



Inorganic anions dependent orientation of ammonium cations in crown ether–ammonium cation–inorganic anion system



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ARTICLE INFO

Article history:

Received 20 September 2013

Accepted 26 November 2013

Available online 2 December 2013

Keywords:

Rotator–stator assembly

Crown ether

Inorganic anions

Orientation

ABSTRACT

Five supramolecular assembly complexes: 2-hydroxypropane-1,3-diammonium-perchlorate-18-crown-6 ($[(C_3H_{12}N_2O-(18\text{-crown-6})_2]^{2+} \cdot 2[ClO_4]^-$, **1**); 2-hydroxypropane-1,3-diammonium-tetrafluoroborate-18-crown-6 ($[(C_3H_{12}N_2O)_2-(18\text{-crown-6})_2]^{2+} \cdot 2[BF_4]^-$, **2**); 4-methylanilinium perchlorate-18-crown-6 ($[C_7H_{10}N-(18\text{-crown-6})]^+ \cdot [ClO_4]^-$, **3**); 4-iodineanilinium-tetrafluoroborate-18-crown-6 ($[C_6H_7NI-(18\text{-crown-6})]^+ \cdot [BF_4]^-$, **4**); 4-methylanilinium tetrafluoroborate-18-crown-6 ($[C_7H_{10}N-(18\text{-crown-6})]^+ \cdot [BF_4]^-$, **5**), for the investigation of the influence of different inorganic anions on the orientation of ammonium cation and host–guest interaction of crown ethers, have been synthesized and characterized. The results revealed that ClO_4^- anion lead to the 2:1 composition of crown and ammonium cation in monoclinic space group and 3:2 composition of crown and ammonium cation in the presence of BF_4^- anion for double-anilinium system (complexes **1** and **2**). While for the single-anilinium system (complexes **3**, **4**, and **5**), the different inorganic anions lead to quite different orientation of the ammoniums in orthorhombic space group. We also studied the TGA/DSC properties, Raman spectroscopy and hot stage microscopy for the five complexes.

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1. Introduction

Anions, which play a vital role in the construction of molecules and affect the resulting properties, are ubiquitous substances both in man-made and natural systems [1–3]. For example, they are vital in many biological systems for the maintenance of life and in the field of environment as anionic pollutants. Consequently, synthetic receptors that bind anions are increasingly being pursued for applications in waste remediation, sensing, treatment of disease, and obtain of attractive properties [4–6].

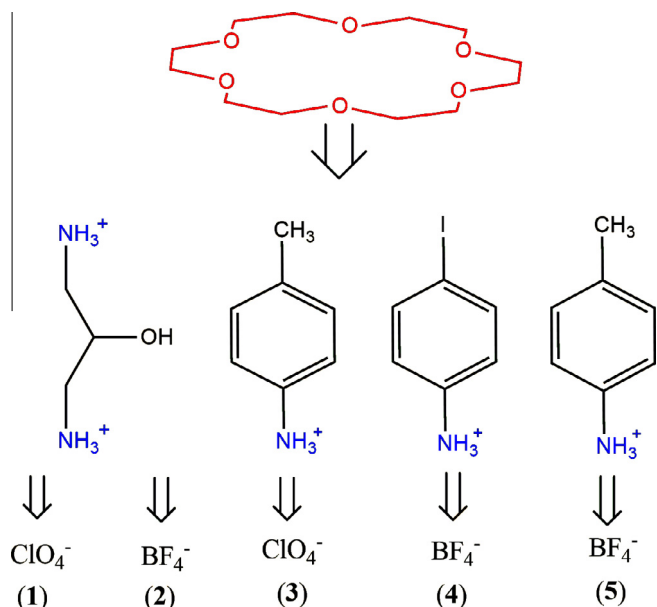
As one of the well-known symbols in supramolecular chemistry, crown ethers been the subject of various studies and have occupied a special position not only because of their extensive utilization for constructing the complex superstructures in supramolecular chemistry and crystal engineering, but also for their abilities to form stable complexes with alkali and transition-metal ions and hydrogenate cations via hydrogen bonds due to their the modest flexibilities [5a,7–12]. Especially, crown ethers act as ideal candidate for the formation of molecular stator for the design of phase change materials and ferroelectric molecular materials [13,14]. To date, numerous derivatives and complexes based on crown ethers have been synthesized and characterized [10, 15–17]. For example, Luo [18] and his co-workers utilized

dichloroacetate as the pendulum-like motions combined with the 18-crown-6 molecular rotor, which formed a novel supra-molecular potassium hydrogen bis (dichloroacetate)-18-crown-6 displays a reversible phase transition. Xiong [19] and his co-workers have introduced 4-methoxyanilinium into the cavity of 18-crown-6 and obtained a novel supra-molecular bola-like second-order ferroelectric phase-transition material. In the field of molecular machine design, the crown ethers often act as good molecular stators which can easily anchored the protonated $R-NH_3^+$ cation (R = aryl ring) into the cavity of 18-crown-6, and the utilization of the R group as a molecular rotor or pendulum unit to create desirable properties also have been investigated [19]. However, investigation of different inorganic anions on the supramolecular structures of crown ether–ammonium cation–inorganic anion system still remains unexplored.

Hence in this work, we studied detailed the influences of two different inorganic anions (BF_4^- , ClO_4^-) on the five members of crown ether–ammonium cation–inorganic anion system (Scheme 1): 2-hydroxypropane-1,3-diammonium-perchlorate-18-crown-6 ($[C_3H_{12}N_2O-(18\text{-crown-6})_2]^{2+} \cdot 2[ClO_4]^-$, **1**); 2-hydroxypropane-1,3-diammonium-tetrafluoroborate-18-crown-6 ($[(C_3H_{12}N_2O)_2-(18\text{-crown-6})_2]^{2+} \cdot 2[BF_4]^-$, **2**); 4-methylanilinium perchlorate-18-crown-6 ($[C_7H_{10}N-(18\text{-crown-6})]^+ \cdot [ClO_4]^-$, **3**); 4-iodineanilinium-tetrafluoroborate-18-crown-6 ($[C_6H_7NI-(18\text{-crown-6})]^+ \cdot [BF_4]^-$, **4**); 4-methylanilinium tetrafluoroborate-18-crown-6 ($[C_7H_{10}N-(18\text{-crown-6})]^+ \cdot [BF_4]^-$, **5**). We found that the

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Scheme 1. Molecular Structure of the five crown ether–ammonium cation–inorganic anion complexes.

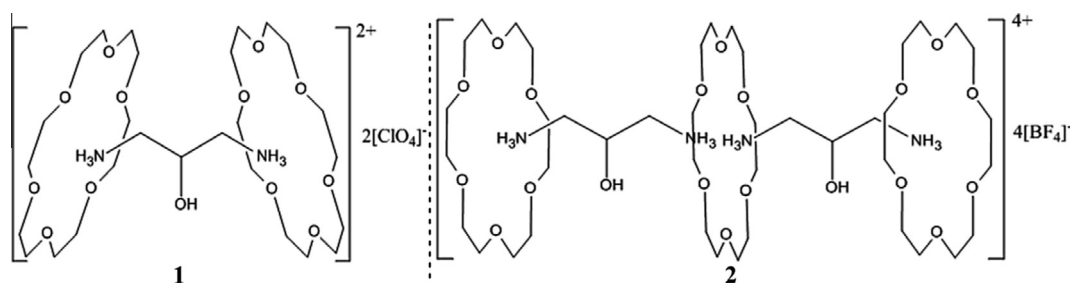
different inorganic anions lead to different orientation of the anilinium rotors, which result quite another supramolecular structures. These results are of importance not only for the evaluation of the specific case of the crown ether–ammonium cation–inorganic anion system but also for other host–guest systems where fascinating structures and properties are possible. The influences of different inorganic anions on the dielectric properties will be investigated in the future.

2. Results and discussions

2.1. Influences of different inorganic anions on double-anilinium system

Complexes **1** (2-hydroxypropane-1,3-diammonium-perchlorate-18-crown-6) and **2** (2-hydroxypropane-1,3-diammonium-tetrafluoroborate-18-crown-6) were selected in this section, the only difference between **1** and **2** belongs to the lattice inorganic anions. Crystal structural determinations reveal that **1** and **2** were all crystallizes in monoclinic space group, the basic unit of **1** is composed of one $C_3H_{12}N_2O-2(18\text{-crown-6})]^{2+}$ complex cation and two ClO_4^- anion, While the basic unit of **2** is composed of one $2(C_3H_{12}N_2O)-3(18\text{-crown-6})]^{4+}$ complex cation and four BF_4^- anion (Scheme 2 and Fig. 1). For complex **1**, the protonated 2-hydroxypropane-1,3-diammonium cation joins with two 18-crown-6 molecules to form a rotator-stator assembly $N-H\cdots O$ hydrogen-bonding interaction. For complex **2**, the change of ClO_4^- to BF_4^- anion leads to quite another formation style, the basic unit containing three 18-crown-6 molecules and two 2-hydroxypropane-1,3-diammonium cations, where the two 18-crown-6 at both ends join with one 2-hydroxypropane-1,3-diammonium cation through a rotator-stator assembly $N-H\cdots O$ hydrogen-bonding interaction, while the 18-crown-6 at middle position join with two 2-hydroxypropane-1,3-diammonium cations, and the BF_4^- anion ornament at the gap between two 18-crown-6 molecules.

The symmetry of the 18-crown-6 macrocycle in complexes **1** and **2** were shown in Fig. 2. All the macrocycle in **1** (Fig. 2, 1a and 1b) and two of the three macrocycle in **2** (Fig. 2, 2a) encountered nearly ideal crown “round” D_{3d} like conformations, where oxygen atoms of the 18-crown-6 in the structure are, as a common, displaced alternately above and below the media plane of the ring, forming two approximately parallel and nearly equilateral triangles. For **1**, O1, O3, and O5 atoms are located below the mean



Scheme 2. The basic unit of complexes **1** and **2**.

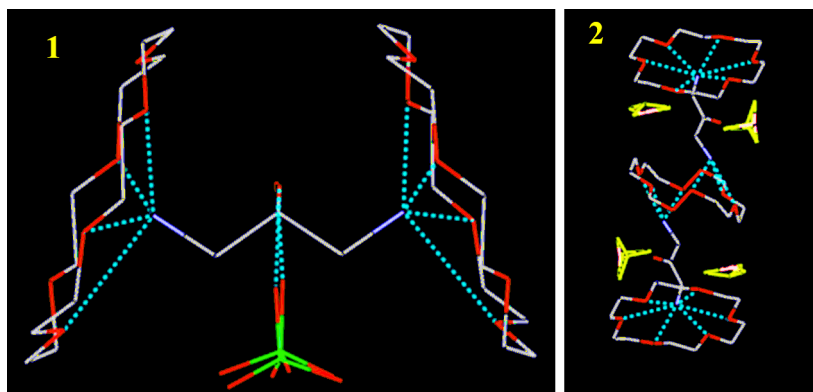


Fig. 1. The motif image of the basic unit of complexes **1** and **2**, hydrogen bonds are shown in dashed line and hydrogen atoms are omitted for clarity.

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