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Dedicated to blessed memory of Prof. A.A. Pasynskii

First Pentanuclear Molybdenum Iodide Cluster $(Bu_4N)[Mo_5OI_{13}]$: Synthesis and Structure

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Abstract—The first iodide cluster of molybdenum with the metal cage in the form of a tetragonal pyramid $(Bu_4N)[Mo_5OI_{13}]\cdot$THF (**I**) and cocrystallizate $(Bu_4N)\{[Mo_5OI_{13}]_{0.9}[Mo_6I_{14}]\cdot$THF (**II**) are synthesized for the first time by heating a LiI–I_2–Mo mixture in a temperature range of 300–400°C followed by the extraction of the product. Complexes **I** and **II** are studied by X-ray diffraction analysis (CIF files CCDC nos. 2063029 (**I**) and 2063030 (**II**)). The molybdenum atoms in $[Mo_5OI_{13}]^-$ form a square pyramid with Mo–Mo distances of 2.67 Å between the basal molybdenum atoms and the Mo–Mo distances equal to 2.72 Å between the apical and basal molybdenum atoms. The oxygen atom is coordinated to the pyramid base (Mo–μ_4-O 2.10 Å). The cluster anion $[Mo_5OI_{13}]^-$ can be presented as the octahedral cluster anion $[Mo_6I_{14}]^{2-}$ in which the position of the $\{MoI\}^-$ fragment (d^0, 6e) is occupied by the isoelectronic oxygen atom (s^2p^4, 6e). In the structure of compound **II**, the $[Mo_5OI_{13}]^-$ and $[Mo_6I_{14}]^{2-}$ cluster anions occupy close atomic positions.

Keywords: clusters, molybdenum, iodine, oxoiodides, self-assembling, crystal structure
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INTRODUCTION

The formation of stable cluster groups with metal–metal bonds of various multiplicity is a characteristic feature of lower molybdenum and tungsten halides [1]. The clusters containing the cluster cores $\{M_6X_8\}^{4+}$ (M = Mo, W; X = Cl, Br, I) are most studied [2]. Active interest in them is presently evoked by the ability of these clusters to exhibit bright red phosphorescence, which can find use in diverse areas [3]. As a rule, the structures of metal cages of the clusters of lower nuclearity (3–5 metal atoms) can formally be removed from the octahedron by the removal of one (square pyramid), two ("butterfly" or square), and three (triangle) vertices (Fig. 1), although the tetrahedral clusters are also known [4, 5]. The pentanuclear clusters with the square pyramid structure are of interest as possible precursors of heterometallic octahedral clusters of the $\{M_5M'X_8\}^{4+}$ type (M' is heteroatom), especially in the case of X = I, since these are the iodide cluster complexes of molybdenum $[Mo_6I_8L_6]^z$ (L are terminal ligands, and z is the charge of the coordination sphere) that demonstrate the highest quantum yields and lifetimes [3]. It can be expected that the replacement of one of the molybdenum atom by a heterometal would increase the range of quantitative characteristics of phosphorescence (maximum of emission wavelength, quantum yield, and lifetime). The pentanuclear iodide clusters both in the composition of binary phases [5] and as anionic complexes $[W_5I_{13}]^{-/2-}$ and $[W_5(\mu_4\text{-}C)I_{13}]^-$ [6] were described for tungsten, while only the chloride and bromide clusters $[Mo_5X_{13}]^{2-}$ (X = Cl, Br) were synthesized for molybdenum [7–10].

The first example of the molybdenum iodide cluster $(Bu_4N)[Mo_5OI_{13}]\cdot$THF with the metal cage structure as a square pyramid was obtained and studied by X-ray diffraction analysis (XRD) in this work.

EXPERIMENTAL

Organic solvents (tetrahydrofuran (THF), acetonitrile, and ethanol) were purified using standard procedures, and hexane (special purity grade) and diethyl ether were used as received. The starting reagents (Mo,