



Synthesis And Characterization Of Two New Bromo Complexes, [[C₄H₉]₄N][MoO₃Br] And [[C₄H₉]₄N][AlCl₃Br]

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ABSTRACT

The reaction between tetrabutylammonium bromide and AlCl₃ and MoO₃ produced two new ionic bromocomplexes with tetrabutylammonium cation. One of them is tetrabutylammonium bromotrioxomolybdate (VI), (C₄H₉)₄N[MoO₃Br], TBABM, that is easily synthesized in a nearly quantitative yield using a direct reaction of MoO₃ and tetrabutylammonium bromide. Another is tetrabutylammonium bromotrichloroaluminate (III), [(C₄H₉)₄N][AlCl₃Br], TBABA, that has been synthesized by reaction of tetrabutylammonium bromide with AlCl₃ salt. These compounds were characterized by IR, UV/Visible, ¹³C-NMR and ¹H-NMR techniques. The electronic and vibrational spectra of TBABM and TBABA have been measured and studied.

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KEYWORDS

Synthesis;
Characterization;
Tetrabutylammonium
bromotrioxomolybdate (VI);
Tetrabutylammonium
bromotrichloroaluminate
(III).

INTRODUCTION

In recent years there has been a great deal of interest in the metal oxohalo compounds. This is because of the important prerequisites for an oxidant to be useful for its mildness, versatility, selectivity and operational simplicity. Considering these, development of oxidizing agents based upon higher-

valent metal oxo derivatives specially transition metals has been the objective of many research laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, tungsten, vanadium and chromium have all proven to be capable of alcohol oxidation. While halochromates of type CrO₃X⁻ (X= F, Cl, Br) having isolated tetrahedral anions, have been known for some time and

are readily accessible by reaction in solution^[1-3] the corresponding molybdates and aluminates are not found in analogous manner. We had prepared and reported synthesis of a number of $[\text{CrO}_3\text{F}]^-$ and $[\text{CrO}_3\text{Cl}]^-$ anions with tetraethylammonium counter ion previously^[4,5]. We have managed to prepare two new bromocompounds of molybdenum and aluminum that are the analog of the above chromium compounds. Oxohalochromates(VI) have been known for many years and many methods have been used to synthesize them^[6-8], but the compounds, bromotrioxomolybdate (VI) and bromotrichloro aluminate (III) have not been synthesized and reported so far. In this paper a direct, simple and one-step method has been used to synthesize these compounds. There were two primary incentives for selection of $(\text{C}_4\text{H}_9)_4\text{N}^+$ as the counter ion. Firstly, quaternary ions such as tetrabutylammonium are often used as phase transfer catalysts. Secondly, quaternary ions such as tetrabutylammonium are used as crystal growing agents.

RESULTS AND DISCUSSION

We had reported the synthesis of a number of halochromates(VI), with the belief that those reagents could be used for the oxidation of organic substrates. It has been shown that halochromates were useful new oxidants for organic chemists^[9,10]. Those compounds showed oxidative properties like as other previous reported halochromates^[11-13]. We now report the synthesis of the TBABM that is analog of the above chromium compounds.

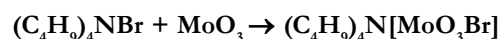
The reported methods for their preparation involved non-mild or hard conditions such as high tem-

peratures or use of acids such as HF. The method used for the synthesis of TBABM and TBABA does not involve direct use of HF or reaction of MHF_2 ($\text{M}=\text{NH}_4, \text{K}$) with MoO_3 and AlCl_3 , and is based on the concept of high reactivity of tetrabutyl ammonium bromide, $(\text{C}_4\text{H}_9)_4\text{NBr}$ and its power to bromide addition to other compounds.

The advantages of the new method are: a) there is no side product, b) the reaction is quite fast, c) mild conditions and d) the accompanied color change that providing visual means for ascertaining the progress of the reaction.

Tetrabutylammonium bromotrioxochromate (VI), $(\text{C}_4\text{H}_9)_4\text{N}[\text{MoO}_3\text{Br}]$, TBABM

$(\text{C}_4\text{H}_9)_4\text{N}[\text{MoO}_3\text{Br}]$ was prepared by the reaction of $(\text{C}_4\text{H}_9)_4\text{NBr}$ and MoO_3 in a 1:1 ratio in MeCN solvent as follows:



In the vibrational spectrum of this compound the known bands of cation and anion were seen^[14,15,16] such as $\nu_{\text{Mo=O}}$ (A_1) that was found at 872.16 cm^{-1} that confirmed with literature data (TABLE 1). There is an absorption in the compound electronic spectrum (Figure 1). Electronic spectrum of TBABM shows a transition in acetonitrile at 228 nm ($\epsilon=336.2 \text{ mol}^{-1}\text{lit. cm}^{-1}$) that belongs to $^1A_1 \rightarrow ^1E$ ($a_2 \rightarrow e$) transition. This transition is expected as in mono substituted molybdate ions, because of the position of molybdenum in the second series of transition metal elements and making of strong crystalline field complexes.

The expected signals were found in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

TABLE 1: The frequencies (cm^{-1}) and assignment of cation and anion of TBABM

$\nu(\text{cm}^{-1})$	Assignment	Intensity	$\nu(\text{cm}^{-1})$	Assignment	Intensity
	$(\text{C}_4\text{H}_9)_4\text{N}^+$		1476	ν_{16}	(s)
3473	$\nu_{\text{CH}_3} + \nu_{19}$	(w, br.)	1402	ν_{16}	(m)
3380	$\nu_{\text{CH}_3} + \nu_8$	(w, br.)	1921	ν_{rock}	(w)
3105	$\nu_{\text{CH}_3, \text{asym.str}}$	(sh.)	940	ν_{18}	(vs)
3010	$\nu_{13}, \nu_{\text{CH}_3, \text{asym.str}}$	(w, br.)	475	ν_{19}	(ms)
2955	$\nu_{14}, \nu_{\text{CH}_3, \text{asym.str}}$	(w, br.)	438	ν_{19}	(ms)
2785	$\nu_{14}, \nu_{\text{CH}_3, \text{asym.str}}$	(w, br.)		MoO_3Br^-	
2625	$\nu_7 + \nu_{16}$	(w)	911	$\nu_{\text{as Mo=O}}$ (E)	911
2568	$\nu_3 + \nu_8 + \nu_{16}$	(w)	874	$\nu_{\text{a Mo=O}}$ (A)	874

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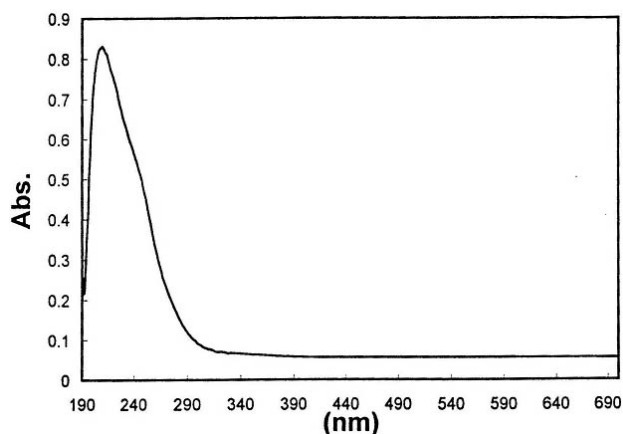
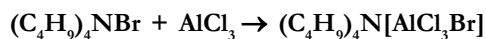


Figure 1: UV/Visible spectrum for the $(C_4H_9)_4N[MoO_3Br]$ ($C=9.4 \times 10^{-4}$, solvent:acetonitrile)

Tetrabutylammonium bromotrichloroaluminate (III), $[(C_4H_9)_4N][AlCl_3Br]$

$(C_4H_9)_4N[AlCl_3Br]$ was prepared by the reaction of $(C_4H_9)_4NBr$ and $AlCl_3$ in a 1:1.1 ratio in MeCN solvent as follows:



In the vibrational spectrum of TBABA the cationic and anionic bands were seen^[14,17] such as ν_{Al-Cl} that was found at 686.4 cm^{-1} that along the literature data. There are three absorption bands in this compound electronic spectrum (TABLE 2). The expected signals were found in the 1H -NMR and ^{13}C -NMR.

TABLE 2: Transitions specifications of TBABA

λ (nm)	λ (nm)	λ (nm)
$(\epsilon, M^{-1}cm^{-1})$	$(\epsilon, M^{-1}cm^{-1})$	$(\epsilon, M^{-1}cm^{-1})$
575	375	305
(458)	(478)	(485)

EXPERIMENTAL

Material and instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentoxide before use, thereby reducing its water content to $<4 \text{ ppm}$. Tetrabutylammonium bromide was bought from Merck. $AlCl_3$ and MoO_3 (Merck, p.a.) were used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. 1H and ^{13}C -NMR were recorded on a Bruker AVANCE DRX 500 spectrometer. All the chemical

shifts are quoted in ppm using the high-frequency positive convention; 1H and ^{13}C -NMR spectra were referenced to external $SiMe_4$. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tetrabutylammonium bromotrioxochromate(VI), $[(C_4H_9)_4N][MoO_3Br]$

Tetrabutylammonium bromotrioxomolybdate (VI), $[(C_4H_9)_4N][MoO_3Br]$ was prepared by dissolving MoO_3 (0.31 g, 2.2 mmol) in MeCN and addition of this solution to a solution of tetrabutylammonium bromide (0.70 g, 2.2 mmol) in MeCN under stirring at room temperature until a bright green precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with isopropyl alcohol and dried at room temperature. The tetrabutylammonium salts are somewhat hygroscopic, and it better stored under a layer of hexane, whereas all of the salts are photosensitive and moisture-sensitive, both in solution and solids. UV/Visible, IR, 1H -NMR and ^{13}C -NMR were all consistent with the TBABM structure. Mp: $111^\circ C$. Anal. Calcd for $C_{16}H_{36}BrMoNO_3$ (%): C, 41.20; H, 7.72; N, 3.00. Found: C, 42.53; H, 8.01; N, 3.12.

Synthesis of Tetrabutylammonium bromotrichloroaluminate(III), $[(C_4H_9)_4N][AlCl_3Br]$

To a solution of aluminium trichloride $AlCl_3$ (0.29 g, 2.2 mmol) in MeCN the solid powder tetrabutylammonium bromide (0.78 g, 2.42 mmol) was added under stirring at room temperature until a white solid precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with 1-butanol, and dried at room temperature. UV/Visible, IR, 1H -NMR and ^{13}C -NMR were all consistent with the TBABA structure. Anal. Calcd for $C_{16}H_{36}AlBrCl_3N$ (%): C, 42.15; H, 7.90; N, 3.07. Found: C, 42.94; H, 8.17; N, 3.22.

CONCLUSION

Two tetrabutylammonium bromide salts of $AlCl_3$ and MoO_3 were synthesized simply. $(C_4H_9)_4N[MoO_3Br]$ was prepared by the reaction of $(C_4H_9)_4NBr$ and MoO_3 in a 1:1 ratio in MeCN solvent and $(C_4H_9)_4N[AlCl_3Br]$ was prepared by the reaction of $(C_4H_9)_4NBr$ and $AlCl_3$ in a 1:1.1 ratio in MeCN solvent. Electronic and vibrational spectra of these two new

bromocomplexes studied. These compounds were characterized by IR, UV/Visible, and ^{13}C -NMR and ^1H -NMR techniques. Production of these compounds shows the ability of tetrabutylammonium bromide in bromide addition to transition metal and main group elements compounds.

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