Synthesis and characterization of new bromomolybdate complex

\[(\text{C}_6\text{H}_{13})_4\text{N}\text{MoO}_3\text{Br}\]

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Abstract

The reaction between tetrahexylammonium bromide and MoO\textsubscript{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 \(^{81}\text{Br}\)-NMR techniques.

Keywords: Synthesis; Characterization; Tetrahexylammonium bromotrioxomolybdate(VI); \(^{81}\text{Br}\)-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\textsubscript{3}X \((X = \text{F, Cl, Br})\) 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 tetralkylammonium 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) (Sajjadi and Ghammami, 2006) (Sarrafi 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 pentaoxide before use, thereby cutting its water content to <4 ppm. Tetrahexylammonium bromide purchased from E. Merck. MoO\textsubscript{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 Campspec model M 350 spectrometer. \(^{81}\text{Br}\)-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,
(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 C42H72NBrMoO3 (%): 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 there 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 MHF3 (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:

(C6H13)4NBr + MoO3 → (C6H13)4N[MoO3Br]

In the vibrational spectrum of THexABM the cationic and anionic bands were seen such as vMo=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 225 nm (ε = 385.2 mol⁻¹ cm⁻³) 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.

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<tr>
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Conclusion

(C\textsubscript{6}H\textsubscript{13})\textsubscript{4}N[MoO\textsubscript{3}Br] was prepared by the reaction of (C\textsubscript{6}H\textsubscript{13})\textsubscript{4}NBr with MoO\textsubscript{3} in a 1:1.1 ratio in MeCN solvent. The compound was characterized by a combination of IR, UV/Visible, and \textsuperscript{13}C-NMR, \textsuperscript{1}H-NMR and \textsuperscript{81}Br-NMR techniques. Production of this compound shows the ability of tetrahexylammonium bromide addition to transition metals compounds.

Acknowledgements

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