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Density functional theory studies of structural properties, energies and natural band orbital for two new aluminate compounds

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ABSTRACT

Two new aluminate compounds was prepared by the reaction of $AlCl_3$ with KX (X = SCN^-, CN^-) in a 1:1 mole ratio. In these salts the aluminum atom is surrounded by three chlorine atoms and a ligand (X = SCN^-, CN^-). In $AlCl_3SCN$ anion, the SCN coordinates to the Al through sulfur and $AlCl_3CN$ anion the CN^- coordinates to the Al center through carbon. The molecular geometry, vibrational frequencies, energies and natural bond orbital (NBO) in the ground state are calculated by using the DFT (B3LYP) methods with 6-311G* basis sets. The geometries and normal modes of vibrations obtained from B3LYP calculations are in good agreement with the experimentally observed data.

1. Introduction

In the present work we explore complexes formation between a Lewis acid and the anion which should delocalize the negative charge of the anion and thereby decrease the Coulombic attractions between cations and anions. These salt/Lewis acid adducts usually result in either ionic liquids or crystalline materials with low melting points. Salts containing large organic cations, such as butylpyridinium chloride or 1,3-dialkylimidazolium chloride, interact with $AlCl_3$ to form ionically conducting liquids at room temperature [1–4]. Solid $AlCl_3$ has a melting temperature at 193 °C. Upon melting, $AlCl_3$ consists primarily of discrete Al_2Cl_6 dimers, and appears as a molecular liquid with high vapor pressure. It is well known [5] that the melting point of $AlCl_3$ can be lowered upon mixing with MCl (M denotes an alkali metal), which is believed to originate from the Lewis acid–base interactions of $AlCl_3$ with MCl and the formation of large-sized complex anions, such as $AlCl_4^-$, $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$. From the binary phase diagram, it is found that a low-lying eutectic occurs in the 2:1 composition of $AlCl_3$–MCl. Melting temperature of the eutectic is well below that of the $AlCl_3$, representing the minimum liquidus temperature throughout the entire system. SCN^- resembles halides in their chemical and physical properties, and is known as pseudohalides. It has been reported [5] that the phase behavior of the $AlCl_3$–MSCN system is very similar to that of $AlCl_3$–MCl because of the Lewis acid–base interactions between $AlCl_3$ and SCN^- and the formation of $AlCl_3$–KSCN complex anions. Compared with the $AlCl_3$–MCl system, however, the $AlCl_3$–MSCN system exhibits the lower liquidus temperature and is easier to form glasses over an extended composition range [6].

In this letter, we report the synthesis, spectroscopic characterization, density functional theory calculations of two compounds by using B3LYP method with the 6-311G* basis set. The molecular geometry and vibrational frequencies, energies, molecular orbitals and NBO in the ground state are calculated by using the B3LYP at 6-311G* method.

2. Experimental

2.1. Materials and instruments

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. 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.

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2.2. Synthesis of $KSCN/AlCl_3$ **(1)**

Compound **(1)** was prepared by dissolving $AlCl_3$ (0.29 g, 2.17 mmol) in acetonitrile and adding this solution to a solution of KSCN (0.21 g, 2.16 mmol) in acetonitrile under stirring at room temperature until a light brown precipitate was formed. After 3 h stirring, the mixture was filtered, washed with ether and hexane. Yield 0.43gr, 92%; MS, *m/z* (%) = 230 (M^+), 192, 183, 177, 171, 152, 133, 121, 101, 97, 81; IR (KBr) cm^{-1}: 2108 ν(C≡N), 655 ν(C–S), 613 ν(Al–Cl), 429 ν(Al–Cl); m/e = 230.

2.3. Synthesis of $KCN/AlCl_3$ **(2)**

Compound **(2)** was prepared by dissolving $AlCl_3$ (0.34 g, 2.54 mmol) in acetonitrile and adding this solution to a solution of KCN (0.16 g, 2.46 mmol) in acetonitrile under stirring at room temperature until a light blue precipitate was formed. After 3 h stirring, the mixture was filtered, washed with ether and hexane. Yield 0.41 gr, 82%; MS, *m/z* (%) = 332 (M^+), 198, 185, 173, 157, 112, 97, 89, 53; IR (KBr) cm^{-1}: 2121 ν(C≡N), 631 ν(Al–C), 554 ν(Al–Cl); m/e = 198.

2.4. Computational method

All computations are carried out using Gaussian98 program [7]. The isomers and their vibrational frequencies were calculated at the DFT/B3LYP level of theory using the standard 6-311G* basis set. Intrinsic reaction coordinate calculations are carried out at the same levels.

3. Results and discussion

The optimized geometries, including 6 isomers found in [$AlCl_3$, S, C, N] system and involving 2 isomers in [$AlCl_3$, C, N] system at B3LYP/6-311G* of theory are shown in Fig. 1 Among these 6 isomers found in [$AlCl_3$, S, C, N] system, only $AlCl_3NCS$ and $AlCl_3SCN$ were observed and characterized experimentally [4]. Their associated energies are included in Table 1. The $AlCl_3CN$ anion is stable than $AlCl_3NC$ by 0.00826 a.u. and also the $AlCl_3SCN$ is stabilized by

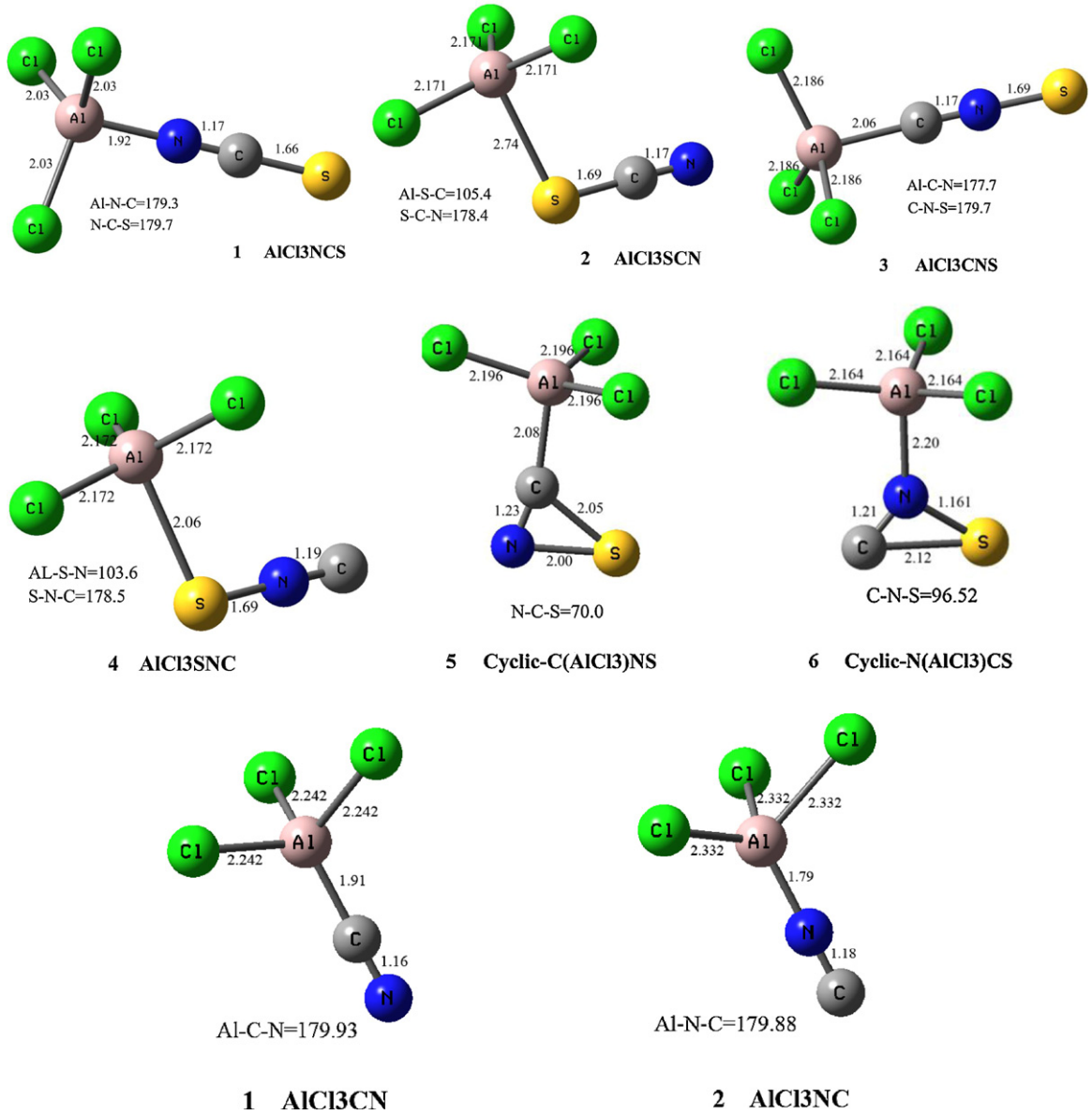

Fig. 1. Optimized structures of isomers [$AlCl_3$, S, C, N] system and [$AlCl_3$, C, N] system at the B3LYP/6-311G*.