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Mononuclear Molybdenum Oxohalide Complexes $(Bu_4N)[MoOCl_4(H_2O)]$ and $(Bu_4N)[MoOBr_4(H_2O)]$: Synthesis and Crystal Structures

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Abstract—The oxidation of $K_3[MoCl_6]$ with air oxygen in aqueous solutions of HX (X = Cl, Br) in the presence of *n*-tetrabutylammonium salts affords mononuclear heteroligand complexes $(Bu_4N)[MoOCl_4(H_2O)]$ (**I**) and $(Bu_4N)[MoOBr_4(H_2O)]$ (**II**). The complexes are characterized by X-ray diffraction analysis (CIF files CCDC nos. 1812657 (**I**) and 1812658 (**II**).

Keywords: molybdenum, halide complexes, heteroligand complexes, X-ray diffraction analysis

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INTRODUCTION

The most part of low-valence molybdenum halide complexes known today are clusters [1–4]. The exception is the Mo(III) derivatives: the majority of structurally characterized compounds of this type are mononuclear ($[MoX_6]^{3-}$) (X = Cl, Br, I) [5–9]. Single examples of the bi- and trinuclear complexes are also known [10–12]. Although this class of compounds has been known long ago, their chemical properties are studied rather weakly. Based on the general concepts of the chemistry of halometallates [13–15], one can assume the ability of $[MoX_6]^{3-}$ to act as "building blocks" for the synthesis of heterometallic complexes of higher nuclearity.

The initial purpose of this work was to obtain tetrabutylammonium salts $[MoX_6]^{3-}$ (X = Cl, Br) that are hypothetically highly soluble in polar organic solvents, which would allow us to use them for the synthesis of heterometallic derivatives. We found that the exchange reactions $K_3[MoCl_6]$ + tetrabutylammonium salt in solutions of HX (X = Cl, Br) in air did not give desirable products: in the presence of air oxygen, $[MoX_6]^{3-}$ undergoes oxidation to form the mononuclear heteroligand complexes of Mo(V). Salts $(Bu_4N)[MoOCl_4(H_2O)]$ (**I**) and $(Bu_4N)[MoOBr_4(H_2O)]$ (**II**) were also isolated and structurally characterized.

EXPERIMENTAL

The reactions were carried out in air. The starting reagents (HCl, HBr, and tetrabutylammonium chloride and bromide) were purchased from commercial sources and used as received. Salt $K_3[MoCl_6]$ were prepared according to a previously published procedure [16].

Synthesis of complex I. A weighed sample of $K_3[MoCl_6]$ (100 mg, 0.23 mmol) was dissolved on heating (70°C) in concentrated HCl (5 mL). A dark red solution was gradually formed, and an excess of Bu_4NCl (326 mg, 1.2 mmol) in H_2O (3 mL) was added. The resulting mixture was cooled down to room temperature and kept for 24 h at 6°C. Green crystals of compound **I** were formed, filtered off, and dried in air. The yield was 89% (based on Mo).

For $C_{16}H_{38}NO_2Cl_4Mo$

Anal. calcd., %	C, 37.4	H, 7.4	N, 2.7
Found, %	C, 37.2	H, 7.5	N, 2.7

Synthesis of complex II was carried out similarly to compound **I** using HBr instead of HCl and Bu_4NBr instead of Bu_4NCl (378 mg in 3 mL of H_2O). Yellow-

Table 1. Crystallographic characteristics and details of diffraction experiments for the structures of compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	514.21	692.05
Temperature, K	130	130
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P4/n$
a, Å	10.2943(2)	12.1670(3)
b, Å	14.5474(3)	12.1670(3)
c, Å	16.9540(3)	8.3509(4)
α, deg	108.652(2)	90
β, deg	96.313(1)	90
γ, deg	97.225(1)	90
V, Å^3	2355.84(8)	1236.23(8)
Z	4	2
μ, mm^{-1}	1.02	7.00
Crystal sizes, mm	0.22 × 0.15 × 0.15	0.12 × 0.10 × 0.06
Range of data collection over θ, deg	3.3–29.0	3.4–29.6
Ranges of reflection indices	$-13 \le h \le 14$, $-19 \le k \le 18$, $-22 \le l \le 20$	$-16 \le h \le 12$, $-16 \le k \le 10$, $-11 \le l \le 6$
Measured reflections	21072	3333
Independent reflections	10274	1495
Reflections with $I \ge 2\sigma(I)$	8687	1323
Number of refined parameters	445	47
GOOF	1.05	1.07
R_1 (for $\|F\|^2$ for reflections with $I > 2\sigma(I)$)	0.034	0.038
wR_2 (for $\|F\|^2$ for all reflections)	0.090	0.093
Residual electron density (max/min), e/Å^3	1.12/–1.07	0.89/–1.09

brown crystals of compound **II** were formed. The yield was 91% (based on Mo).

For $C_{16}H_{38}Br_4NO_2Mo$

Anal. calcd., %	C, 27.8	H, 5.5	N, 2.0
Found, %	C, 27.6	H, 5.6	N, 2.0

X-ray diffraction analysis. The structures of compounds **I** and **II** were determined using a standard procedure on an Xcalibur (Agilent Technologies) diffractometer at 130 K (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator). The reflection intensities were measured using φ scan of narrow (0.5°) frames. An absorption correction was applied using the SCALE3 ABSPACK algorithm [17]. The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation using the SHELX 2017/1 algorithm [18] in the ShelXle program package [19]. The coordinates of the hydrogen atoms of the coordinated water molecule in the crystal structure of compound **I** were

Table 2. Selected geometric parameters for the structures of compounds **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Mo(1)–O(1)	1.6494(18)	Mo(2)–Cl(6)	2.3812(6)
Mo(1)–O(2)	2.3966(19)	Mo(2)–Cl(7)	2.3616(7)
Mo(2)–O(3)	1.6552(18)	Mo(2)–Cl(8)	2.3590(6)
Mo(2)–O(4)	2.3871(19)	Mo(1)–O(1)	1.645(6)
Mo(1)–Cl(1)	2.3606(7)	Mo(1)–O(2)	2.492(12)
Mo(1)–Cl(2)	2.3545(7)	Mo(2)–O(2)	1.504(13)
Mo(1)–Cl(3)	2.3926(6)	Mo(1)–Br(1)^{i}	2.4972(4)
Mo(1)–Cl(4)	2.3826(6)	Mo(2)–Br(1)^{i}	2.4858(12)
Mo(2)–Cl(5)	2.3953(6)		

* Symmetry codes: ^{i} $-x + 1/2$, $-y + 1/2$, z.

found experimentally and refined with the thermal parameter –1.2. In the crystal structure of complex **II**, the $\{OMo(H_2O)\}$ group is orientationally disordered due to location on the crystallographic axis 4. Therefore, the direct localization of the hydrogen atoms of the coordinated water molecule is impossible. The crystallographic data and the results of refinement for the structures of compounds **I** and **II** are presented in Table 1.

The coordinates of atoms and other parameters of the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1812657 (**I**) and 1812658 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

It has earlier been mentioned that the Mo(III) halide complexes in solutions in the presence of air oxygen are unstable. For example, trinuclear $(PPh_4)_3[Mo_3I_{12}]$ undergoes oxidation to form $(PPh_4)[MoOI_4]$ in a yield of 50% for 5 h [20]. A similar behavior was observed for the binuclear Mo(II) carboxylates in solutions of HX [21]. Thus, the formation of compounds **I** and **II** cannot be considered unusual. It is most likely that the tetrabutylammonium salts $[MoX_6]^{3-}$ should be prepared by the reaction in an inert atmosphere.

According to the data in the Cambridge Structural Database, the most number of compounds containing an anion of the $[MoOX_4(H_2O)]^-$ type was described for X = Cl (16, including the monoclinic polymorphous modification of $(Bu_4N)[MoOCl_4(H_2O)]$ [22]), whereas the bromide and iodide complexes are presented to a lower extent (8 [21, 23–28] and 2 [21, 29], respectively). The structure of the anionic moieties of complexes **I** and **II** (including the Mo–O and Mo–X bond lengths, where X = Cl, Br; Table 2) is consistent with published data. In both cases, the coordination sphere of Mo(V) is a strongly distorted octahedron. In the case of complex **I**, the Cl···H–C contacts play a substantial role in crystal packing formation. Some types of Cl···H–C contacts are shown in Fig. 1. The

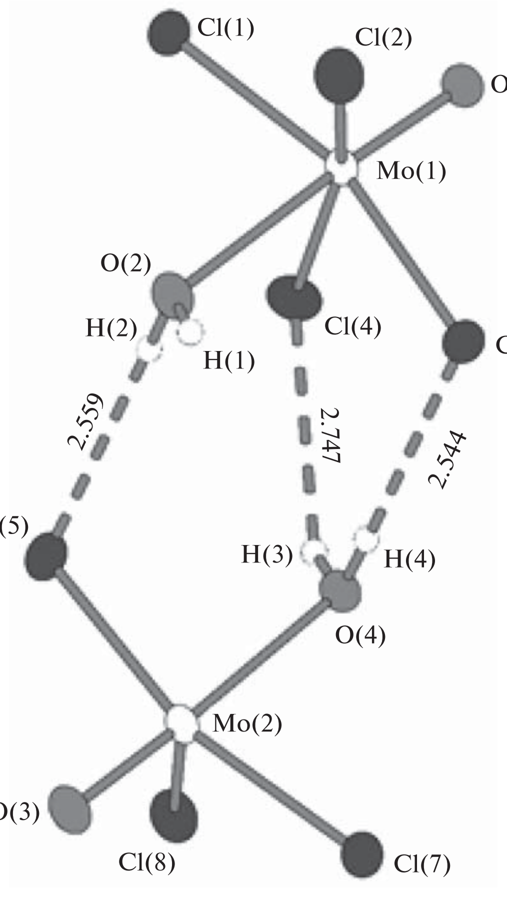

Fig. 1. Associate $\{MoOCl_4(H_2O)\}_2^{2-}$ in the crystal structure of compound **I** formed by contacts H···Cl between the aqua and chloride ligands. Ellipsoids of 50% probability.

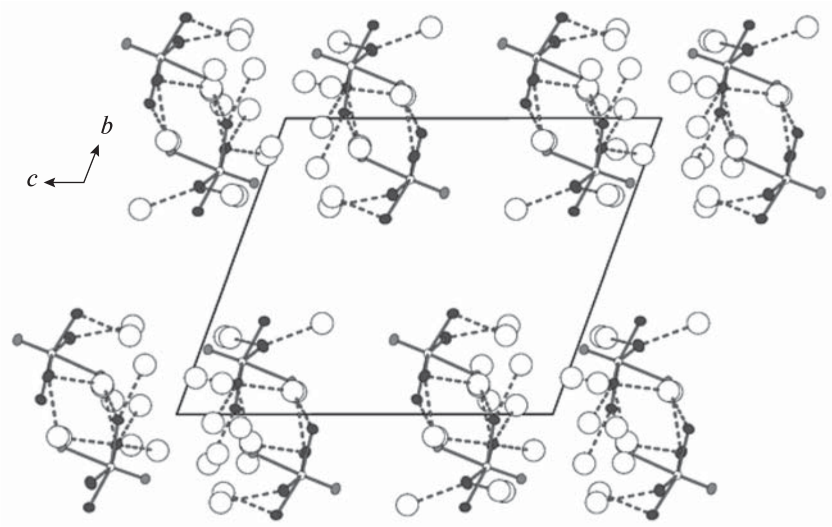

Fig. 2. Crystal packing of complex **I**. Ellipsoids of 50% probability.

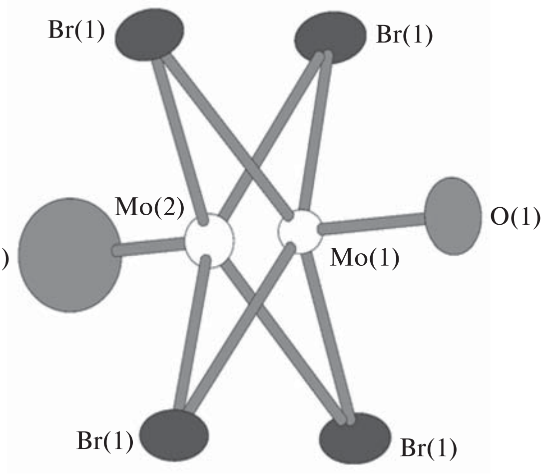

Fig. 3. Orientational disordering of the {OMo(H_2O)} group in the crystal structure of complex **II**.

difference in energies of these interactions leads to the appearance of two types of intermolecular Mo–Mo distances along the crystallographic axis *c*: 9.5 and 9.3 Å, respectively. The crystal packing of complex **I** is shown in Fig. 2. The orientational disordering of the {OMo(H_2O)} fragment is observed in the structure of compound **II** (Fig. 3).

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