



Scholars Research Library

Der Pharma Chemica, 2014, 6(1):466-471  
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X  
CODEN (USA): PCHHAX

## Synthesis and characterization of a new combination of nano-trichloroiodoaluminate (III)

Mohamad Mehdi Akbarzade\* and Ali Naderi

Department of Chemistry, Ardabil Branch, Islamic Azad University, Ardabil, Iran

### ABSTRACT

There is provided a nano aluminate complex that has a quaternary ammonium cation. This nano system has an equal molar ratio of Al to N that has been prepared by reaction of an organic salt  $R^+X^-$  such as  $[(CH_3)_4NBr]$ , and a Lewis acid such as  $AlCl_3$ , compounds. The synthesized compound was characterized by IR, Mass, X-Ray diffraction measurements. In addition, the structure of synthesized compound was optimized at the theoretical level of the Moller-Plesser perturbations of the second order (MP2) with LanL2DZ basis set and molecular specifications such as band length and angle were extracted using Gaussian 98 program. Theoretical data show good agreement with the experimental result.

**Keywords:** Nano particles, Aluminate complex, Tetrabutylammonium Trichloroiodoaluminate (III), XRD, Theoretical calculation.

### INTRODUCTION

Many of complex compounds are formed by at least two components. The first component is contained an organic salt or mixture of salts such as phosphonium, sulfonium, or quaternary ammonium halides including one or more alkyl moieties. The second component is contained a Lewis acid (metal halide) such as  $ZnCl_2$ ,  $GaCl_3$ ,  $InBr_3$ ,  $AlCl_3$ ,  $HfCl_4$ ,  $ZrCl_4$ ,  $GeCl_4$ ,  $SiCl_4$ ,  $WCl_6$ ,  $SbCl_3$  and  $RuCl_3$  [1-2]. The properties of these complexes can be varied by changing the constituent ions.

Whereas symmetric  $R_4NX$  have been studied by different experimental techniques and they have special characteristics, we focus my attention on tetra-alkyl-ammonium halides [3-5].

In order to make a complex compound, reaction of metal halide with organic salt such as quaternary ammonium halide solution may be performed at  $-10$  to  $100^\circ C$  and the 2 to 9 Al/N molar ratio [1-2].

Of course in the literature were found the mole ratio less than 2 according to the following reactions [6]:



It is noteworthy that if the molar ratio,  $q/p$ , is less than 1, reaction consist of  $R^+AlX_4^-$  and  $R^+Al_2X_7^-$  [7-9]. When  $q/p$  is greater than 1 but less than 2, reaction products consist of  $R^+X^-$  and  $R^+AlX_4^-$  [7-9]. Those compound for which  $q/p=1$  contain only  $R^+AlX_4^-$ .

Furthermore the solution chemistry of these complexes has been studied in some molecular solvents. It was found that some metal halide complexes undergo the following hydration and hydrolysis reactions in aqueous solution [6 & 10].



Therefore, in order to avoid hydrolysis reaction, some nonaqueous molecular solvent, such as acetonitril, can be used in place of water.

These reactions and complex compounds can be employed in a very wide range of applications such as alkylation, isomerization, hydrocracking, polymerization, dimerization, oligomerization, acylation, acetylation, metathesis, copolymerization, hdroformylation, dehalogenation, etc [11-15]. For example an isobutane-butene alkylation catalyzed with butyl pyridinium chloroaluminate, and co-catalyzed with t-butyl chloride, in literature has been mentioned [1].

Special series of mentioned complex compounds are called Aluminates complex which are produce by reaction of alkyl-ammonium salts and aluminum chloride according to a reported general procedure [16]. Some of the chloroaluminate complexes are used for alkylation of benzene instead of  $AlCl_3$  as a catalyst. These compounds solve problems such as the formation of aluminate waste, low yield, cumbersome product recovery, and nonreuse of the catalyst. An advantage of the chloroaluminate compounds is their adjustable Lewis acidity. Acidity can be altered by varying the molar ratio of the two components and can be used to produce specific catalysts or compounds [17].

Extended practical applications of these materials have motivated us to improve our knowledge. In this direction, in order to gain insight into neoteric material, a Nano quaternary ammonium haloaluminate complex was synthesized by using an equal molar ratio of a quaternary ammonium salt and aluminum chloride compounds and then was identified by different experimental methods and finally was determined stable configuration of complex via an ab initio calculations.

## MATERIALS AND METHODS

Tetrabutylammonium iodide and aluminum chloride were purchased from Merck Corporation. In this study all the chemical solvents were of analytical grade and were used as received without purification. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 (420 models) FT-IR spectrometer, using the pressing potassium bromide disk. The ranges of DTGS were  $4000-400\text{ cm}^{-1}$ . The Nano particles were characterized by X-ray diffraction (XRD; PMD-3000).

Mass spectrum was recorded by mass spectroscopy (Mass; Agilent Technology (HP), 5973 Network Mass Selection Detector).

2.0mmol (0.27g) aluminum chlorides was placed in a round flask and in this flask, 5 ml  $CH_3CN$  (without water) was added. The mixture was stirred at room temperature for ~ten minuets until the solution became yellow. Then 2.0mmol (0.73 g) Tetrabutylammonium iodide (dried) was mixed with 5 ml  $CH_3CN$  (without water) in other round flask and stirred for 1 h until solution became milky and was then added to first flask. The resulting solution was then kept for 3 h at room temperature with stirring. Reaction was exothermic and the resultant became orange.

The nano-particles were centrifuged at 5000 rpm for 20 min and the precipitates were collected and redispersed in diethyl ether. The precipitate was centrifuged again at 5000 rpm for 20 min and the precipitates were redispersed in hexane. At the end of the solution was centrifuged at 5000 rpm for 20 min once more, and the precipitates were collected and redispersed in  $CH_3CN$ . The light orange precipitate was extracted in ceramic dish, dried in sand-bath and kept in desiccator. Weight and yield of dried Nano-particles was 0.80 g and 80%, respectively. These washed

and dried Nano-particles were used for spectroscopic, SEM and XRD measurement. Spectroscopic data of synthesized aluminates complex are reported as IR (KBr): 3380, 3315, 3225, 3010, 2958, 2874, 2735, 2360, 1950, 1475, 1382, 1158, 463, 453, 1061, 879, 885  $\text{cm}^{-1}$ ; MS,  $m/z=360$  ( $\text{M}^+$ ), 353, 333, 313, 290, 279, 254, 239, 203, 184, 167, 142, 133, 121, 98, 85, 63, 50 (Figure 1, 4).

The ab initio calculations were carried by means of the Gaussian 98 software. The structure of anionic segment  $[\text{AlCl}_3\text{I}]^-$ , and synthesized compound  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  was optimized at the theoretical level of the Moller- Plesser perturbations of the second order (MP2) with LanL2DZ basis set. Calculations were done in the gas phase. Optimization procedures and frequency calculations were done in order to extract most stable structure, bond length and angle, vibratory frequencies and finally results checked for more confidence and theoretical data were compared with experimental results.

## RESULTS AND DISCUSSION

Fist of all, It was synthesized with an equal molar ratio of Al to I in order to synthesize only one product,  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$ , without impurity. Non-aqueous molecular solvent, acetonitril, was used with initial substances in order to avoid hydrolysis reaction. Then the resultant nano aluminate complex after purification was characterized by IR, Mass, X-Ray diffraction measurements.

The solubility of synthesized ionic liquid was verified in common solvents. The results of solvation shows that soluble in solvents such as methanol, water, slightly soluble in ethanol and dimethyl solfoxide and insoluble in toluene, acetonitrile, chloroform, hexane.

The cationic segment and synthesized structure of  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  were optimized by MP2 method using LanL2DZ basis set in the gas phase (Figure 2). Structure formation energy ( $E(\text{HF})$ ), RMS force and displacement, maximum force and displacement demonstrate stability of structures (global minimum). Also Table 1 consists of calculated molecular parameters (bond length and angle), anionic segments and synthesized  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  in sequence. Results of Table 1 for  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  show, Al-I bond length is 2.826 Å, Al-Cl(2) bond length is 1.875 Å, Al-Cl(3) bond length is 1.875 Å, Al-Cl(4) bond length is 1.930 Å, I-Al-Cl(2) bond angles are 106.5°, and I-Al-Cl(3) bond angel is 106.5°, Cl(3)-Al-Cl(2) bond angel is 120.5° Cl(4)-Al-Cl(2) bond angel is 118.9°, Cl(4)-Al-Cl(3) 109.505°.

Table 2 show calculated IR frequencies (theoretical) in 1-4000  $\text{cm}^{-1}$  without correction.

FTIR spectrum of  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  which were recorded by a Bruker instrument, are shown in Figure 1. The experimental bands and assignments for FTIR spectra of  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  are presented in Table 2.

X-ray powder diffraction measurement was performed at room temperature and data on crystallite size was obtained. Figure 3 shows typical XRD patterns of the tested sample. Then the crystallite size of  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  powders was calculated by classical Debye-Scherrer Eq (1):

$$d = K \cdot \lambda / \beta \cdot \cos \theta \quad (1)$$

Wherein  $d$  is the crystallite size,  $\lambda$  is the X-ray wavelength ( $\lambda=0.154$  nm),  $\beta$  is the width of the peak (full width at half maximum (FWHM) or integral breadth) after correcting for instrumental peak broadening ( $\beta$  expressed in radians) ( $\beta=0.0039^\circ$ ),  $\theta$  is the Bragg angle ( $2\theta=22.7^\circ$ ) and  $K$  is the Scherrer constant ( $K=0.9$ ). Whereas the crystallite size is related to the diffraction peak broadening and this method is applicable to crystallites in the range of 3–100 nm then the value of crystallite size determined from X-ray diffraction for  $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{AlCl}_3\text{I}]^-$  powders, ( $d=36$  nm).

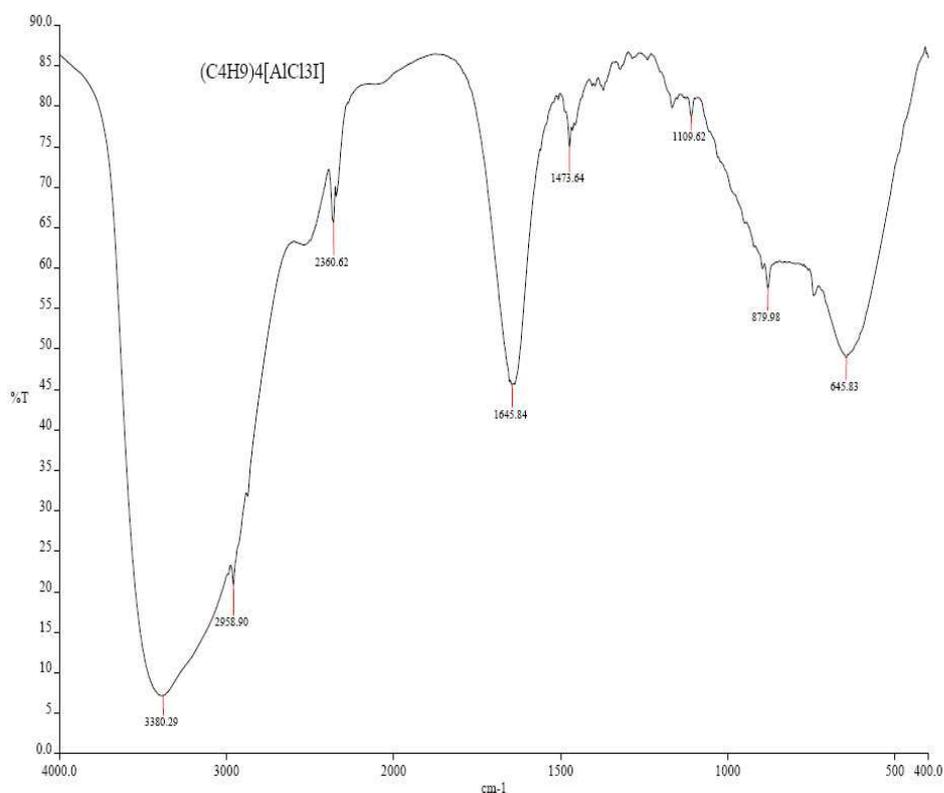
Mass spectrometry was used to prove the structure of the notified nano aluminate complex. The mass spectrum of mentioned sample is shown in figure 3.

Table1. Optimized parameters of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$  based on Gaussian 98

Bond	Bond lengths[Å]	angles	Bond angles [°]
Al-I	2.826	I-Al-Cl(2)	106.5
Al-Cl(2)	1.875	I-Al-Cl(3)	106.5
Al-Cl(3)	1.875	Cl(3)-Al-Cl(2)	120.5
Al-Cl(4)	1.930	Cl(4)-Al-Cl(2)	118.9
		Cl(4)-Al-Cl(3)	118.9

Table2. Experimental frequencies of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$  ( $cm^{-1}$ )

( $cm^{-1}$ ) $\nu$	Vibration	Intensity
<b><math>(C_4H_9)_4N^+</math></b>		
3380	$\nu_{CH_2} + \nu_{19}$	(m, br)
3315	$\nu_{CH_2} + \nu_8$	(w, br)
3225	$\nu_{CH_2}$ , asym. str	(sh)
3010	$\nu_{13}, \nu_{CH_2}$ , asym. str	(w, br)
2958	$\nu_{14}$ , asym. str	(w, br)
2874	$\nu_{14}, \nu_{CH_2}$ , asym. str	(w, br)
2735	$\nu_7 + \nu_{16}$	(w)
2360	$\nu_3 + \nu_8 + \nu_{16}$	(w)
1950	$\nu_8 + \nu_{15}$	(w, br)
1475	$\nu_{15}, CH_2$ , asym. def	(ms)
1382	$\nu_{16}, CH_2$ , sym. str	(s)
1158	$\nu_{rock}, CH_2$ , rocking $\nu_{14}$	(m)
463	$\nu_{19}, \nu_{C_4}$ , dif.	(w, br)
453	$\nu_{19}, \nu_{C_4}$ , dif.	(w, br)
<b><math>[AlCl_3I]^-</math></b>		
1061	Al-Cl	(s)
879	Al-I	(s)
885	B-I	(m)

Figure1. FTIR spectrum of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$

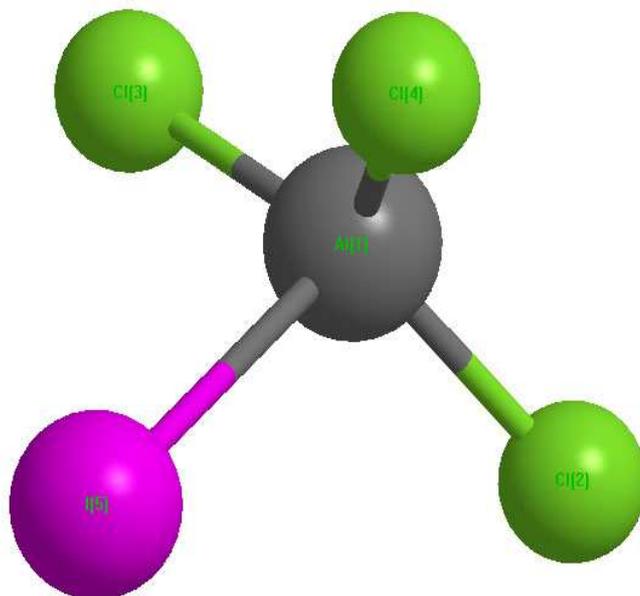


Figure2. Optimized cationic structure of  $[(C_4H_9)_4N]^+$

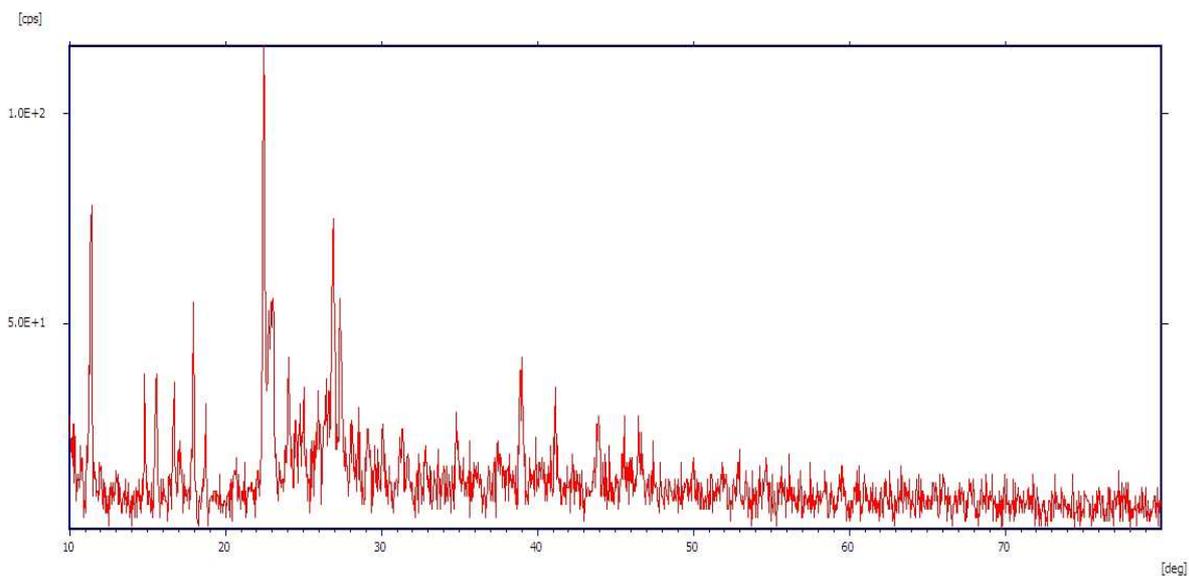


Figure3. XRD patterns of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$

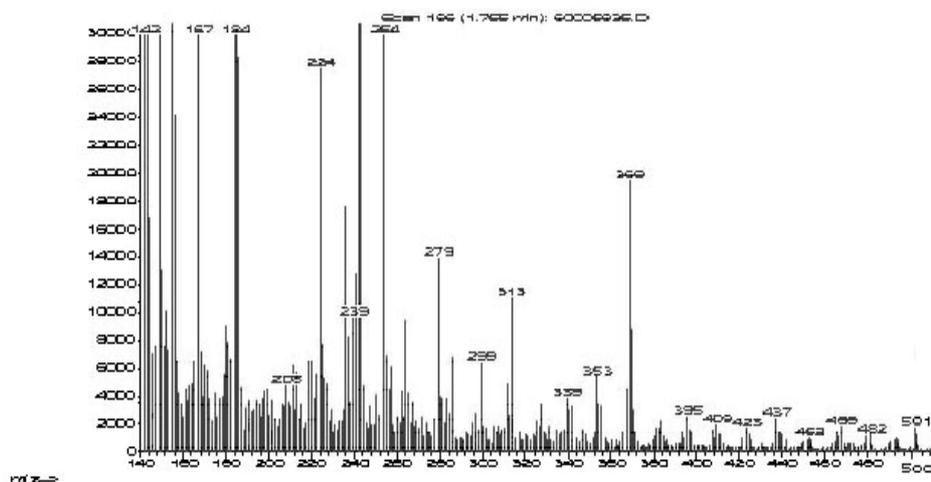


Figure4. Mass spectra of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$

### CONCLUSION

We present the mentioned results as recommendations in order to increase information with respect to  $[(C_4H_9)_4N]^+[AlCl_3I]^-$  and continue the quest for more details.

In summary, the molecular structure of  $[(C_4H_9)_4N]^+[AlCl_3I]^-$  is confirmed by presence of functional groups in FTIR spectra and fragment ion in mass spectrometric. Also theoretical data show good agreement with the experimental result.

In addition, the value of crystallite size in Nano scale are demonstrated by X-ray diffraction method for  $[(C_4H_9)_4N]^+[AlCl_3I]^-$  Nano crystalline powders.

### REFERENCES

- [1] Blanco L. H.; Gomez A.; Bermudez G. *Acta. Sud. Quim.* **1981**, 1, 107.
- [2] Amado E.; Blanco L. H. *Phys. Chem. Liq.* **2000**, 38, 451.
- [3] Blanco L. H.; Vargas E. F. *J. Sol. Chem.* **2006**, 35, 21.
- [4] Hussey Ch. L.; *Pure & Appl. Chem.* **1988**, 60, 1763.
- [5] Gale R. J.; Gilbert B.; Osteryoung R. A. *Inorg. Chem.* **1978**, 17, 2728.
- [6] Matsumoto T.; Ichikawa K.; *J. Am. Chem. Soc.* **1984**, 106, 4316.
- [7] Takahashi S.; Koura N.; Murase M.; Ohno H. *J. Chem. Soc.* **1986**, 2, 49.
- [8] Appleby D.; Hussey C. L.; Seddon K. R.; *J. E. Turp, Nature* **1986**, 323, 614,
- [9] Forsyth S. A.; Pringle J. M.; MacFarlane D. R.; *Aust. J. Chem.* **2004**, 57, 113.
- [10] Endres F.; *Chem. Phys. Chem.* **2002**, 3, 144.
- [11] Buzzeo M. C.; Evans R. G.; Compton R. G. *Chem. Phys. Chem.* **2004**, 5, 1106.
- [12] Endres F.; El Abedin S. Z. *Chem. Phys. Chem.* **2006**, 8, 2101.
- [13] John S. Wilkes, *Green Chemistry* **2002**, 4, 73-80.
- [14] Hussey C. L.; *Pure Appl. Chem.* **1988**, 60, 1763.
- [15] Verevkin S. P.; Kozlova S. A.; Emel'yanenko V. N.; Goodrich P. C. *J. Phys. Chem.* **2008**, 112, 11273.
- [16] Sheldon R. R. *Chem. Common.*, **2001**, 413, 2399
- [17] Verevkin S. P.; Emel'yanenko V. N.; Toktonov A. V. *J. Phys. Chem.* **2009**, 113, 12704