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SYNTHESIS AND CHARACTERIZATION OF TWO ALUMINATE (III) COMPLEXES $Na[AlCl_3 X]$ (X =F, I), SPECTROSCOPY AND ANTIBACTERIAL PROPERTIES

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***Abstract*— The present investigation, we report The synthesis and characterization of two new aluminate (III) complexes of general formula $Na[AlCl_3 X]$, derived from one dentate Ligands CL, X (X =F, I). Sodium Trichlorofluoroaluminate, SCFA, Sodium Trichloroiodatoaluminate, SCIA, produced two ionic aluminate complexes. They easily synthesized in a nearly quantitative yield using by direct reaction of $AlCl_3$ with relative ligands. The complexes were characterized by physico-chemical and spectroscopic methods. Theoretical calculation has been used for extraction of structural and spectroscopic data of these new synthesized complexes. The antibacterial activities of synthesized compounds were studied against the *Staphylococcus aureus, Escherichia coli*, *Staphylococcus Epidermidis, Estreptococo B and Shigella*.**

Keywords— **Theoretical calculation, aluminate complexes, Synthesis, Characterization, SCFA, SCIA, Antibacterial activities.**

I. INTRODUCTION

In the last of twentieth century, scientist found that unlike traditional view about the melting points of salts, there is a class of salts or salt mixtures with melting points below 100°C, which are referred to as ionic liquids (IL). Room-temperature ionic liquids (RTIL) are ILs with melting points at or below room temperature. Some ionic liquids (RTIL) are non-flammable, non-volatile or thermally stable and can be used as promising replacements for the traditional organic solvent. Moreover, the growing interest to synthesis and study of ionic liquids has been observed. The facility of applying ionic liquids in organic reaction comes from that often the organic product in these reactions can be removed easily from the ionic liquid by extraction with organic solvent without resorting to an aqueous workup or needing to solvent evaporation in high temperature. This is useful when metal catalyst is used in the reaction that this catalyst often remains in the ionic liquid and can be directly reused. In addition, ionic liquids as a class of novel environmental "green solvents", have remarkable new properties and promising applications in many fields. The first RTIL, ethyl ammonium nitrate (mp 13–14 °C), was reported in 1914. However, ILs did not draw much attention from chemists till 1992, when Wilkes and co-workers reported air- and water-stable RTILs based on imidazolium salts. Subsequently, research on the synthesis, properties, and applications of RTILs has increased substantially. However, a recent report indicated that several ionic liquids have been applied in separation of various mixtures [1,2]. Moreover, ionic liquid properties such as heat capacities and refractive index [3], luminescence properties [4], osmotic coefficients [5], enthalpy, density, heat capacity [6], and thermo physical properties [7] have been studies since their first synthesis. Therewith, following our previous studies about ionic liquids chemistry [8-10], we decide to improve our knowledge about these compounds by synthesis, characterisation, and theoretical study of some new aluminium-based ionic liquids. In this investigation, we report on the synthesis, spectroscopic characterization, and antimicrobial activity of aluminate (III) complexes with trichloro ligands: $Na^+[AlCl_3F]^-$, $Na^+[AlCl_3I]^-$. Although the synthesis of the trichloro has been reported earlier, no research has been done so far on the aluminate complexes of these ligands. Al (III) can form stable pyramid complexes with tetra coordinating atoms, 3Cl, X(F,I) atoms can be coordinated to the (Al) ion. Thus, the geometry of the molecule is a distorted pyramid with the 3Cl, X (F,I) symmetry group. The antibacterial activities of synthesized compounds were studied against the *Staphylococcus aureus, Escherichia coli, Staphylococcus Epidermidis, Estreptococo B and Shigella*.

II. METHODS AND MATERIALS

All chemicals and reagents used for the syntheses were commercial products (Merck) and used without further purification. Solvents used for reactions were purified and dried by standard procedures. The molar conductance values of the complexes were measured in acetonitrile solution in room temperature with a Jenway 4510 conductometer instrument. Melting points were determined using an electrothermal apparatus and are uncorrected. The electronic

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spectroscopic data in 200–900 nm range were recorded in acetonitrile on a Perkin-Elmer lambda spectrophotometer. Infrared spectra were recorded as KBr disks on a Bruker Tensor model 420 spectrophotometer. Mass spectra were recorded on a Agilent Technology (HP) model Network Mass Selective Detector 5973 spectrophotometer.

Antibacterial activity tests

The in vitro activity tests were carried out using the Growth Inhibitory zone (well method), *against the staphylococcus aureus, Escherichia coli, Staphylococcus Epidermidis, Estreptococo B and Shigella*. Microorganisms (obtained from enrichment cultures of the microorganisms in 1 mL Muller–Hinton broth, incubated at 37 °C for 24 h) were cultured on Muller–Hinton agar medium. The inhibitory activities were compared with those of the standard antibiotic gentamicin (0.5 Mg). After drilling wells in the medium using a 6 mm cork borer, 100 L of solutions of the test compounds were poured into each well. The plates were incubated at 37 °C overnight. The diameter of the inhibition zone was measured to the nearest millimeter. Each test was carried out in triplicate and the average was calculated for inhibition zone diameters. A blank containing only methanol showed no inhibition in a preliminary test. The macro-dilution broth susceptibility assay was used for the evaluation of minimal inhibitory concentration (MIC). Twelve test tubes was used for the macro-dilution method. By including 1 mL Muller–Hinton broth in each test and then adding 1 mL extract with concentration 100 mg/mL in the first tube, we made serial dilutions of this extract from first tube to last tube. Bacterial suspensions were prepared to match the turbidity of 0.5 Mcfarland turbidity standards. Matching this turbidity provides a bacterial inoculum concentration of $1.5*10^8$ cfu/mL. Then 1 mL of bacterial suspension was added to each test tube. After incubation at 37 °C for 24 h, the last tube in the series without turbidity was determined as the minimal inhibitory concentration (MIC) (Table 1).

Table 1 In vitro antibacterial studies of the synthesized Compound.

Compound	Staphylococcus aureus	Staphylococcus Epidermidis	Streptococcus B	Escherichia coli	Shigella
Na[AlCl3F]	-	-	7mm	-	5mm
Na[AlCl3I]	-	3mm	-	6mm	4mm

A. **Synthesis of Sodium Tri chloro fluoro aluminate (III), Na [$AlCl_3F$]**

Sodium Trichlorofluoroaluminate(III), Na [$AlCl_3F$] was prepared by dissolving $AlCl_3$ (0.38g, 2.85 mmol) in acetonitrile and adding this solution to a solution of NaF (0.12 g, 2.86 mmol) in acetonitrile under stirring at room temperature until a white precipitate was formed. After 3 hours stirring, the mixture was filtered, washed with ether and hexane. Precipitate amount was 0.4gr. MP: 280˚C *.m/e* (%): 175(M^+), 157, 152, 149, 140, 133, 129, 125, 121, 117, 113, 105, 98, 94, 90, 85, 81, 77, 69, 63, 59, 55, 50, 46, 42; IR (KBr): 1172, 874, 604, 415 cm^{-1} (Fig 1,2).

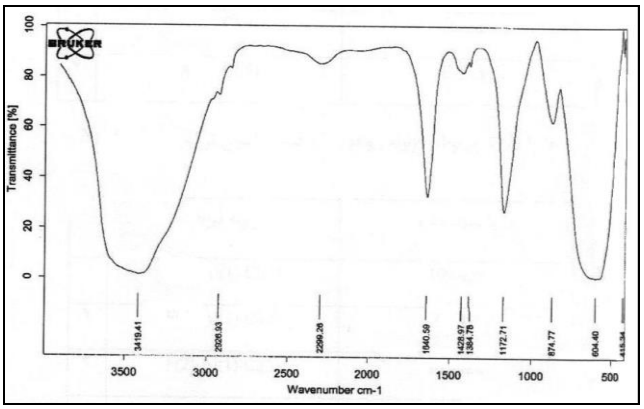

Fig 1 The FT-IR spectrum of Na+[AlCl3F]- (KBr Disk)

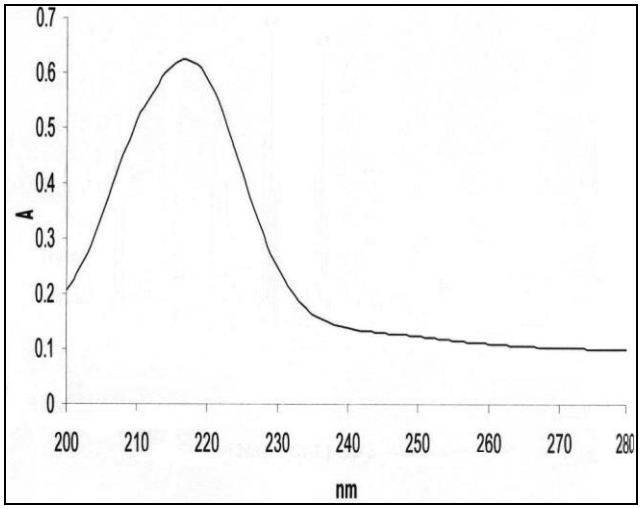

Fig 2 The UV/Vis spectrum of Na+[AlCl3F]-

B. **Synthesis of Sodium Trichloroiodatoaluminate (III), Na [$AlCl_3I$]**

Sodium Trichloroiodatoaluminate(III), Na [$AlCl_3I$] was prepared by dissolving $AlCl_3$ (0.24g, 1.8 mmol) in acetonitrile and adding this solution to a solution of NaI (0.264 g, 1.8 mmol) in acetonitrile under stirring at room

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temperature until a brown precipitate was formed. After 3 hours stirring, the mixture was filtered, washed with ether and hexane. Precipitate amount was 0.4gr. *MP:* 280˚C. *m/e* (%): 284(M^+), 260, 257, 248, 234, 225, 221, 212, 198, 189, 185, 177, 162, 156, 154, 150, 133, 121, 98, 94, 85, 63, 59, 50; IR (KBr): 1145, 715, 422 cm^{-1}(Figure3, 4) and (Table 2)

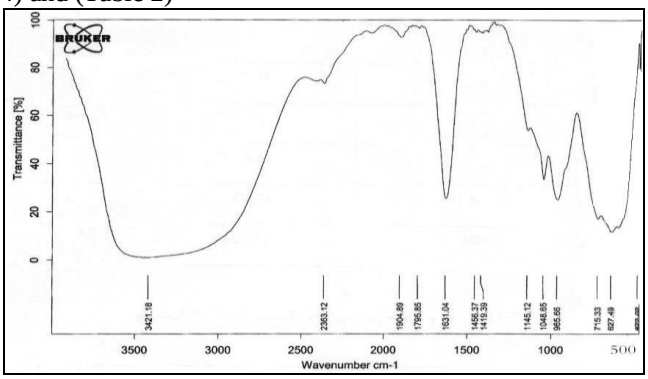

Fig 3 The FT-IR spectrum of Na+[AlCl3I]- (KBr Disk)

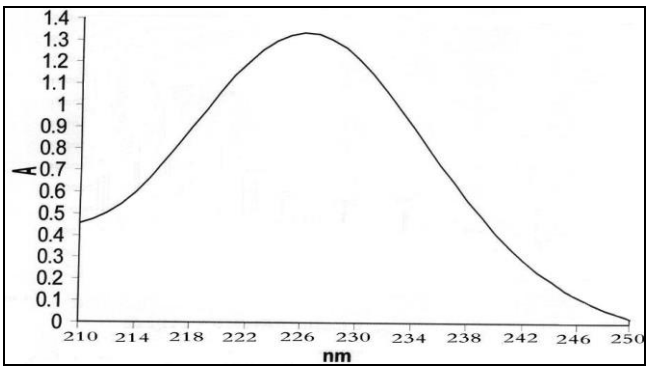

Fig 4 The UV/Vis spectrum of Na+[AlCl3I]-

Table 2 The IR Spectra Data Compounds of Na [AlCl3 F] and Na [AlCl3 I]

$[AlCl_3\ F]^-$			$[AlCl_3\ I]^-$		
Vibration	$(Cm^{-1})_v$	Intensity	Vibration	$(Cm^{-1})_v$	Intensity
Al-F	874	(S)	Al-I	422	(S)
Al-Cl	415	(S)	Al-Cl	715	(S)
Al-Cl	604	(S)	Al-Cl	1145	(S)
Al-Cl	1172	(S)			

III. Computational Methods

All computational are carried out using Gaussian 98 program [11-12] which combines the exact Hartree-Fock exchange with Becke's and uses the Lee-Yang-Parr correlation function in order to include the most important correlation effects. The structures of the molecules were completely optimized without any symmetry in all the levels. The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima [13]. Infrared intensities (int) in Kilometer per mole of all compounds were performed at the same level on the respective fully optimized geometries. These compounds and their data are in accordance with recent works on the formation of four coordinate intermediates.

IV. Results

$[AlCl_3X]^-$ can be prepared by the reaction of NaX and $AlCl_3$ derivative in purified acetonitrile. The complexes were found to be little soluble in DMSO and display good stability in air at room temperature. The structures of the ligands were confirmed by IR, UV, and Mass data. The spectroscopic data of the $Na[AlCl_3X]$ complex and its complex show tri bands at 874,422 cm^{-1} and these can be attributed to X(F,I respectively). The comparison of experimental and accounting IR spectra's shown wich these two spectra have convergence relatively well together (Table3).

Table 3 The comparison of experimental IR spectra results with accounting IR spectra

IR	**Accounting**	**Experimental**	**Vibration species**
SCFA	476	415	Al-Cl
	733	874	Al-F
SCIA	471	422	Al-I

The electronic spectra of the complexes were measured in acetonitrile solution. In general, the electronic transitions for Aluminate (III) systems are spin forbidden and hence weak, and are often masked by charge transfer bands. $AlCl_3X$ was the most impotent antibacterial agent, indicating that the iodine plays an important role in the antibacterial activity. The two Aluminate (III) complexes that were tested have moderate activity (inhibitory zones (15 mm) against all four gram-positive bacteria, except Na $[AlCl_3X]$ that has weak activity toward S. aureus. Also indicate that the all two complexes are moderately active against the two gram-negative bacteria (inhibitory zones (15 mm), except for $AlCl_3X$ which shows weak activity toward pneumoniae.

V. Discussion

Sodium Trichlorofluoroaluminate(III), $Na^+[AlCl3\ F]$:-

$Na^+[AlCl_3\ F]^-$ was prepared by the reaction of $AlCl_3$ and NaF in acetonitrile solvent as follows:

$NaF + AlCl_3 \rightarrow Na\ [AlCl_3\ F]$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{Al\text{-}F}$ that was

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found at 874 cm^{-1} and confirmed with literature data. In the Mass spectra Na [$AlCl_3$ F] complex peak related to m/e=175 has been observed.

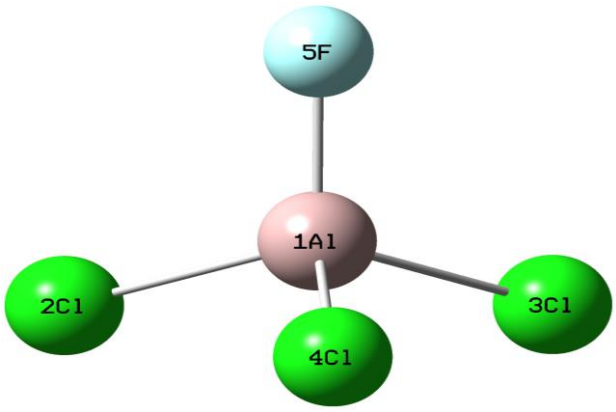

Fig 5 Optimized molecular structures of Na+[AlCl3F]- complex

From the optimized structure of the title compounds, molecular parameters can be extracted. Molecular parameters can depict a useful representation of molecular structure. Therefore, we extracted important bond lengths and bond angles of computed complex and listed them in (Table 4).

Table 4 Bond lengths [Å] and Bond angles [°] for composition Na+[AlCl3 F]-

No	Bond lengths	[Å]
1	Al(1)-F(2)	1.735
2	Al(1)-Cl(3)	2.253
3	Al(1)-Cl(4)	2.253
4	Al(1)-Cl(5)	2.253
No	Bond angles	[°]
1	F(2) Al(1)-Cl(3)	109.429
2	F(2) Al(1)-Cl(4)	109.422
3	F(2) Al(1)-Cl(5)	109.428
4	Cl(3) Al(1)-Cl(4)	109.52
5	Cl(3) Al(1)-Cl(5)	109.505
6	Cl(4) Al(1)-Cl(5)	109.524

Sodium Trichloroiodatoaluminate(III), $Na^+[AlCl3\ I]^-$:
$Na^+[AlCl3\ I]^-$ was prepared by the reaction of AlCl3 and NaI in acetonitrile solvent as follows:

$NaI + AlCl_3 \rightarrow Na\ [AlCl_3\ I]$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{Al\text{-}I}$ that was found at 422 cm^{-1} and confirmed with literature data. In the Mass spectra Na [$AlCl_3$ I] complex peak related to m/e=284 has been observed.

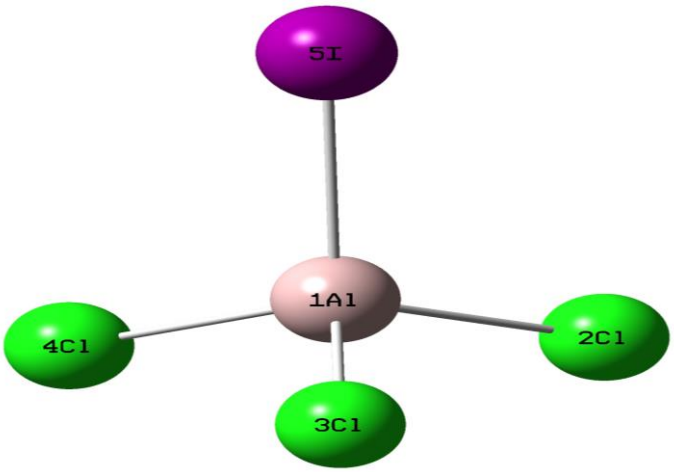

Fig 6 Optimized molecular structures of Na+[AlCl3I]- complex

From the optimized structure of the title compounds, molecular parameters can be extracted. Molecular parameters can depict a useful representation of molecular structure. Therefore, we extracted important bond lengths and bond angles of computed complex and listed them in (Table 5).

Table 5 Bond lengths [Å] and Bond angles [°] for composition Na+[AlCl3 I]-

No	Bond lengths	[Å]
1	Al(1)-I(2)	2.648
2	Al(1)-Cl(3)	2.255
3	Al(1)-Cl(4)	2.255
4	Al(1)-Cl(5)	2.255
No	Bond angles	[°]
1	I(2) Al(1)-Cl(3)	109.449
2	I(2) Al(1)-Cl(4)	109.43
3	I(2) Al(1)-Cl(5)	109.441
4	Cl(3) Al(1)-Cl(4)	109.501
5	Cl(3) Al(1)-Cl(5)	109.505
6	Cl(4) Al(1)-Cl(5)	109.501

VI. CONCLUSION

Na [$AlCl_3F$] was prepared by the reaction of NaF and $AlCl_3$ in acetonitrile solvent and Na [$AlCl_3I$] was prepared by the reaction of NaI and $AlCl_3$ in acetonitrile solvent. Electronic and vibrational and Mass spectra of these two Aluminate-

complexes were studied. These compounds were characterized by IR, and UV/Visible and Mass techniques. The electronic spectra indicate pyramid geometry for the complexes.

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