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PROPIOLATE CLUSTER COMPLEXES
$(Bu_4N)_2[Mo_6X_8(OOC–C≡CH)_6]$ (X = Br, I)

M. A. Mikhailov[1]*, A. S. Berezin[1], T. S. Sukhikh[1],
D. G. Sheven'[1], A. L. Gushchin[1],
and M. N. Sokolov[1,2,3]

Two new cluster complexes $(Bu_4N)_2[Mo_6X_8(OOC–C≡CH)_6]$ (**1**) (X = Br) and (**2**) (X = I) are synthesized by the reaction of $(Bu_4N)_2[Mo_6X_8(OOCCH_3)_6]$ (X = Br, I) with HOOC–C≡CH propiolic acid, their crystal structures are determined, and the luminescent properties are studied for powder samples at different temperatures. According to X-ray crystallographic data, molybdenum atoms are monodentately coordinated by oxygen atoms of the carboxyl group at Mo–O distances of 2.108(2)-2.121(16) Å. The propiolate complexes are characterized by electrospray mass spectrometry, ^{1}H and ^{13}C NMR, elemental analysis, and IR spectroscopy.

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INTRODUCTION

Carboxylate complexes $[Mo_6X_8(RCOO)_6]^{2-}$ (X = Br, I) exhibit intense phosphorescence in the red spectral range [1-3], which is accompanied by singlet oxygen generation, and they are considered as promising components of materials for photocatalysis, antibacterial coatings, drugs for photodynamic therapy [1, 4-13]. In many cases, the design of materials and devices based on $[Mo_6I_8(RCOO)_6]^{2-}$ implies the chemical binding of the cluster with other components. This can be achieved, for instance, by introducing an additional function into the carboxylate residue. Thus, the isonicotinate complex $[Mo_6I_8(C_5H_4NCOO)_6]^{2-}$ can be directly bonded to porphyrines by coordinating with zinc porphyrinate through the nitrogen atom [14] or by oxidative coupling resulting in the formation of a bond between the nitrogen atom and carbon mesoatoms of the porphyrine ring [15]. The vinyl group of methacrylate complexes $[Mo_6I_8(CH_2{=}C(CH_3)COO)_6]^{2-}$ formed in situ from $[Mo_6I_8(NO_3)_6]^{2-}$ and methacrylic acid can be involved in the copolymerization reaction [16]. Palladium coordination to phosphorus atoms in $Na_2[Mo_6I_8(OOCC_6H_4P(C_6H_5)_2)_6]$ was used to prepare a new efficient heterogeneous catalyst for the Suzuki–Miyaura reaction [17]. In this work, we synthesized and structurally characterized propiolate complexes $(Bu_4N)_2[Mo_6X_8(OOCC≡CH)_6]$ (X = Br, I), containing two potential centers for further functionalization: a triple bond and the methine group containing a proton with increased acidity.

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[1] Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia; *mikhajlovmaks@yandex.ru. [2] Novosibirsk State University, Novosibirsk, Russia. [3] Kazan (Volga region) Federal University, Kazan, Russia. Original article submitted July 1, 2021; revised July 13, 2021; accepted July 13, 2021.