds for the synthesis of complexes $[W_6I_8L_6]$ [14]. However, the terminal halide ligands in the anionic clusters $[M_6I_8X_6]^{2-}$ (M = Mo, W; X = Cl, Br, I) are substitutable rather difficultly and, hence, it is preferable to perform the primary synthesis of complexes $[\{M_6I_8\}X_6]^{2-}$ with more labile ligands X, such as triflate ($CF_3SO_3^-$) or *para*-toluenesulfonate (tosylate, $CH_3C_6H_4SO_3$, Pts), which are considered to be "good leaving groups." A series of similar compounds was synthesized and structurally characterized in the previous works: compound $(PhCH_2NMe_3)_2[Mo_6Cl_8(O_3SCF_3)_6]$ [15] and solvates $(Bu_4N)_2[Mo_6Cl_8(O_3SC_6H_4CH_3)_6] \cdot 2CH_3CN$ and $(Bu_4N)_2[Mo_6Cl_8(O_3SC_6H_4CH_3)_6] \cdot 2CH_2Cl_2$ [16]. Complexes $(Bu_4N)_2[W_6Cl_8(O_3SCF_3)_6]$ and $(Bu_4N)_2[W_6Cl_8(O_3SC_6H_4CH_3)_6]$ were described for tungsten. They were used for the preparation of a wide range of anionic complexes $[W_6Cl_8X_6]^{2-}$ with halide, pseudo-halide, and other ligands (X = F^-, Cl^-, Br^-, I^-, NCO^-, NCS^-, $NCSe^-$, N_3^-, CH_3COO^-, $\{(NC)Mn(CO)_2Cp\}^-$), as well as cationic complexes $[W_6Cl_8L_6]^{4+}$ (L = $OPPh_3$, $(NC)Ru(PPh_3)_2Cp$, $(NC)Os(PPh_3)_2Cp$) [17–19]. The triflate complex $(Bu_4N)_2[W_6I_8(O_3SCF_3)_6]$ was synthesized in a yield of 81% from $(Bu_4N)_2[W_6I_{14}]$ and silver triflate [14], but its chemical properties were not studied. The molybdenum tosylate complex $[Mo_6I_8(O_3SC_6H_4CH_3)_6]^{2-}$ in

the form of a salt with the (2-methacryloyloxyethyl)dimethyldodecylammonium cation has recently been proposed for use in the production of poly(methyl methacrylate) materials by the copolymerization with methyl methacrylate. An enhanced lability of the tosylate ligands toward the solvent (tetrahydrofuran, THF) was observed that can exert a negative effect on the properties of the samples [20].

The synthesis and some properties of $(Bu_4N)_2[Mo_6I_8(Pts)_6]$ (**I**) and $(Bu_4N)_2[W_6I_8(Pts)_6]$ (**II**) are reported in this work. Single crystals of mixed solvate $(Bu_4N)_2[Mo_6I_8(Pts)_6] \cdot 2Et_2O \cdot 2MeCN$ (**I'**) for which the crystal structure was determined were obtained by the crystallization from an acetonitrile–diethyl ether mixture. The processes of solvolysis of the complexes in acetonitrile and dimethyl sulfoxide solutions were studied using ^{1}H NMR and mass spectrometry. The electrochemical characteristics of solutions of compounds **I** and **II** before and after solvolysis were determined using cyclic voltammetry (CV).

EXPERIMENTAL

The starting compounds were synthesized using known procedures [21, 22]. Silver tosylate AgPts was obtained according to a known procedure [23]. Organic solvents were purified using standard procedures. IR spectra were recorded on Scimitar FTS 2000 and Specord IR 75 spectrometers in a range of 4000–400 cm^{-1}. ^{1}H NMR spectra were measured on a Bruker Avance 500 spectrometer at room temperature using $Si(CH_3)_4$ as an internal standard.

Mass spectra were recorded on an Agilent (6130 QuadrupoleMS, 1260 infinityLC) liquid chromatograph coupled with a mass spectrometer. The multimode ionization source adjusted to chemical ionization under atmospheric pressure (MM-APCI) was used. The instrument operated in the mass spectrum scan mode (SCAN) for negatively or positively charged ions in the range m/z 400–3000. The following parameters were used: nitrogen as a drying gas, temperature 350°, flow rate 5 L/min, spraying gas (nitrogen) pressure 20 psig, evaporator temperature 250°C, voltage on the capillary 2000 V, and voltage on the charging electrode 2000 V. To retain weakly bound forms in the mass spectrum, the voltage on the fragmentator was established to be 0 V in all experiments. A solution (5 μL) of the studied compound in deuterated acetonitrile with the concentration about 10^{-4} g/mL was injected into the mobile phase consisting of acetonitrile (special purity grade), deionized water, and formic acid (special purity grade) in a ratio of 70 : 30 : 0.5 was passed through the preliminary column ZORBAX Eclipse Plus-C18 4-Pack Narrow Bore Guard Column 2.1 × 12.5 mm 5-micron (to protect the system from possible nondissolved impurities in the sample) with a rate of 0.4 mL/min, sprayed, and ionized. All scans of the mass spectrum of the analyte (that was eluted within approximately 0.5 min) were summated. The peaks in the mass spectra were interpreted by both experimentally obtained masses of the ions and a comparison of the calculated and experimental isotopic peak distributions. The Molecular Weight Calculator by Matthew Monroe program was used for the calculations.

Electrochemical measurements were performed by the CV method on a VAComputrace analyzer (Metrohm, Switzerland) in a 10-mL three-electrode cell. A platinum rod served as an auxiliary electrode, and the silver chloride (Ag/AgCl) electrode filled with a saturated solution of KCl was a reference electrode. A glassy carbon disc with a diameter of 2 mm was used as a working electrode. A 0.1 M solution of Bu_4NPF_6 in acetonitrile or dimethyl sulfoxide served as an electrolyte.

Synthesis of compound I. Compound $(Bu_4N)_2Mo_6I_{14}$ (0.15 g, 0.053 mmol) was dissolved in CH_2Cl_2 (10 mL) in a small round-bottom flask preliminarily wrapped with aluminum foil to avoid irradiation with the daylight. Then a sevenfold molar excess of solid AgPts (0.103 g, 0.37 mmol) was added to the obtained red solution. The reaction mixture was magnetically stirred for 48 h and filtered through a paper filter, and the product was precipitated with diethyl ether. The precipitate was filtered off on a glass filter, washed with ether, and dried on the filter. The yield of the product as a dark orange powder was 77 mg (47%).

IR (KBr), ν, cm^{-1}: 2958 m, 2929 m, 2872 m, 1600 w, 1492 w, 1457 w, 1382 w, 1272 s, 1156 s, 1101 s, 1024 m, 979 s, 813 m, 677 s, 563 m, 403 w. Electrospray mass spectrum (MeCN), m/z: average 1308.4 ($[Mo_6I_8(O_3SC_6H_4CH_3)_6]^{2-}$), calcd. 1309. ^{1}H NMR ($(CD_3)_2SO$, normalized to 24 protons of CH_3 groups of Bu_4N^+), δ, ppm: 2.37 (s, 18 H, CH_3 groups of Pts), 7.24 (d, $^1J_{H,H}$ = 8 Hz, 12 H, *o*-protons to CH_3 group), 7.59 (d, $^1J_{H,H}$ = 8 Hz, 12 H, *m*-protons to CH_3 group). ^{13}C NMR ($(CD_3)_2SO$), δ, ppm: 20.49 (CH_3 group of ligand), 126.55 (*o*-carbon toward carbon at CH_3 group), 128.80 (*m*-carbon toward to carbon at CH_3 group), 140.42 (*ipso*-carbon or carbon at CH_3 group), 141.36 (carbon at sulfonate group).

For $C_{74}H_{114}N_2O_{18}S_6I_8Mo_6$

anal. calcd., %:	C, 28.6;	H, 3.7;	N, 0.9;	S, 6.2.
Found, %:	C, 28.2;	H, 3.5;	N, 0.9;	S, 6.1.

Single crystals of solvate **I'** suitable for X-ray diffraction analysis were obtained by the diffusion of diethyl ether vapor to an acetonitrile solution of complex **I**.

Synthesis of compound II. Compound $(Bu_4N)_2W_6I_{14}$ (0.24 g, 0.071 mmol) was dissolved in CH_2Cl_2 (10 mL) in a small round-bottom flask preliminarily wrapped with aluminum foil to protect from

the light. A tenfold molar excess of solid AgPts (0.20 g, 0.717 mmol) was added to the orange solution formed. The reaction mixture was magnetically stirred for 48 h and filtered through a paper filter, and the product was precipitated with diethyl ether. The precipitate was filtered off on a glass filter, washed with ether, and dried on the filter. The yield of the product as a light orange powder was 109 mg (42%).

IR (KBr), ν, cm^{-1}: 2958 m, 2929 m, 2872 m, 1599 w, 1493 w, 1457 w, 1381 w, 1277 m, 1158 s, 1100 s, 1024 m, 975 s, 813 m, 677 s, 562 m, 399 w. Electrospray mass spectrum (MeCN), *m/z*: 1572.4 ($[W_6I_8(O_3SC_6H_4CH_3)_6]^{2-}$), calcd. 1572.7. ^{1}H NMR ($(CD_3)_2SO$, normalized to 24 protons of CH_3 groups of Bu_4N^+), δ, ppm: 2.34 (s, 18 H, CH_3 group of Pts), 7.28 (d, $^1J_{H,H}$ = 8 Hz, 12 H, protons in *o*-position to CH_3 group), 7.46 (d, $^1J_{H,H}$ = 8 Hz, 12 H, protons in *m*-position to CH_3 group). ^{13}C NMR ($(CD_3)_2SO$), δ, ppm: 21.42 (CH_3 group of ligand), 126.52 (*o*-carbon toward carbon at CH_3 group), 129.56 (*m*-carbon toward carbon at CH_3 group), 139.92 (carbon at CH_3 group), 141.41 (carbon at sulfonate group).

For $C_{74}H_{114}N_2O_{18}S_6I_8W_6$				
anal. calcd., %:	C, 22.5;	H, 3.7;	N, 0.8;	S, 5.3.
Found, %:	C, 22.9;	H, 3.1;	N, 0.8;	S, 5.0.

X-ray diffraction analysis of compound I'. All measurements were carried out using a standard procedure on a Bruker Apex2 Duo automated four-circle diffractometer equipped with a CCD two-coordinate detector (MoK_α detector, λ = 0.71073 Å, graphite monochromator). Reflection intensities were measured using φ and ω scan modes for narrow (0.5°) frames. An absorption correction was applied empirically using the SADABS program [24]. The structure was solved by a direct method (SHEXLS-2014) [25]. The *para*-tolyl groups of two of three crystallographically independent cluster anions were disordered over two close equally probable positions differed in the turns of deviations of the tolyl substituents relative to the C–S bond. The corresponding carbon atoms were refined in the isotropic approximation. The positions of other non-hydrogen atoms were refined in the anisotropic approximation (SHELX-2014) [25]. Hydrogen atoms were refined in the rigid body approximation.

The crystallographic characteristics and diffraction experimental details are presented in Table 1. Relatively high *R* factors of the residual electron density are explained by a low quality of the crystals. The CIF file containing the full information on the studied structure was deposited with the Cambridge Crystallographic Data Centre (CCDC) (CIF file CCDC no. 1027969; www.ccdc.cam.ac.uk/data_request/cif).

The topology of the crystal packing in compound **I'** was determined using the ToposPro program package [26].

RESULTS AND DISCUSSION

Compound **I** and **II** were synthesized by the exchange reactions of anionic cluster complexes $(Bu_4N)_2[M_6I_{14}]$ (M = Mo, W) with silver salt AgPts at room temperature in dichloromethane. The formation of an insoluble precipitate of AgI provided the shift of the equilibrium of the chemical reaction to the right. The purity of the target compounds was confirmed by the methods presented in Experimental. In particular, the ^{1}H NMR spectra of compounds **I** and **II** indicate the absence of signals from free Pts ions. At the same time, the ratio of integral intensities of coordinated tosylate and tetrabutylammonium indicates the complete replacement of halogen by tosylate. The electrospray mass spectra of freshly prepared solutions of compounds **I** and **II** in acetonitrile contain the signals from the two-charge anions $[M_6I_8(O_3SC_6H_4CH_3)_6]^{2-}$ only. The cluster anion in compound **I'** (at the inversion center) has a structure typical of all complexes $[M_6X_8L_6]$ (Fig. 1). Each Mo atom is coordinated by one oxygen atom of the tosylate anion. Several orientational conformers can exist due to rotation relative to the Mo–O and C–S bonds, resulting in the observed disordering of some tolyl groups in the crystal. According to the CCDC data [27], the Mo–Mo and Mo–I bond lengths (Table 2) are close to the values found for 16 known structures containing the $\{Mo_6I_8\}$ fragment (2.673 and 2.781 Å). In the crystal of compound **I'** (Fig. 2), the large cluster anions form a distorted body centered cubic packing with the distance between the centers of the anions ranging from 15.60 to 18.52 Å. The space between the tetrabutylammonium cations and cluster anions is occupied by solvate molecules of diethyl ether and acetonitrile.

Weighed samples (0.02 g) of compounds **I** and **II** were dissolved in deuterated acetonitrile (CD_3CN) and dimethyl sulfoxide ($(CD_3)_2SO$) (0.4 mL in every case). The solutions were transferred to small glass ampules, which were degassed, sealed out, and kept at 100°C. The ^{1}H NMR spectra of the initial solutions before heating were recorded first, and then a series of the spectra after heating for 1.5 and 14.5 h was obtained. The substitution is completed by the formation of an equilibrium mixture within 1 h for solutions in CD_3CN and within 14.5 h for solutions in $(CD_3)_2SO$. A longer heating does not substantially change the patterns of the ^{1}H NMR spectra: after the heating of all solutions, they contain both the signals from the protons of the tosylate ligands coordinated to the cluster cores $\{M_6I_8\}^+$ (M = Mo, W) and the signals from the protons of free tosylate ions (at the same time, the freshly prepared solutions give the signal from the coordinated ligands only). The chemical

Table 1. Main crystallographic data and experimental characteristics for the structure of compound $(Bu_4N)_2[Mo_6I_8(Pts)_6] \cdot 2Et_2O \cdot 2MeCN$ (**I'**)

Parameter	Value
Empirical formula	$C_{86}H_{136}N_4O_{20}S_6I_8Mo_6$
FW	2453.38
Crystal system	Orthorhombic
Space group	*Pbca*
Temperature, K	150
a, Å	17.0044(19)
b, Å	26.151(3)
c, Å	26.227(3)
V, Å^3	11 662(2)
Z	4
F(000)	6448
Radiation	MoK_α
μ, mm^{-1}	2.91
Crystal size, mm	0.22 × 0.21 × 0.07
Diffractometer	Bruker Nonius X8Apex CCD
Scan mode	ϕ
Absorption correction	SADABS (Bruker-AXS, 2004)
T_{min}, T_{max}	0.200, 0.265
$2\theta_{max}$, deg	60.4
Ranges of indices *h, k, l*	$-23 \le h \le 24$, $-36 \le k \le 36$, $-36 \le l \le 36$
Number of measured/independence/observed ($I > 2\sigma(I)$) reflections	129514/16376/12730
R_{int}	0.0515
Number of refined parameters	576
R ($F^2 > 2\sigma(F^2)$), wR (F^2); S	0.089, 0.222; 1.22
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	4.34/–2.81

shifts of coordinated tosylates are insensitive to the degree of substitution: only the ratio of integral intensities of the signals from the protons of the coordinated and uncoordinated ions changes. The values of chemical shifts for the free and coordinated Pts ions for compounds **I** and **II** in various deuterated solvents are presented in Table 3. The fragment of the ^{1}H NMR spectrum of solvates $[Mo_6I_8(Pts)_{6-x}(CD_3CN)_x]^{-(2-x)}$ after the heating of a solution of compound **I** in acetonitrile for 14.5 h is shown in Fig. 3. The arrangement of chemical shifts in the ^{1}H NMR spectra of the solvolysis products of compound **II** is similar. The spectra of the solvates in dimethyl sulfoxide (DMSO) are not presented but, as for solutions of the solvates in acetonitrile, the ratio of the free and coordinated Pts ions is determined by the ratio of integral intensities of the protons of the methyl groups, whose values were obtained by the manual integration of the peaks. The ratios of integral intensities of the protons of the methyl groups of the free and coordinated Pts ions at various heating times are listed in Table 4. As mentioned above, only coordinated and uncoordinated *para*-toluenesulfonate can be distinguished from the chemical shifts in the ^{1}H NMR spectra, whereas solvates $[Mo_6I_8(Pts)_{6-x}((CD_3)_2SO)_x]^{-(2-x)}$ and $[Mo_6I_8(Pts)_{6-x}(CD_3CN)_x]^{-(2-x)}$ with different values of *x* cannot be distinguished because the signals from coordinated *para*-toluenesulfonate coincide in all cases. The mass spectrum of a solution of compound **I** in CD_3CN heated for 14 h contains a series of signals with *m/z* from 2300 to 2900 in the negative range, among which are the signal corresponding to $[Mo_6I_8(Pts)_6]^{2-}$ (*m/z*(average) 1309.0) and the signal with *m/z*(average) 2445.7 probably assigned to the $[Mo_6I_8(Pts)_5]^-$ species. The latter ion forms "clusters" with acetonitrile molecules: $\{(CH_3CN)[Mo_6I_8(Pts)_5]\}^-$ and $\{(CH_3CN)_{10}[Mo_6I_8(Pts)_5]\}^-$. It is most likely that this

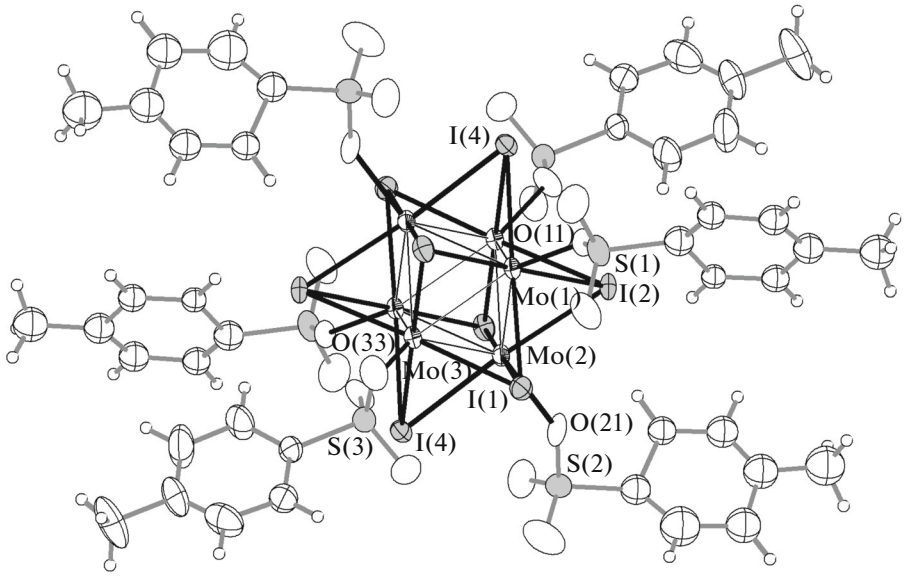

Fig. 1. Structure of the cluster cation in compound **I'** (ellipsoids of 50% probability atomic shifts). The carbon and hydrogen atoms of the disordered *para*-toluenesulfonate ligand are omitted.

clusterization occurs in the gas phase: the solution contains only CD_3CN, and an ion with CH_3CN can be formed only in the ion source upon the reaction with gaseous non-deuterated acetonitrile coming from the mobile phase. The presence of the $\{(CH_3CN)_{10}[Mo_6I_8(Pts)_5]\}^-$ ion confirms indirectly that the signal with m/z 2445.7 can be attributed to the $[Mo_6I_8(Pts)_5]^-$ species. In this case, each tosylate ligand binds two solvent molecules. The positive range exhibits broad signals at m/z 2200–2700 corresponding to the cationic species $[Mo_6I_8(Pts)_{6-x}(CD_3CN)_x]^{-(2-x)}$ (x = 3–6) and their single-charge associates with tosylate $\{[Mo_6I_8(Pts)_{6-x}(CD_3CN)_x](Pts)_y\}^{-(2-x+y)}$ (y = 1–3). The positive range for a solution

Table 2. Selected bond lengths in the cluster anion of the structure of compound **I'***

Bond	d, Å	Bond	d, Å
I(1)–Mo(1)	2.7695(12)	Mo(1)–Mo(3)	2.6724(12)
I(1)–Mo(2)	2.7861(12)	Mo(1)–O(11)	2.130(8)
I(1)–Mo(3)	2.7746(12)	Mo(2)–Mo(3)^i	2.6593(13)
I(2)–Mo(1)	2.8057(11)	Mo(2)–Mo(3)	2.6684(13)
I(2)–Mo(2)	2.7910(12)	Mo(2)–O(21)	2.107(9)
I(2)–Mo(3)^i	2.7960(12)	Mo(3)–O(31)	2.153(8)
I(3)–Mo(1)	2.7642(12)	S(1)–O(11)	1.502(8)
I(3)–Mo(2)^i	2.7667(12)	S(1)–O(12)	1.436(11)
I(3)–Mo(3)	2.7630(12)	S(1)–O(13)	1.420(12)
I(4)–Mo(1)^i	2.7934(12)	S(2)–O(21)	1.483(10)
I(4)–Mo(2)	2.7653(12)	S(2)–O(22)	1.450(13)
I(4)–Mo(3)	2.7839(12)	S(2)–O(23)	1.414(13)
Mo(1)–Mo(2)	2.6602(13)	S(3)–O(31)	1.484(9)
Mo(1)–Mo(2)^i	2.6670(12)	S(3)–O(32)	1.433(11)
Mo(1)–Mo(3)^i	2.6583(13)	S(3)–O(33)	1.430(11)

* The atom is transformed by the symmetry procedure: ^{i} $-x+1, -y+1, -z+1$.

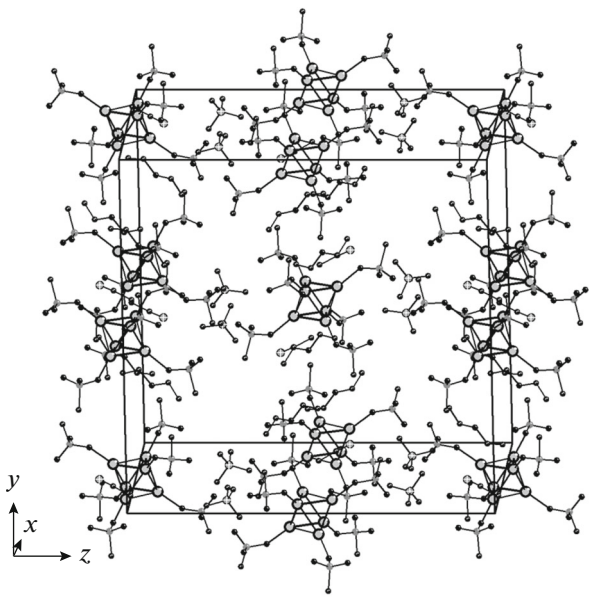

Fig. 2. Crystal packing in compound **I'**. The iodine and hydrogen atoms and the terminal carbon atoms of the cations of the tosylate ligands are omitted.

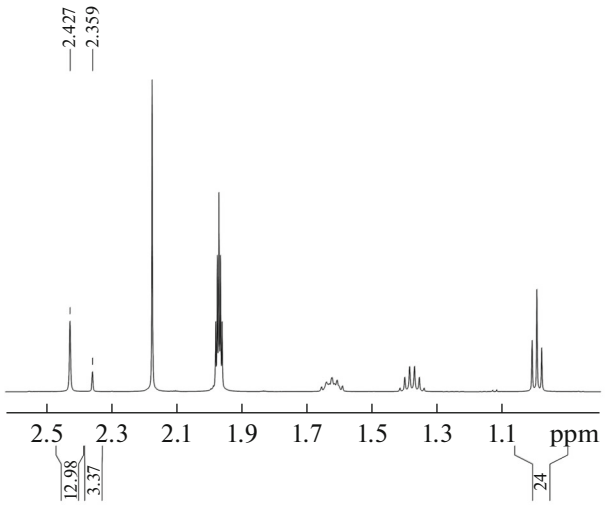

Fig. 3. Fragment of the ^{1}H NMR spectrum of complex **I** in acetonitrile. The integral intensities of the chemical shifts of the protons of the methyl groups of the Pts ions are normalized to 24 protons of the methyl groups of the Bu_4N^+ cations (triplet at the right). Other chemical shifts correspond to the protons of water, solvent, and two methylene groups of tetrabutylammonium observed in the part of the spectrum presented.

of $[Mo_6I_8(Pts)_{6-x}((CD_3)_2SO)_x]$ in $(CD_3)_2SO$ also contains very broad signals in the range m/z 2300–2700 from the cationic complexes $[Mo_6I_8(Pts)_{6-x}((CD_3)_2SO)_x]^{-(2-x)}$ (x = 3–6) and the corresponding adducts $\{[Mo_6I_8(Pts)_{6-x}((CD_3)_2SO)_x](Pts)_y\}^{-(2-x+y)}$ (y = 1–3).

The negative range of the spectra of the tungsten complexes in acetonitrile after heating exhibits a broad signal centered at m/z 1570.7 corresponding to $[W_6I_8(Pts)_6]^{2-}$ (m/z 1572.8), whereas the signal with m/z 2754.8 corresponding to $[W_6I_8(Pts)_3(CH_3CN)_3]^+$ (m/z 2755.1) was detected in the positive range. The signals with m/z 2882, 1397.0, and 901.8 from $[W_6I_8(Pts)_3(C_2D_6SO)_3]^+$, $[W_6I_8(Pts)_2(C_2D_6SO)_4]^{2+}$, and $[W_6I_8(Pts)(C_2D_6SO)_5]^{3+}$, respectively, were detected in the positive range for a solution of compound **II** in $(CD_3)_2SO$.

Clusters $\{M_6X_8\}^{4+}$ (24 skeletal electrons) can reversibly be transformed into the oxidized form $\{M_6X_8\}^{5+}$ (23 skeletal electrons) under the conditions of electrochemical oxidation [1]. The tungsten clusters are oxidized more easily than their molybdenum analogs. The CV method was used in this work for the determination of the oxidation potentials of tosylate complexes **I** and **II**. The corresponding values are given in Table 5. A quasi-reversible process (with a difference in the cathodic and anodic potentials of 70 mV/s) of one-electron oxidation at $E_{1/2}$ = 1.43 V was observed for a solution of complex **I** in acetonitrile. No oxidation was observed in a range of 0–2 V after heating (Fig. 4).

Interestingly, no oxidation is observed in a range of 0–1.5 V in the initial (before heating) solution of complex **I** in DMSO. It cannot be excluded that this process can be manifested at higher potentials. However,

Table 3. Chemical shifts of the free and coordinated Pts ions for compounds **I** and **II** in deuterated acetonitrile and dimethyl sulfoxide

Solvent	$TBA_2[Mo_6I_8(Pts)_6]$		$TBA_2[W_6I_8(Pts)_6]$	
	^{1}H NMR chemical shifts			
	Pts free	Pts coordinated	Pts free	Pts coordinated
CD_3CN	7.63 d, 7.17 d, 2.36 s	7.59–7.56 m, 7.33–7.30 m, 2.43 s	7.63 d, 7.17 d, 2.36 s	7.59–7.56 m, 7.33–7.32 m, 2.43 s
$(CD_3)_2SO$	7.49 d, 7.12 d, 2.30 s	7.60–7.57 m, 7.34–7.32 m, 2.37 s	7.49 d, 7.12 d, 2.30 s	7.61–7.57 m, 7.35–7.33 m, 2.38 s

Table 4. Ratio of integral intensities of the protons of the methyl groups of the free and coordinated Pts ions at various heating times in CD_3CN and C_2D_6SO solutions

Heating time, h	Ratio of integral intensities of protons of methyl groups of free and coordinated Pts ions			
	CD_3CN		C_2D_6SO	
	$TBA_2[Mo_6I_8(Pts)_6]$	$TBA_2[W_6I_8(Pts)_6]$	$TBA_2[Mo_6I_8(Pts)_6]$	$TBA_2[W_6I_8(Pts)_6]$
1	0.24 ± 0.03	0.23 ± 0.03	3.39 ± 0.03	0.11 ± 0.03
5	0.27 ± 0.03	0.24 ± 0.03	3.74 ± 0.03	1.10 ± 0.03
14.5	0.26 ± 0.03	0.25 ± 0.03	5.39 ± 0.03	3.22 ± 0.03

Table 5. Electrode oxidation potentials obtained for solutions of complexes **I** and **II** before and after heating for 14 h

Complex	Oxidation potential, V			
	CH_3CN		DMSO	
	before	after	before	after
$(Bu_4N)_2[Mo_6I_8(Pts)_6]$	$E_{1/2}$ = 1.43		*	
$(Bu_4N)_2[W_6I_8(Pts)_6]$	$E_{1/2}$ = 1.16	1.39	E_a = 1.26	

* Probably, the anodic current corresponding to the oxidation of the complex is not seen against the background of a significant current of DMSO oxidation.

DMSO is also oxidized under these conditions [28] and accompanied by a significant increase in the anodic current. The cyclic voltammogram of a solution of complex **II** in acetonitrile also exhibits a quasi-reversible process (a difference between the cathodic and anodic potentials is 140 mV/s) of one-electron oxidation at $E_{1/2}$ = 1.16 V (Fig. 5), which is by 0.27 V lower than that for complex **I** but is by 0.55 V higher (recalculated to the silver chloride electrode) than that for $[W_6I_{14}]^{2-}$ [13]. After heating, the oxidation potential $E_{1/2}$ is shifted by 0.23 V and becomes equal to 1.39 V (ΔE = 130 mV/s).

Unlike complex **I**, the oxidation process (E_a = 1.26 V) in a range of 0–1.5 V can be detected in the cyclic voltammogram of complex **II** in DMSO, although the process is irreversible. In this case, the oxidation of DMSO does not deteriorate, since complex **II** is oxidized at lower potentials. No oxidation is observed after heating. The CV results confirm the conclusion made on the basis of the mass spectra about the occurrence of solvolysis processes on heating that substantially change the redox properties of the iodide clusters. The shift of the oxidation potentials to the positive range indicates the formation of cationic species containing coordinated solvent molecules.

^{1}H NMR spectroscopy was used for the quantitative estimation of the degree of solvolysis in solutions of compounds **I** and **II**. According to the data in Table 4, the degree of substitution of tosylate ligands in DMSO is higher than that for acetonitrile, which correlates with high Gutmann's donor number of DMSO (29.8) as an aprotic donor solvent compared to that of acetonitrile (14.1) [29]. In the case of the solvolysis of compound **I** in acetonitrile, the ratio of the integral intensity of the protons of the methyl groups of free tosylate ions (δ = 2.36) to the general integral intensity

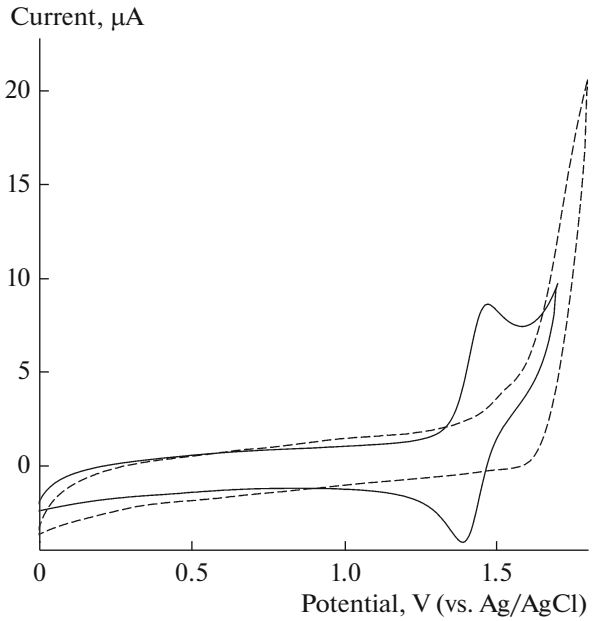

Fig. 4. Cyclic voltammogram of a 1 mM solution of $(Bu_4N)_2[Mo_6I_8(Pts)_6]$ in acetonitrile in the presence of a 0.1 M solution of Bu_4NPF_6 in a range of 0–1.8 V. Solid and dashed lines show the curves for a freshly prepared solution and a solution heated for 14 h, respectively. The scan rate is 0.1 V/s.

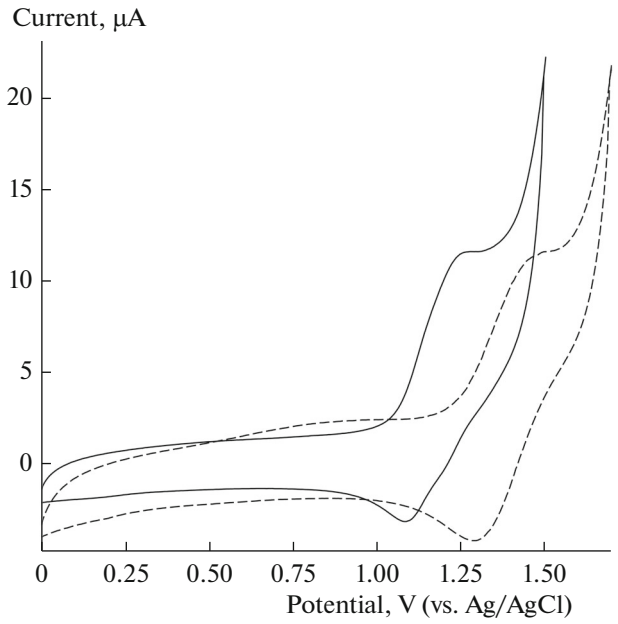

Fig. 5. Cyclic voltammetry of a 1 mM solution of $(Bu_4N)_2[W_6I_8(Pts)_6]$ in acetonitrile in the presence of a 0.1 M solution of Bu_4NPF_6 in a range of 0–1.7 V. Solid and dashed lines show the curves for a freshly prepared solution and a solution heated for 14 h, respectively. The scan rate is 0.1 V/s.

of the protons of the methyl groups achieves an average value of 0.26; i.e., the number of coordinated Pts ions is by 3.9 times higher than that of the uncoordinated ions ($x_{min} = 4.72$, $x_{max} = 4.96$, where x is the average value of the number of coordinated Pts ions with allowance for the determination error of the ratio of integral intensities). This corresponds to the formation of a set of species of the averaged composition $[Mo_6I_8(O_3SC_6H_4CH_3)_{4.72-4.96}(CH_3CN)_{1.04-1.28}]^{-(0.72-0.96)}$ and implies that the species $[Mo_6I_8(O_3SC_6H_4CH_3)_5(CH_3CN)]^-$ predominantly exists in the solution with a minor fraction of $[Mo_6I_8(O_3SC_6H_4CH_3)_4(CH_3CN)_2]$. In the case of the solvolysis of compound **II** under the same conditions, the amount of the coordinated Pts ions is by 4.2 times larger than that of the uncoordinated ions, which corresponds, as in the case of the solvolysis of compound **I**, to the predominant formation of $[W_6I_8(O_3SC_6H_4CH_3)_5(CH_3CN)]^-$ with a minor fraction of $[W_6I_8(O_3SC_6H_4CH_3)_4(CH_3CN)_2]$ ($x_{min} = 4.72$, $x_{max} = 4.96$). Thus, the labilities of the tosylate ligands in complexes **I** and **II** in acetonitrile are similar. The solvolysis of compound **I** in DMSO results in a situation where the average ratio of the intensity of the methyl groups of free tosylate ($\delta = 2.30$) to the intensity of the signal from the protons of the methyl groups of the ligands ($\delta = 2.37$) becomes equal to 5.39. This formally corresponds to $[Mo_6I_8(O_3SC_6H_4CH_3)_{0.93-0.94}(DMSO)_{5.06-5.07}]^{(3.06-3.07)+}$ and can be interpreted as the coexistence of the cationic complexes $[Mo_6I_8(O_3SC_6H_4CH_3)(DMSO)_5]^{3+}$ with a minor fraction of $[Mo_6I_8(DMSO)_6]^{4+}$. The ratio of signals of the chemical shifts for the solvolysis of compound **II** is 3.2. This is due to the formation of $[W_6I_8(O_3SC_6H_4CH_3)_{1.41-1.43}(DMSO)_{4.57-4.59}]^{(2.57-2.59)+}$ corresponding to the coexistence of the cationic complexes $[W_6I_8(O_3SC_6H_4CH_3)_2(DMSO)_4]^{2+}$ and $[W_6I_8(O_3SC_6H_4CH_3)(DMSO)_5]^{3+}$. The kinetic lability, or an increase in the degree of solvolysis depending on the heating time, for compound **I** is higher than that for complex **II**. However, the mass spectral data indicate a more complicated solvolysis process occurring to some average degree of substitution. A set of forms with a broader distribution over x than it follows from the ^1H NMR data are at equilibrium, including the presence of some amount of the starting compounds **I** and **II**. This behavior is characteristic of donor solvents of a medium strength, which are acetonitrile and DMSO toward $[M_6I_8(Pts)_6]^{2-}$. Unfortunately, the peak intensities in the mass spectra cannot be used for the calculation of the relative content of the species, since they are related to specific features of the ionization of the individual species. The absence of peaks from the monosubstituted species $[M_6I_8(Pts)_5(CH_3CN)]^-$ in the negative part of the mass spectra can be due to the easiness of the loss of a neutral acetonitrile molecule in the gas phase to form $[M_6I_8(Pts)_5]^-$, the signals from which predominate in the mass spectra. It can be asserted on the basis of the obtained data that, on the one hand, clusters $\{Mo_6I_8\}$ are more labile than $\{W_6I_8\}$ in the solvolysis reactions. On the other hand, the tosylate ligand in compounds **I** and **II** turned out to be somewhat less labile than triflate $CF_3SO_3^-$ in $[Mo_6Cl_8(CF_3SO_3)_6]^{2-}$, which is completely replaced by $(CH_3)_2SO$ (but not by CH_3CN) [1].

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