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The new study compound structural of tree new aluminate complexes [$AlCl_3X$] (X= NO_3, CH_3COO, N_3) and study of antimicrobial activities

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ABSTRACT

The synthesis and characterization is reported of Tri aluminate (III) complexes of general formula Na[$AlCl_3$ X], derived from monoanionic Ligands CL_3X (X = No_3, CH_3COO, N_3). Sodium Trichloronitratoaluminate, SCNA, Sodium Trichloroacetatoaluminate, SCAA, Sodium Trichloroazidoaluminate, SCAZA produced tri ionic aluminate complexes. They easily synthesized in a nearly quantitative yield using by direct reaction of $AlCl_3$ with relative ligands. These compounds were characterized by IR, UV/Visible and Mass techniques. Concerning the molecular structure of the compound, the AL(III) cation ($2S^2$,$2P6^6$) with four sp^3 hybrided orbitals can form stable hero complex with two kind coordinating atoms, 3Cl , X atoms can be coordinated to the (AL) ion. The AL and Cl ,X atoms and the title ligand are disordered. Suggestion structural distortions away from the idealized C_3V geometry. The antibacterial activities of synthesized compounds were studied against the four Gram-positive bacteria: Streptococcus pyogenes, Streptococcus agalactiae, Staphylococcus aureus, Bacillus anthracis, also against the two Gram negative bacteria: Klebsiella pneumoniae and Pseudomonas aeruginosa.

Keywords: Synthesis, Characterization, SCNA, SCAA, SCAZA, Antibacterial, Activities.

INTRODUCTION

Bioinorganic model chemistry has made extensive use of monoanionic ligands to mimic the active sites in metalloproteins and metalloenzymes [1,2]. The design, synthesis, and characterization of Aluminate complexes with ligands has prepared useful synthetic models for the Aluminate-containing enzymes [3–5]. In this investigation, we report on the synthesis, spectroscopic characterization, and antimicrobial activity of Aluminate (III) complexes with TrichloroX ligands: $Na^+[AlCl_3(No_3)]^-$, $Na^+[AlCl_3(CH_3COO)]^-$, $Na^+[AlCl_3(N_3)]^-$. Although the synthesis of the TrichloroX has been reported earlier, no research has been done so far on the Aluminate complexes of these ligands. AL(III) can form stable hero complex with tetra coordinating atoms, 3Cl, X(No3, CH3COO, N3) atoms can be coordinated to the (Al) ion. Thus, the geometry of the molecule is a distorted hero with the 3Cl, X(No_3, CH_3COO, N_3) symmetry group. Ligands No_3^-, CH_3COO^-, N_3^- in the basis state to belong to point group D_3h, D_3h, $D_\infty h$ respectively. The Al(1)–Cl(3) bond distance in the $Na^+[AlCl_3(No_3)]^-$, $Na^+[AlCl_3(CH_3COO)]^-$, $Na^+[AlCl_3(N_3)]^-$, complexes respectively is 2.2367Å, 2.2485 Å, 2.2507 Å and also bond angle in the mentioned complexes respectively is Cl(3)- Al(1)-Cl(4) 112.8263, 111.145, 109.4175.

However, a recent report indicated that several ionic liquids have been applied in separation of various mixtures [6,7]. Moreover, ionic liquid properties such as heat capacities and refractive index [8], luminescence properties [9], osmotic coefficients [10], enthalpy, density, heat capacity [11], and thermo physical properties [12] have been

studies since their first synthesis. Therewith, following our previous studies about ionic liquids chemistry [13-15], we decide to improve our knowledge about these compounds by synthesis, characterisation, and theoretical study of some new Aluminium-based ionic liquids.

The antimicrobial activities of synthesized compounds were studied against the four Gram-positive bacteria: Streptococcus pyogenes, Streptococcus agalactiae, Staphylococcus aureus, and Bacillus anthracis (RITCC 1036) and also against the two Gram negative bacteria: Klebsiella pneumoniae (RITCC 1249) and Pseudomonas aeruginosa (RITCC 1547).

MATERIALS AND METHODS

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 ascertained using an electrothermal apparatus and are uncorrected. The electronic 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 an Agilent Technology (HP) model Network Mass Selective Detector 5973 spectrophotometer.

1.1. Antibacterial activity tests

The in vitro activity tests were carried out using the Growth Inhibitory zone (well method), against the four Gram-positive bacteria: Streptococcus pyogenes, Streptococcus agalactiae, Staphylococcus aureus, and Bacillus anthracis (RITCC 1036) and also against the two Gram negative bacteria: Klebsiella pneumoniae (RITCC 1249) and Pseudomonas aeruginosa (RITCC 1547). 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). 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).

1.2. Sodium Trichloronitratoaluminate(III), $Na^+[AlCl_3(No_3)]^-$

Sodium Trichloronitratoaluminate(III), $Na^+[AlCl_3(No_3)]$ was prepared by dissolving $AlCl_3$ (0.3g, 2.3 mmol) in acetonitrile and adding this solution to a solution of $NaNo_3$ (0.195 g, 2.3 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 0.46gr; reaction randeman efficiency was 92%. Synthesized composition doesn't melt until 280°C temperature.

IR (KBr): 1384, 1283, 1049, 835, 638, 566 cm^{-1}.

1.3. Sodium Trichloroacetatoaluminate (III), $Na^+[AlCl_3(CH_3COO)]^-$

Sodium Trichloroacetatoaluminate (III), $Na^+[AlCl_3(CH_3COO)]^-$ was prepared by dissolving $AlCl_3$ (0.25g, 1.88 mmol) in acetonitrile and adding this solution to a solution of $NaCH_3COO$ (0.25 g, 1.84 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 0.44gr; reaction randeman efficiency was 88%. Synthesized Composition doesn't melt until 280°C temperature.

IR (KBr): 1578, 1473, 1354, 1098, 1045, 702, 642, 522, 499, 420 cm^{-1}.

1.4. Sodium Trichloroazidoaluminate(III), $Na^+[AlCl_3(N_3)]^-$

Sodium Trichloroazidoaluminate (III), $Na^+[AlCl_3(N_3)]$was prepared by dissolving $AlCl_3$ (0.34g, 2.6 mmol) in acetonitrile and adding this solution to a solution of NaN_3 (0.16 g, 2.5 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 0.45 gr, reaction randeman efficiency was 90%. Synthesized composition doesn't melt until 280°C temperature.

IR (KBr): 2041, 1465, 639, 529, 471 cm^{-1}.

RESULTS AND DISCUSSION

$[AlCl_3X]^-$ can be prepared by the reaction of NaX and $AlCl_3$ derivative in purified acetonitrile. The complexes were found to be unsoluble in toluene 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 $Na[AlCl_3 X]$ complex and its complex show tri bands at (566,1283),702,529 cm^{-1} and these can be attributed to X(No_3 ,CH_3COO, N_3 respectively). The comparison of experimental and accounting IR spectra's shown wich these two spectra have convergence relatively well together.(Table1-3) 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. From the spectra of these Aluminate (III) complexes, it can be seen that all of them exhibit one permissible transition at $A_1 \rightarrow A_1^*$ which in the visible light is seen. This transition was from kind, transfer band (CT) and isn't seen d→d transition. $AlCl_3X$ was the most impotent antibacterial agent, indicating that the iodine plays an important role in the antibacterial activity. The tri 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 tri complexes are moderately active against the two gram-negative bacteria (inhibitory zones (15 mm), except for $AlCl_3X$ which shows weak activity toward pneumoniae.

2.1. Sodium Trichloronitratoaluminate(III), $Na^+[AlCl_3(No_3)]^-$

$Na^+[AlCl_3(No_3)]^-$ was prepared by the reaction of $AlCl_3$ and $NaNo_3$ in acetonitrile solvent as follows:

$Na\ No_3 + AlCl_3 \rightarrow Na\ [AlCl_3(No_3)]$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{Al\text{-}O\text{-}N}$ that was found at 566, 1283 cm^{-1} and confirmed with literature data. In the Mass spectra Na $[AlCl_3$ (No3)] complex peak related to m/e=218 has been observed.

FIGURE 1. Optimized molecular structures of $Na^+[AlCl_3(No_3)]^-$ 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-a, 4-b).

2.2. Sodium Trichloroacetatoaluminate (III), $Na^+[AlCl_3(CH_3COO)]^-$

$Na^+[AlCl_3(CH_3COO)]^-$ was prepared by the reaction of $AlCl_3$ and $NaCH_3COO$ in acetonitrile solvent as follows:

$NaCH_3COO + AlCl_3 \rightarrow Na\ [AlCl_3(CH_3COO)]$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{Al\text{-}O}$ that was found at 702cm^{-1} and confirmed with literature data. In the Mass spectra Na $[AlCl_3(CH_3COO)]$ complex peak related to m/e=215.5 has been observed.

FIGURE 2. Optimized molecular structures of $Na^+[AlCl_3(CH_3COO)]^-$ 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-a, 5-b).

2.3. Sodium Trichloroazidoaluminate(III), $Na^+[AlCl_3(N_3)]^-$

$Na^+[AlCl_3(N_3)]^-$ was prepared by the reaction of $AlCl_3$ and NaN_3 in acetonitrile solvent as follows:

$NaN_3 + AlCl_3 \rightarrow Na\ [AlCl_3(N_3)]$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{Al\text{-}N}$ that was found at 529cm^{-1} and confirmed with literature data. In the Mass spectra Na $[AlCl_3(N_3)]$ complex peak related to m/e=198 has been observed.

FIGURE3. Optimized molecular structures of Na $[AlCl_3(N_3)]$ 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 6-a, 6-b).

Table1. the comparison of experimental IR spectra results with accounting IR spectra results for composition SCNA

Accounting	Experimental	Vibration species
566	473	Al-O
493	638	Al-Cl

Table 2. the comparison of experimental IR spectra results with accounting IR spectra results for composition SCAA

Accounting	Experimental	Vibration species
466	420	Al-Cl
481	499	Al-Cl
617	702	Al-O

Table 3. the comparison of experimental IR spectra results with accounting IR spectra results for composition SCAZA

Accounting	Experimental	Vibration species
546	529	Al-N

Table 1-a. Bond lengths [Å] for composition $Na^+[AlCl_3(No_3)]^-$

	Bond lengths	[Å]
1	Al(1)-Cl(2)	2.2399
2	Al(1)-Cl(3)	2.2367
3	Al(1)-Cl(4)	2.237
4	Al(1)-O(5)	1.8615
5	Al(1)-O(8)	3.0116
6	O(5)-N(6)	1.3819
7	N(6)-O(7)	1.2483
8	N(6)-O(8)	1.2612

Table 1-b. Bond angles [°] for composition $Na^+[AlCl_3(No_3)]^-$

	Bond angles	[°]
1	Cl(2) Al(1)-Cl(3)	110.0965
2	Cl(2) Al(1)-Cl(4)	110.0522
3	Cl(2) Al(1)-O(5)	100.7906
4	Cl(3) Al(1)-Cl(4)	112.8263
5	Cl(3) Al(1)-O(5)	111.2329
6	Cl(3) Al(1)-O(8)	85.5864
7	Cl(4) Al(1)-O(5)	111.2019
8	Al(1)-O(5)-N(6)	122.9855
9	O(5)-N(6)-O(7)	116.2822
10	O(5)-N(6)-O(8)	117. 5541
11	O(7)-N(6)-O(8)	126.1637
12	Al(1)-O(8)-N(6)	70.9102

Table 2-a. Bond lengths [Å] for composition $Na^+[AlCl_3(CH_3COO)]^-$

	Bond lengths	[Å]
1	Al(1)-Cl(2)	2.2531
2	Al(1)-Cl(3)	2.2485
3	Al(1)-Cl(4)	2.2485
4	Al(1)-O(5)	1.7941
5	O(5)-C(6)	1.3442
6	C(6)-C(7)	1.5146
7	C(6)-O(8)	1.241
8	C(7)-H(9)	1.0913
9	C(7)-H(10)	1.0952
10	C(7)-H(11)	1.0952

Table 2-b. Bond angles [°] for composition $Na^+[AlCl_3(CH_3COO)]^-$

	Bond angles	[°]
1	Cl(2) Al(1)-Cl(3)	108.8671
2	Cl(2) Al(1)-Cl(4)	108.868
3	Cl(2) Al(1)-O(5)	104.6356
4	Cl(3) Al(1)-Cl(4)	111. 145
5	Cl(3) Al(1)-O(5)	111. 5321
6	Cl(4) Al(1)-O(5)	111.5279
7	Al(1)-O(5)-C(6)	137.5027
8	O(5)-C(6)-C(7)	112.4235
9	O(5)-C(6)-O(8)	124.4139
10	C(7)-C(6)-O(8)	123.1626
11	C(6)-C(7)-H(9)	110.0802
12	C(6)-C(7)-H(10)	109.6941
13	C(6)-C(7)-H(11)	109.6928
14	H(9) -C(7)-H(10)	110.0624
15	H(9) -C(7)-H(11)	110.059
16	H(10) -C(7)-H(11)	107.2057

Table 3-a. Bond lengths [Å] for composition $Na^+[AlCl_3(N_3)]^-$

	Bond lengths	[Å]
1	Al(1)-Cl(2)	2.2511
2	Al(1)-Cl(3)	2.2507
3	Al(1)-Cl(4)	2.251
4	Al(1)-N(5)	1.8087
5	N(5)-N(6)	1.2021
6	N(6)-N(7)	1.1709

Table 3-b. Bond angles [°] for composition $Na^+[AlCl_3(N_3)]^-$

	Bond angles	[°]
1	Cl(2) Al(1)-Cl(3)	109.4173
2	Cl(2) Al(1)-Cl(4)	109.4134
3	Cl(2) Al(1)-N(5)	109.5476
4	Cl(3) Al(1)-Cl(4)	109.4175
5	Cl(3) Al(1)-N(5)	109.4902
6	Cl(4) Al(1)-N(5)	109.5412
7	Al(1)-N(5)-N(6)	179.2262

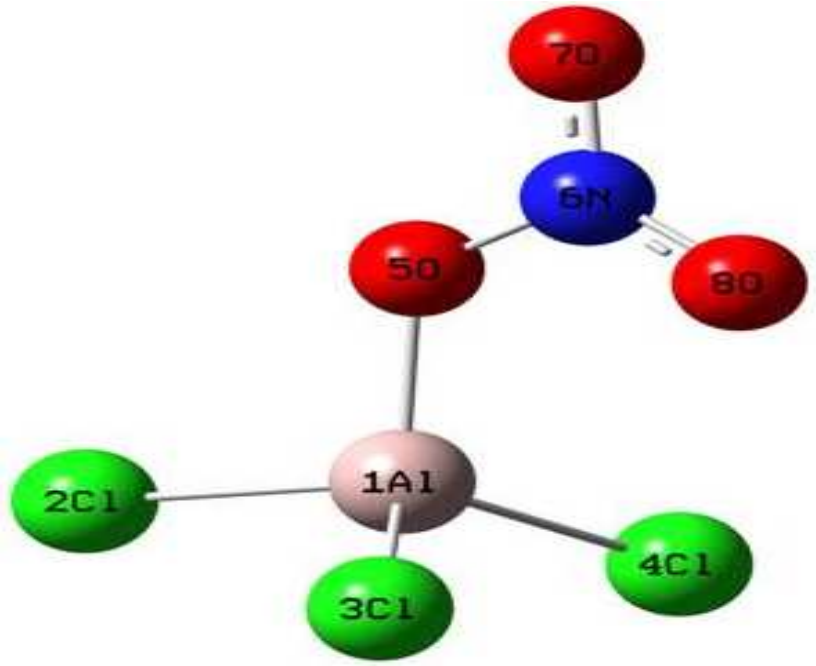

FIGURE 1. Optimized molecular structures of $Na^{+}[AlCl_3(No_3)]^{-}$ complex

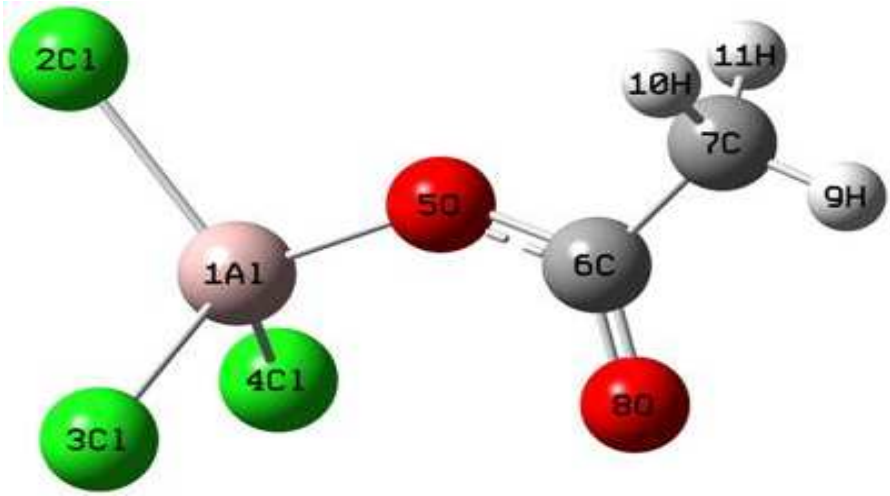

FIGURE 2. Optimized molecular structures of $Na^{+}[AlCl_3(CH_3COO)]^{-}$ complex

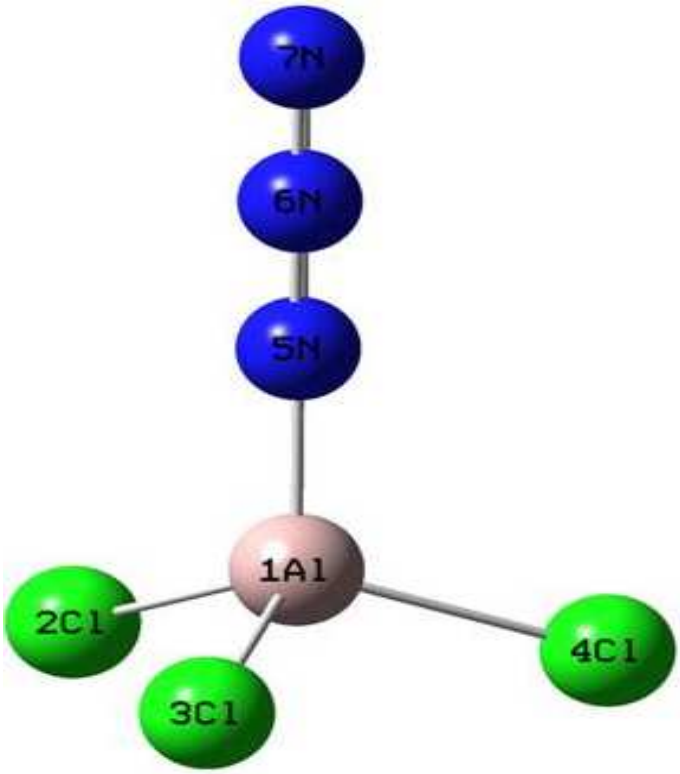

FIGURE3. Optimized molecular structures of Na [$AlCl_3(N_3)$] complex

CONCLUSION

Na [$AlCl_3$(No_3)] was provided by the reaction of $NaNo_3$ and $AlCl_3$ in acetonitrile solvent and Na [$AlCl_3(CH_3COO)$] was prepared by the reaction of Na CH_3COO and $AlCl_3$ in acetonitrile solvent, Na [$AlCl_3$(N_3)] was prepared by the reaction of NaN_3 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. Ligands No_3^-, CH_3COO^-, N_3^- in the basis state to belong to point group D_3h, D_3h, $D_\infty h$ respectively. The electronic spectra indicate hero geometry for the complexes.

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