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Short Communication

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Synthesis and characterization of new bromomolybdate complex



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Abstract

The reaction between tetrahexylammonium bromide and MoO_3 produced a new bromo salt (bromotrioxomolybdate (VI)). $(\text{C}_6\text{H}_{13})_4\text{N} [\text{MoO}_3\text{Br}]$, characterized by IR, UV/Visible and ^{81}Br -NMR techniques.

Keywords: Synthesis; Characterization; Tetrahexylammonium bromotrioxomolybdate(VI); ^{81}Br -NMR; UV/Visible

Introduction

Because of the important prerequisites for an oxidant to be useful, mildness, versatility, selectivity and operational simplicity, there is a great deal of interest in the metal oxo halo compounds. Considering these, development the oxidizing agents based on higher-valent metal oxo derivatives specially transition metals the end of many research laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, tungsten, vanadium and chromium have all proved to be capable of alcohol oxidation. When halochromates of type CrO_3X^- (X = F, Cl, Br) having isolated tetrahedral anions, known for some time and are readily accessible by reaction in solution (Brauer, 1960; Ghammami and Sadjadi, 2005; Mahjoub *et al.*, 2003) the corresponding molybdates are not found in similar way. We had prepared and reported synthesis of some $[\text{CrO}_3\text{F}]^-$ and $[\text{CrO}_3\text{Cl}]^-$ anions with tetraalkylammonium counter ion previously (Ghammamy *et al.*, 2006; Mahjoub *et al.*, 2000). We have managed to prepare a new bromo compound of molybdenum which is analog of the above chromium compounds. Oxohalochromates(VI) known for many years and many methods have been used to synthesize them, (Vadera *et al.* 2010) (Sajadi and Ghammami, 2006) (Sarraf *et al.*, 2012) but tetrahexylammonium bromotrioxomolybdate (VI) has not been synthesized and reported so far. In this paper a direct, simple and one-step method has been used to synthesize this compound. There were two primary

incentives for selection of $(\text{Hex})_4\text{N}^+$ as the counter ion. First, quaternary ions such as tetrahexylammonium are often used as phase transfer catalysts. Second, such quaternary ions are used as crystal growing agents.

Materials and methods

Materials and instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentoxide before use, thereby cutting its water content to <4 ppm. Tetrahexylammonium bromide purchased from E. Merck. MoO_3 (Merck, p.a.) and used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Bruker Tensor model 27 spectrophotometer. The UV/Visible measurements were made on Camspec model M 350 spectrometer. ^{81}Br -NMR was recorded on a Bruker AVANCE DRX 500 spectrometer. All the chemical shifts are quoted in ppm using the high-frequency positive convention. Elemental analyses were performed by Microanalytical Laboratories, Department of Chemistry, OIRC, and Tehran.

Synthesis of Tetrahexylammonium Bromotrioxomolybdate (VI), $[(\text{C}_6\text{H}_{13})_4\text{N}] [\text{MoO}_3\text{Br}]$

Tetrahexylammonium bromotrioxomolybdate (VI), $[(\text{C}_6\text{H}_{13})_4\text{N}] [\text{MoO}_3\text{Br}]$ was prepared by dissolving MoO_3

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(0.35 g, 2.4 mmol) in MeCN and addition of this solution to a solution of tetrahexylammonium bromide (1.1 g, 2.4 mmol) in MeCN under stirring at room temperature until a light green precipitate was formed. After 3 hours stirring, the mixture was filtered, washed with isopropyl alcohol and dried at room temperature. The tetrahexylammonium salts are somewhat hygroscopic, and stored under a layer of hexane, though all the salts are photosensitive and moisture-sensitive, both in solution and solids. UV/Visible, IR, ⁸¹Br-NMR were all consistent with the THexABM structure. Mp: 175°C. Anal Calc for C₂₄H₅₂NBrMoO₃ (%): C, 42.15; H, 7.90; N, 3.07. Found: C, 42.94; H, 8.17; N, 3.22.

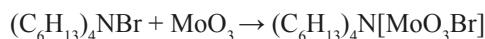
Results and discussions

We reported the synthesis of several halochromates (VI), with the belief that these reagents could be used for oxidizing organic substrates. It was shown that halochromates were useful new oxidants for organic chemists (Ghammamy and Bhattacharjee *et al.* 1982; Mazareey *et al.*, 2005). Those compounds showed oxidative properties like as other previous reported halochromates (Chaminade *et al.*, 1986; Ghammamy *et al.* 2009; Nakamoto, 2009). We now report the synthesis of THexABM, an analog of the above chromium compounds.

The method used for the synthesis of THexABM does not involve direct use of HF or reaction of MHF₂ (M = NH₄, K) with MoO₃, and is based on high reactivity of tetrahexylammonium bromide, (C₆H₁₃)₄NBr and its ability to bromide addition to other compounds. The advantages of the new method are:

a) there is no side product, b) the reaction is fast, c) mild conditions and d) the accompanied color change that provides visual means for ascertaining the progress of the reaction.

(C₆H₁₃)₄N[MoO₃Br] was prepared by the reaction of (C₆H₁₃)₄NBr with MoO₃ in a 1:1.1 ratio in MeCN solvent in as follows:



In the vibrational spectrum of THexABM the cationic and anionic bands were seen such as ν_{Mo-O} that was found at 863.4 cm⁻¹ that along the literature data (Table I). Electronic spectrum of THexABM shows a transition in acetonitrile at 225nm ($\epsilon = 385.2 \text{ mol}^{-1}\text{lit.cm}^{-1}$) that belongs to ¹A₁ → ¹E (a₂ → e) transition. This transition is expected as in mono substituted molybdate ions, because of the position of molybdenum in the second series of transition metal parts and making of strong crystalline field complexes. Also the signals were found in ⁸¹Br-NMR shows the bond between Mo and Br.

Table I. The frequencies (cm⁻¹) and assignment of cation and anion of THexABM

ν Assignment Intensity (cm ⁻¹)			ν Assignment Intensity (cm ⁻¹)		
(C ₆ H ₁₃) ₄ N ⁺			1462	ν_{16}	(s)
3460	$\nu \text{ CH}_3 + \nu_{19}$	(w, br.)	1396	ν_{16}	(m)
3370	$\nu \text{ CH}_3 + \nu_8$	(w, br.)	1921	ν_{rock}	(w)
3113	$\nu \text{ CH}_3, \text{asym.str}$	(sh.)	940	ν_{18}	(vs)
3015	$\nu_{13}, \nu \text{ CH}_3, \text{asym.str}$	(w, br.)	475	ν_{19}	(ms)
2926	$\nu_{14}, \nu \text{ CH}_3, \text{asym.str}$	(w, br.)	438	ν_{19}	(ms)
2861	$\nu_{14}, \nu \text{ CH}_3, \text{asym.str}$	(w, br.)	MoO ₃ Br ⁻		
2625	$\nu_7 + \nu_{16}$	(w)	918	$\nu_{\text{as Mo=O}}$ (E)	911
2568	$\nu_3 + \nu_8 + \nu_{16}$	(w)	863	$\nu_{\text{a Mo=O}}$ (A)	874

Conclusion

(C₆H₁₃)₄N[MoO₃Br] was prepared by the reaction of (C₆H₁₃)₄NBr with MoO₃ in a 1:1.1 ratio in MeCN solvent. The compound was characterized by a combination of IR, UV/Visible, and ¹³C-NMR, ¹H-NMR and ⁸¹Br-NMR techniques. Production of this compound shows the ability of tetrahexylammonium bromide addition to transition metals compounds.

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