Asian Journal of Chemistry Vol. 20, No. 3 (2008), 1733-1740

Synthesis, Characterization, ^{81}Br NMR and Electronic Spectra of $[(C_4H_9)_4N][CrO_3Br]$ and $[(C_4H_9)_4N][FeCl_3Br]$

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Two new ionic complexes of transition metals with tetrabutylammonium cation were synthesized. One of them is tetrabutylammonium bromotrioxochromate(VI), $(C_4H_9)_4N$ $[CrO_3Br]$ (TBABC), that easily synthesized in a nearly quantitative yield using a direct reaction of Cr(VI) oxide and tetrabutylammonium bromide. Another is tetyrabutylammonium bromotrichloroferrate(III), $[(C_4H_9)_4N][FeCl_3Br]$, (TBABF), that has been synthesized by reaction of tetrabutylammonium bromide with $FeCl_3$ salt. These compounds were characterized by IR, UV/Visible, ^{81}Br NMR, ^{13}C NMR and ^{1}H NMR techniques. The electronic and vibrational spectra of TBABC and TBABF have been measured and studied. In TBABC the intervening band has been identified with oxygen-to-chromium charge transfer. This band exhibits a partially resolved vibrational progression or vibronic coupling due to excitation of a symmetric stretching mode in the CrO_3 group.

Key Words: Synthesis, ^{81}Br NMR, Tetrabutylammoniumbromotrioxochromate(VI), Electronic spectra, Tetra-butylammonium bromotrichloroferrate(III).

INTRODUCTION

Oxidation in modern organic chemistry is one of the most important reactions. Chromium(VI) is the most widely employed among oxidizing agents based upon transition metal derivatives such as reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium. There is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. In recent years, significant improvements were achieved by the use of new oxidizing agents[1-4] such as pyridinium

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dichromate (PDC)[5], pyridinium fluorochromate (PFC)[6]. Triphenylmethylposphonium chlorochromate[7], chromium trioxide-3,5-dimethylpyrazole complex (CrO_3 3,5-DMP)[8], Tributylammonium chlorochromate (TriBACC)[9], 3,5-dimethylpyrazolium fluorochromate (DmpzHFC)[10], quinolinium fluorochromate (QFC)[11], 2,2'-bipyridinium chlorochromate (BiPCC)[12]. In this research $(C_4H_9)_4N^+$ was used as counter ion. There were two primary incentives for selection of $(C_4H_9)_4N^+$ as the counter ion. Firstly, quaternary ions such as tetrabutylammonium are often used as phase transfer catalysts. This could make tetrabutylammonium bromochromate(VI), $[(C_4H_9)_4N][CrO_3Br]$, TBABC a more efficient and stronger oxidizing agent. This compound can be used for quantitative oxidation of several organic substrates. Secondly, quaternary ions such as tetrabutylammonium are used as crystal growing agents.

EXPERIMENTAL

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before use, thereby reducing its water content to < 4 ppm. Tetrabutylammonium bromide was bought from Merck. $FeCl_3$ and CrO_3 (Merck) 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 and ^{81}Br NMR was recorded on Bruker Avance DRX 300 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 $SiMe_4$ and ^{81}Br NMR spectra was referenced to external NaBr. The per cent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of tetrabutylammonium bromotrioxochromate(VI), $[(C_4H_9)_4N][CrO_3Br]$ (TBABC): Tetrabutylammonium bromotrioxochromate(VI), $[(C_4H_9)_4N][CrO_3Br]$ was prepared by dissolving CrO_3 (0.23 g, 2.3 mmol) in MeCN and addition of this solution to a solution of tetrabutylammonium bromide (0.76 g, 2.3 mmol) in MeCN under stirring at room temperature until a brown precipitate was formed. After 2 h stirring, the mixture was filtered, washed with diethylether and hexane and dried at room temperature. The tetrabutylammonium salts are some what hygroscopic and best stored under a layer of hexane, whereas all of the salts are photosensitive and moisture-sensitive, both in solution and solids. TBABC was recrystallized from methylene chloride by addition of hexane. UV/Visible, IR, ^{81}Br NMR, ^1H NMR and ^{13}C NMR were all consistent with the TBABC structure. m.p. over 350 ºC. Anal. Calcd. for $C_{16}H_{36}BrNO_3Cr$ (%): C, 45.49; H, 8.53; N, 3.31. Found: C, 46.02; H, 8.75; N, 3.43.

Synthesis of tetrabutylammonium bromotrichloroferrate(III), $[(C_4H_9)_4N][FeCl_3Br]$ (TBABF): Tetrabutylammonium bromotrichloroferrate(III), $[(C_4H_9)_4N][FeCl_3Br]$ was prepared to a solution of tetrabutylammonium bromide (0.66 g, 0.002 mol) in MeCN was added a solution of $FeCl_3$ (0.33 g, 0.002 mol) in MeCN under stirring at room temperature until an orange precipitate was formed. After 2 h stirring, the mixture was filtered, washed with diethyl ether and dried at room temperature. UV/Visible, IR, ^{81}Br NMR, ^1H NMR and ^{13}C NMR were all consistent with the TBABF structure. m.p., 125 ºC. Anal. Calcd. for $C_{16}H_{36}NBrCl_3Fe$ (%): C, 39.63; H, 7.43; N, 2.89. Found: C, 40.02; H, 7.78; N, 3.01.

RESULTS AND DISCUSSION

Tetrabutylammonium bromotrioxochromate(VI), $(C_4H_9)_4N][CrO_3Br]$: $(C_4H_9)_4N[CrO_3Br]$ was prepared by the reaction of $(C_4H_9)_4NBr$ and CrO_3 in a 1:1 ratio in MeCN solvent as follows:

$$(C_4H_9)_4NBr + CrO_3 \longrightarrow [(C_4H_9)_4N][CrO_3Br]$$

The following are the main points emerged out of the electronic spectrum of TBABC (Fig. 1). The transitions in CrO_3Br^- ion of TBABC are charge transfer, because of the chromium oxidation state +6 and d^0 electronic configuration. The ground and excited states energies and symmetries have been studied before[1]. This ion has three electronic transitions that are summarized in Table-1.

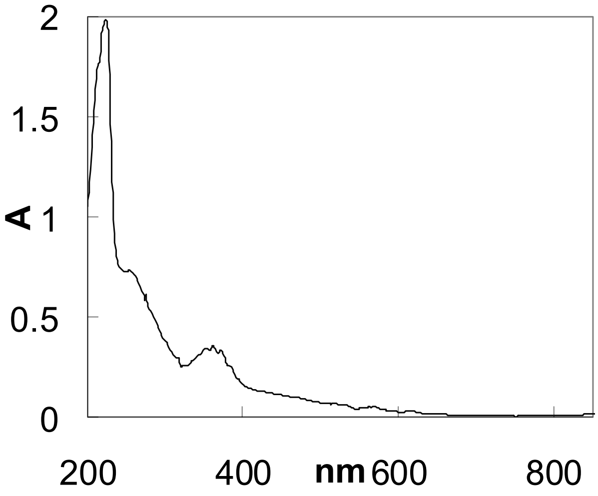

Fig. 1. Electronic spectrum of $(C_4H_9)_4N[CrO_3Br]$ (Solvent: acetonitrile)

TABLE-1
TRANSITIONS SPECIFICATIONS OF TBABC

$\lambda_{C.T}$(LMCT) (ε, $M^{-1}cm^{-1}$)	$\lambda_{C.T}$(LMCT) (ε, $M^{-1}cm^{-1}$)	$\lambda_{C.T}$(LMCT) (ε, $M^{-1}cm^{-1}$)
520	362	254
(69)	(356)	(646)
$a_2 \rightarrow e$	$e \rightarrow e$	$a_1 \rightarrow e$

On the basis of the results in CrO_4^{2-} and the correlation $t_1(T_d) \rightarrow a_2 + e(C_{3v})$, the highest filled orbitals in CrO_3X^- are anticipated and found to have a_2 and e symmetry. The a_2 orbital has the higher energy, a node at the halogen and only a slight chromium character. Hence, the highest occupied orbital retains an oxygen lone-pair description. The highest filled e orbital has somewhat greater, although still small, chromium character and a significant halogen contribution. The latter is expected from *e.g.*, the relative electronegativities, which should tend to concentrate the bromine character in lower energy levels. The lowest unoccupied level has e symmetry and predominantly chromium 3*d* character, as anticipated from the correlation $e(T_d) \rightarrow e(C_{3v})$. Its chromium contribution decreases and its oxygen contribution increases in the order of CrO_4^{2-}, CrO_3F^-, CrO_3Cl^-, CrO_3Br^- but the changes are small. The halogen contribution is very small and similar in both halochromates. The $a_2 \rightarrow e$ and $e \rightarrow e$ excitations derived from the parent $1t_1 \rightarrow 2e$ (T_d) excitation have the lowest energies with $a_2 \rightarrow e$ lowest by ≈ 0.4 e.V in both anions. The results confirm that the calculations suggest that the $^{1,3}E$ states arising from $a_2 \rightarrow e$ are the lowest lying excited states with a very small singlet-triplet splitting. However, this prediction disregards the multiplet splitting among the nearby states arising from the $e \rightarrow e$ excitation $(^{1,3}A_1 + {}^{1,3}A_1 + {}^{1,3}E)$[13].

The spectral correlation between CrO_4^{2-}, CrO_3F^- and CrO_3Br^- is very good. The low lying $^1T_1$ state of CrO_4^{2-} should split into a ^1E state and a $^1A_2$ and, as the $^1A_1 \rightarrow {}^1A_2$ transition is forbidden in C_{3v} symmetry, we should observe $^1A_1 \rightarrow {}^1E$ more prominently. A $^1T_2$ state, on the other hand, should split into ^1E and $^1A_1$ states. The spectral results allow us to conclude that replacement of an oxide ligand by a bromide has almost no effect on a tetrahedral t_1 orbital; to a good approximation it remains oxygen-localized and non-bonding. For the second $^1A_1 \rightarrow {}^1T_2$ transition of CrO_4^{2-}, however, the situation is quite different. The MO scheme for MO_4^{n-} complexes shows that there are three filled π-orbitals generated from oxide 2*p*-orbitals, e, t_2 and t_1. An e orbital is strongly π-bonding, t_1 is non-bonding and t_2 is nearly non-bonding. Upon replacement of an oxide by a halide, strong t_2 splitting to orbitals of e and a_1 symmetries is expected, as the e orbital will have halide pπ character. For bromide, the low-lying excitation may therefore be characterized as a $a_1 \rightarrow e^*$ one electron transition. The $^1A_1$ component of the parent $^1T_2(T_d)$ is evidently a high-lying state, as inferred from the polarization measurements. The fact that the energy and structure of the $^1A_1 \rightarrow {}^1E$ band agrees well with the parent complex indicates that the a_1 orbital remains an oxide non-bonding orbital. In contrast to the transitions at lower energy, however, the effect of the X ligand is not merely to perturb weakly the parent molecule transitions[1].

The IR spectrum of the CrO_3Br^- ion has been the subject of several publications[14] (Fig. 2). The XY_3Z ions have a number of infrared active vibrations. These infrared active vibrations are $\nu_1(A_1)$ or $\nu(XY_3)$, $\nu_2(A_1)$ or $\nu(XZ)$, $\nu_4(E)$ or $\nu(XY3)$ and $\nu_5(E)$ or $\delta(XY_3)$ that correspond to 910, 398, 958 and 375 cm^{-1} for CrO_3Br^- ion, respectively.

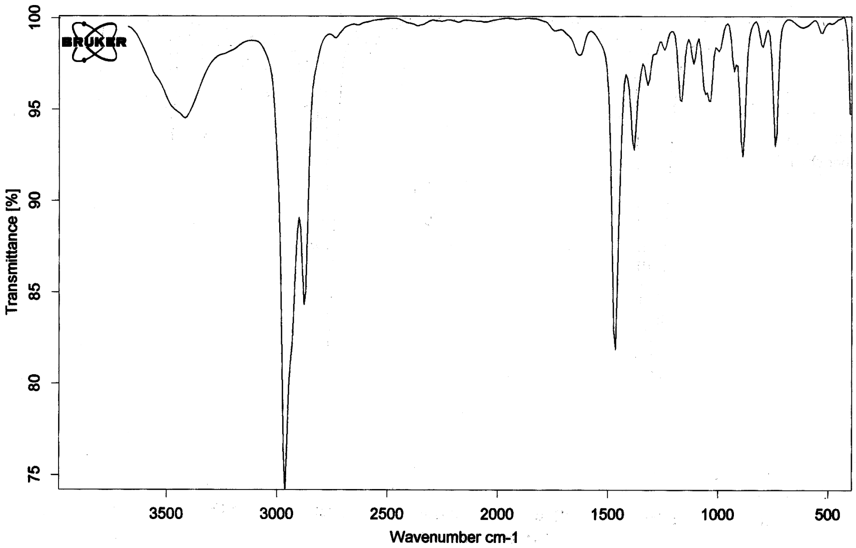

Fig. 2. IR spectrum of $[(C_4H_9)_4N][CrO_3Br]$

Vibrational assignments were made after examination of the region just above 400 nm and Table-2 shows the vibronic intervals. As seen these data are not equal with any of the CrO_3Br^- ground state vibrational frequencies. Vibrational intervals in the electronic spectra have been assigned by the reference to the ground state values, on the assumption that they correspond to the totally symmetric modes. It is assumed that these intervals are related to excited symmetric stretching mode in the CrO_3 group. The CrO_3 ground state symmetric stretching frequency is 910 cm^{-1} in CrO_3Br^- while is significantly lower in the excited state. With this information it is clear that the vibrational progression below 400 nm fits the series $0 \to 0$, $0 \to 1$, $0 \to 2$,. . . $0 \to n$[15]. Therefore, it is concluded that excited state bonds are weaker and probably longer than ground state. Reductions of frequencies of 10-20 % observed in the excited states are of about the same magnitude as found in the spectra of MO_4^- complexes[16]. Experimental data show that the ν_{max} in CrO_3Br^- anion of TBACB occurs near ν_{03} (Fig. 1, Table-2). In the IR spectra, ^1H NMR and ^{13}C NMR cationic signals were seen[17]. In ^{81}Br NMR, a signal was seen in -5.56 ppm due to bonding between bromide and chromate ions (Fig. 3).

TABLE-2
MEASURED CENTER FREQUENCIES AND THE VIBRATIONAL SPACINGS (cm^{-1}) FOR CrO_3Br^- OF TBABC IN ACETONITRILE

λ (nm)	Assignment	ν (cm^{-1})	Δν (cm^{-1})	
334	$0 \to 0$	29940.1	–	$\nu_{max} \pm 10 = 27624.30$
344	$0 \to 1$	29069.7	870.4	
352	$0 \to 2$	28409.1	660.6	$\nu_{vib} \pm 20 = 781.27$
362	$0 \to 3$	27624.3	784.8	
372	$0 \to 4$	26881.7	742.6	$\nu_{00} \pm 50 = 29940.10$
382	$0 \to 5$	26178.0	703.7	
396	$0 \to 6$	25252.5	925.5	

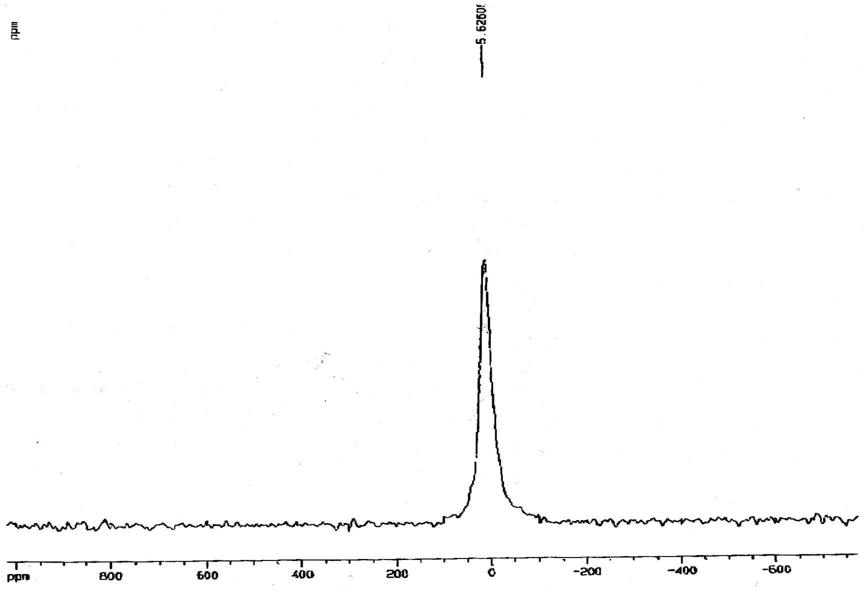

Fig. 3. ^{81}Br NMR spectrum of $[(C_4H_9)_4N][CrO_3Br]$ (Solvent: D_2O)

Tetrabutylammoniumbromotri chloroferrate(III), $[(C_4H_9)_4N][FeCl_3Br]$: The compound was crystallized by the slow evaporation method by use of a solution of MeCN after one week. In the vibrational spectrum the cationic and anionic signals were seen[3,9], $\nu_{3Fe\text{-}Cl}$ (stretching) was found at 464.8 cm^{-1} that along the literature data (Fig. 4). There are four absorptions in this compound electronic spectrum (Table-3). The expected signals were found in the ^1H NMR and ^{13}C NMR. In the ^{81}Br NMR a signal is seen in the 5.62 ppm that confirmed the bonding between bromide and iron (Fig. 5).

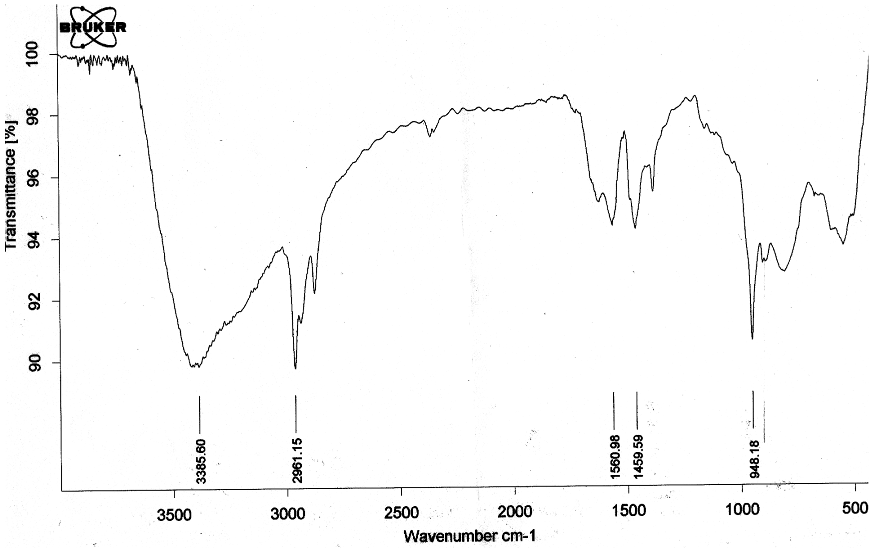

Fig. 4. IR spectrum of $[(C_4H_9)_4N][FeCl_3Br]$

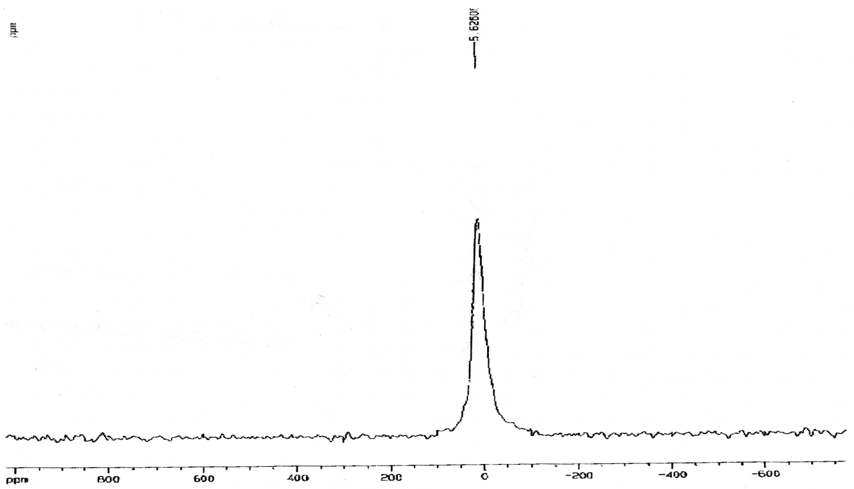

Fig. 5. ^{81}Br NMR spectrum of $[(C_4H_9)_4N][FeCl_3Br]$ (Solvent: D_2O)

TABLE-3
TRANSITIONS SPECIFICATIONS OF TBABF

$\lambda(\varepsilon, M^{-1}cm^{-1})$	$\lambda(\varepsilon, M^{-1}cm^{-1})$	$\lambda(\varepsilon, M^{-1}cm^{-1})$	$\lambda(\varepsilon, M^{-1}cm^{-1})$
572 (152)	362 (2908)	306 (2317)	242 (2383)

Conclusion

Two tetrabutylammonium bromide salts of $FeCl_3$ and CrO_3 were synthesized simply. The electronic and vibrational spectra of these two new bromo complexes studied. TBABC shows vibronic coupling in its second transition that is similar to another mono substituted chromate such as CrO_3F^-, CrO_3Cl^- and so on. These compounds were characterized by IR, UV/Visible, ^{13}C NMR, ^{1}H NMR and ^{81}Br NMR techniques. In ^{81}Br NMR of both new bromocomplexes, TBABC and TBABF have been found a signal that confirmed the bonding between bromide and metal ions.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Gh. Rezaei Behbahani and Dr. Mahjoub for valuable discussions.

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(*Received*: 18 December 2006; *Accepted*: 22 October 2007) AJC-6035