

丙二胺 18 冠 6 醚包合物的合成、晶体结构及介电性质

赵敏敏 戈加震* 张 毅* 熊仁根

(东南大学有序物质科学研究中心, 南京 211189)

摘要: 丙二胺盐酸盐, 18 冠 6 醚和三价的氯化铁在甲醇溶液中反应, 产生了 1 个新的超分子包合物, $[(C_3N_2H_{12}) \cdot (18\text{-Crown-6})_2][Fe_2OCl_6]$ (**1**)。双质子化的丙二胺包含 2 个 $-NH_3^+$ 取代基团, 阳离子 $-NH_3^+$ 基团和冠醚的氧原子间通过 $N-H \cdots O$ 氢键作用, 形成了 1 个三明治式的超分子结构。化合物 **1** 的介电常数分别在不同温度和频率下进行了测量, 结果表明没有出现介电异常, 也就是说, 在测量温度范围内, **1** 应该没有结构相变发生。

关键词: 超分子; 包合物; 双质子化; 三明治; 介电常数

中图分类号: O614.81+1

文献标识码: A

文章编号: 1001-4861(2011)06-1212-07

Synthesis, Crystal Structure and Dielectric Property of Clathrate Based on 18-Crown-6 with Biprotonated 1,3-Propane-diamine

ZHAO Min-Min GE Jia-Zhen* ZHANG Yi* XIONG Ren-Gen

(Ordered Matter Science Research Center, Southeast University, Nanjing 211189, China)

Abstract: The reaction of 1,3-propane-diamine hydrochloride, 18-crown-6 and trivalent ferric chloride in methanol solution yields an unusual supramolecular clathrate, 18-crown-6 and 1,3-propane-diaminium (μ_2 -oxo)-hexachloro-di-iron(III) clathrate, $[(C_3N_2H_{12}) \cdot (18\text{-Crown-6})_2][Fe_2OCl_6]$ (**1**). The biprotonated 1,3-propane-diaminium cation contains two $-NH_3^+$ ammonium cations, resulting in a sandwich-type $[(C_3N_2H_{12})^2 \cdot (18\text{-crown-6})_2]$ supramolecular structure, through $N-H \cdots O$ hydrogen bonding interactions within the crystals between the ammonium moieties of cations ($-NH_3^+$) and the oxygen atoms of the crown ethers. Dielectric constants of compound **1** were measured at different temperatures and frequencies, showing there is no distinct dielectric anomaly occurred in this case and suggesting that there may be no phase transition within the measured temperature range. CCDC: 772928.

Key words: supramolecular; clathrate; biprotonated; sandwich-type; dielectric constant

During the past decades, crown ethers have attracted much attention because of their ability to form non-covalent, H-bonding complexes with ammonium cations both in solid and in solution^[1]. Crown ethers are known to make cell membranes selectively permeable to alkali cations, which are similar to biologically important transport agents, such as the macrocyclic antibiotics^[2-3]. In addition, crown ethers' complexation

process can accelerate salt solubility and anion reactivity in non-aqueous solvents, enabling their potential application in areas of mediated ion transport, molecular recognition^[4-10], self-assembly^[11-16], crystal engineering^[17-18], and anion-activated catalysis^[19]. It is therefore vital to design and synthesize novel crown ether clathrates and to explore their various properties.

Diverse weak intermolecular interactions such as

收稿日期: 2010-05-12。收修改稿日期: 2011-03-21。

国家自然科学基金资助项目(No.20871028)。

*通讯联系人。E-mail: zmmzyahfdzg@126.com

hydrogen-bonding, metal-ligand coordination, charge-transfer, hydrophobic-hydrophilic, and so on, can be used to construct supramolecular structures within crystals. It may be possible to achieve novel molecular-assembly structures to get optimum structures for force and directionality of the intermolecular interaction modes by designing abortively^[20]. Host-guest binary compound is one of the fundamental supramolecules, host molecules can selectively recognize a variety of guest ions or molecules, and fix the guest species into their specific binding-sites^[20-21]. The host molecules combine with the guest species by intermolecular interaction, and if the host molecule possess some specific sites, it is easy to realize high selectivity in ion or molecular recognitions.

More recently, a variety of novel complex supramolecular structures, rather than simple host-guest complexes, including crown ether have been isolated^[22-25], in which the interplay of various types of intermolecular interactions plays important role in the complexation process.

Both the size of the crown ether and the nature of the ammonium cation (NH_4^+ , RNH_3^+ , etc.) can influence the stoichiometry and stability of these host-guest complexes^[26-27]. 18-crown-6 have the highest affinity for ammonium cation RNH_3^+ , while most studies of 18-crown-6 and its derivatives invariably show a 1:1 stoichiometry with RNH_3^+ cations in solution and in the solid state^[28], some structurally characterized complexes of crown ethers with RNH_3^+ display a different stoichiometry (2:1). These complexes have a sandwich structure with the ammonium cation placed between two nearly parallel crown rings^[22,29].

Preparation of suitable materials displaying excellent dielectric constant ε (complex dielectric constant $\varepsilon = \varepsilon_1 - i\varepsilon_2$, in which ε_1 and ε_2 are the respective real and imaginary parts of dielectric constant. Dielectric dissipation factor $D = \tan\delta = \varepsilon_2/\varepsilon_1$) has been the focus of current research activity owing to their widespread applications in resonators, filters, and other key components in microwave communication systems^[30]. However, only a limited number of materials have been developed to meet the stringent dielectric

constant requirements imposed by operating frequencies, required power levels, and types of applications. So far, the only commercially available dielectric inorganic material is the tantalate $\text{Ba}_3\text{ZnTa}_2\text{O}_9$ ^[31]. On the side, while there have been a great deal of studies on pure inorganic compounds, examples on supramolecular compounds (which would possess the preponderant properties of both inorganic and organic compounds) as dielectric materials have remained a significant challenge^[32]. Recently, our group has done a great deal of work on dielectric materials. As a continuation of our work, we focus our attention here on crown ethers chelates. The studies have involved the construction of supramolecular cation structures between crown ethers and ammonium cations through designing of cation-oxygen interactions in order to realize a new supramolecular cation structures coupled with electrically active molecular systems.

1 Experimental

1.1 Material and instrument

All commercially available chemicals are of reagent grade and were used as received without further purification. Infrared (IR) spectra were recorded on SHIMADZU IR prestige-21 FTIR-8400S spectrometer in the spectral range $4\,000\sim 400\text{ cm}^{-1}$, with the samples in the form of potassium bromide (KBr) pellets. The X-ray powder diffraction data was obtained on a Rigaku X-ray powder diffractometer D/MAX 2000/PC. The crystal structures were determined by Rigaku SCX mini diffractometer at room temperature. Dielectric studies (or capacitance measurement) and dielectric loss measurements were performed on pure title compounds powder using automatic impedance TH2828 Precision LCR Meter.

1.2 Preparation of the clathrate 1

$\text{NH}_2\text{-C}_3\text{H}_6\text{-NH}_2\cdot 2\text{HCl}$ (2 mmol, 0.294 g) and 18-crown-6 (4 mmol, 1.056 g) were dissolved in methanol solution. After addition of trivalent ferric chloride (4 mmol, 1.08 g) in concentrated hydrochloric acid medium, the precipitate was filtered and washed with a small amount of methanol. Single crystals suitable for X-ray diffraction analysis were obtained from the slow

evaporation of the mixture solution of methanol and DMF at room temperature after several days. Brown and block-like crystals were obtained in *ca.* 90% yield. For **1**: IR (cm⁻¹, KBr): 3 434 (s), 1 617 (m), 1 095 (s), 970 (m) and 867 (w). Anal. calcd. for C₂₇H₆₀Cl₆Fe₂N₂O₁₃(%): C, 34.31; H, 6.40; N, 2.96. Found(%): C, 34.48; H, 6.48; N, 3.13.

1.3 Single-crystal X-ray diffraction measurements

A single crystal of the title compounds with an approximate dimensions of 0.20 mm×0.18 mm×0.15 mm was selected for data collection at 293(2) K, using a Rigaku SCXmini CCD diffractionmeter by the ω scan technique at room temperature with graphite monochromated Mo *K* α radiation (λ =0.071 073 nm). Of the 21 081 reflections collected, there were 8 810 unique

reflections (R_{int} =0.079 9). The absorption correction was carried out by multi-scan method. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97)^[33], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97)^[34]. All the hydrogen atoms were calculated geometrically, with C-H=0.093 nm, N-H=0.089 nm, and refined as riding with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{N})$. The crystal data, details on the data collection and refinement of complexes **1** are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

CCDC: 772928.

Table 1 Crystal data and structure refinement parameters for **1**

Compound	1	<i>T</i> / K	293
Empirical formula	C ₂₇ H ₆₀ Cl ₆ Fe ₂ N ₂ O ₁₃	<i>D_c</i> / (g·cm ⁻³)	1.397
Formula weight	945.17	μ / mm ⁻¹	1.056
Crystal system	Triclinic	<i>F</i> (000)	988
Space group	<i>P</i> $\bar{1}$	θ range / (°)	3.01~26.00
<i>a</i> / nm	1.015 6(2)	Index ranges	-12 ≤ <i>h</i> ≤ 12, -14 ≤ <i>k</i> ≤ 14, -26 ≤ <i>l</i> ≤ 26
<i>b</i> / nm	1.148 4(2)	Collected reflections	21 081
<i>c</i> / nm	2.122 6(4)	Independent reflections (<i>R</i> _{int})	8 810 (0.079 9)
α / (°)	86.46(3)	Data / restraints / parameters	8 810 / 1 / 456
β / (°)	89.95(3)	<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> >2 σ (<i>I</i>))	0.073 4, 0.153 7
γ / (°)	65.43(3)	<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.154 2, 0.180 8
<i>V</i> / nm ³	2.246 4(8)	$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / (e·nm ⁻³)	484, -588
<i>Z</i>	2	GOF	1.042

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2] \}^{1/2}.$$

Table 2 Selected bond lengths (nm) and angles (°) for **1**

C(1)-O(6)	0.142 7(7)	C(1)-C(2)	0.146 9(9)	C(2)-O(1)	0.142 1(7)
C(3)-O(1)	0.141 3(7)	C(3)-C(4)	0.149 6(9)	C(4)-O(2)	0.141 7(6)
C(14)-O(8)	0.141 9(6)	C(15)-O(8)	0.141 1(7)	C(15)-C(16)	0.148 0(8)
C(16)-O(9)	0.141 8(6)	C(17)-C(18)	0.148 9(8)	C(17)-O(9)	0.141 0(6)
C(27)-N(2)	0.148 2(6)	C(26)-N(1)	0.147 9(6)	C(25)-C(27)	0.144 4(5)
C(25)-C(26)	0.146 9(6)	C(5)-O(2)	0.142 0(7)	O(13)-Fe(2)	0.173 38(10)
O(13)-Fe(2) ⁱ	0.173 38(10)	O(14)-Fe(1) ⁱⁱ	0.173 88(10)	Fe(1)-Cl(3)	0.221 74(19)
Fe(1)-Cl(2)	0.222 14(19)	Fe(1)-Cl(1)	0.222 45(19)	Fe(2)-Cl(6)	0.219 75(19)
Fe(2)-Cl(5)	0.221 0(2)	Fe(2)-Cl(4)	0.223 1(2)		
O(6)-C(1)-C(2)	109.3(5)	O(1)-C(2)-C(1)	109.9(5)	O(1)-C(3)-C(4)	109.5(5)
O(2)-C(4)-C(3)	109.8(5)	C(27)-C(25)-C(26)	114.1(4)	C(25)-C(26)-N(1)	114.3(4)
C(25)-C(27)-N(2)	115.3(4)	C(3)-O(1)-C(2)	112.1(5)	C(4)-O(2)-C(5)	111.7(5)

Continued Table 2

O(7)-C(13)-C(14)	109.8(5)	C(15)-O(8)-C(14)	113.1(5)	O(8)-C(14)-C(13)	109.0(5)
C(17)-O(9)-C(16)	113.6(4)	Fe(2)-O(13)-Fe(2)	180.00(4)	O(14)-Fe(1)-Cl(3)	109.86(7)
Fe(1)-O(14)-Fe(1)	180.00(4)	O(14)-Fe(1)-Cl(2)	111.96(6)	Cl(3)-Fe(1)-Cl(2)	105.01(7)
O(14)-Fe(1)-Cl(1)	111.35(6)	Cl(2)-Fe(1)-Cl(1)	107.25(9)	Cl(3)-Fe(1)-Cl(1)	111.21(8)
O(13)-Fe(2)-Cl(6)	109.80(7)	O(13)-Fe(2)-Cl(5)	112.53(8)	Cl(6)-Fe(2)-Cl(5)	107.50(9)
O(13)-Fe(2)-Cl(4)	112.28(7)	Cl(6)-Fe(2)-Cl(4)	108.43(9)		

Symmetry codes: ⁱ $-x+2, -y+1, -z+1$; ⁱⁱ $-x+2, -y+1, -z+2$.

1.4 Dielectric constant measurements

Dielectric studies (or capacitance measurement) and dielectric loss measurements were performed on pure title compound powder which has been pressed into pellet. The measuring AC voltage was 1 V. The pressed-powder sheet (0.602 mm thick and 5.317 mm² in area) deposited with carbon-graphite conducting glue was used for dielectric studies. The samples have been placed inside a dielectric cell whose capacitance was measured with different frequencies and temperatures. The dielectric constant and dielectric loss have been calculated using the following equations (1) and (2).

$$\varepsilon = \frac{cd}{A\varepsilon_0} \quad (1)$$

$$\varepsilon' = \varepsilon \tan \delta \quad (2)$$

Where d is the thickness, A is the area of the sample and c is capacitance. The observations are made in the frequency range 200 Hz to 1 MHz at room temperature and in the measured temperature ranges at different frequencies.

2 Results and discussion

2.1 IR analysis

The presence of strong broad bands around 3 434 cm⁻¹ in the IR spectra of **1** indicates that the stretching of the -NH₃⁺ cation moiety is presented, and the bands at about 1 095 cm⁻¹ indicate the presence of C-O-C groups.

2.2 XRD pattern of compound 1

Compound **1** was characterized by X-ray powder diffraction at room temperature. As shown in Fig.1. The pattern calculated from the single-crystal X-ray data of **1** is in good agreement with the observed one in almost identical peak position but different peak intensities.

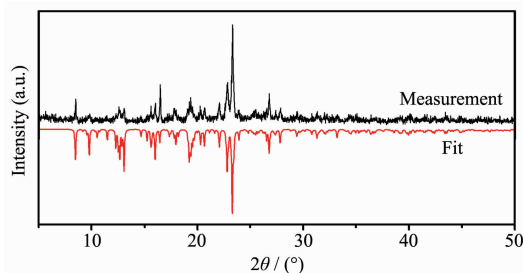


Fig.1 X-ray powder diffraction pattern (XRD) of compound **1**

2.3 Crystal structure of 1

Single crystal X-ray structural determination shows that compound **1** crystallizes in the centrosymmetric triclinic system with space group $P\bar{1}$ (No.2) and $a = 1.015\ 6(2)$ nm, $b = 1.148\ 4(2)$ nm, $c = 2.122\ 6(4)$ nm, $\alpha = 86.46(3)^\circ$, $\beta = 89.95(3)^\circ$, $\gamma = 65.43(3)^\circ$, $V = 2.246(4)$ nm³, $Z = 2$, $R_1 = 0.073\ 4$. The asymmetric unit contains one organic $[(C_3N_2H_{12}) \cdot (18\text{-Crown-6})]^{2+}$ cation and two crystallographically inequivalent half inorganic $Fe_2OCl_6^{2-}$ anions (Fig.2).

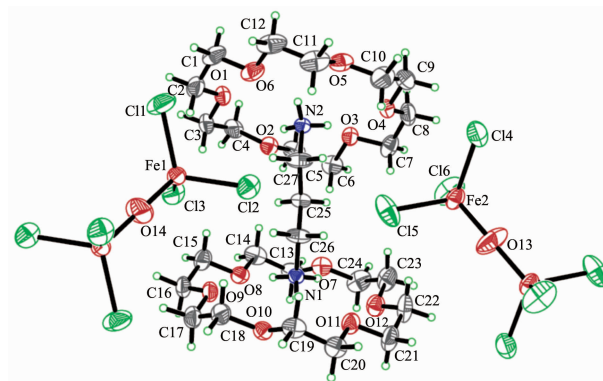
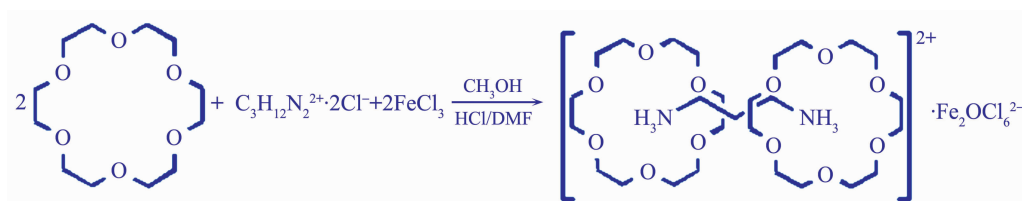


Fig.2 Molecular structure of compound **1** with ellipsoids at the 30% probability

Supramolecular rotators are assembled between biprotonated 1,3-propane-diamine (NH₃-C₃H₆-NH₃)²⁺ and 18-crown-6 by of hydrogen-bonding. The ammonium moieties of (-NH₃⁺) cations are interacted with the six

Scheme 1 Synthesis of compound **1**

oxygen atoms of crown ethers through six simple N–H \cdots O hydrogen bonding, forming 2:1 supramolecular rotator-stator structures. The biprotonated 1,3-propanediamine contains two -NH_3^+ moieties (one crown ether ring per ammonium group), resulting in sandwich-type $[(\text{C}_3\text{N}_2\text{H}_{12}) \cdot (18\text{-Crown-6})_2]^{2+}$ structures.

Supramolecular dication structure, $[(\text{C}_3\text{N}_2\text{H}_{12}) \cdot (18\text{-Crown-6})_2]^{2+}$, are charged as counter cations to balance the $\text{Fe}_2\text{OCl}_6^{2-}$ anions. The biprotonated 1,3-

propane- diamine, with the -NH_3^+ moieties at *trans*-1,3-positions, arrange into the 18-crown-6 within the FeCl_3 salts. The crown adopts a conformation in which the rings show slight distortion. The two crown rings are not parallel to each other, and the centroid-centroid distance between the rings of two crown is 0.639 1 nm. The intramolecular N–H \cdots O hydrogen bonding distances are within the usual range: 0.296 6(5) and 0.281 3(5) nm (Table 3).

Table 3 Hydrogen-bond geometry for **1**

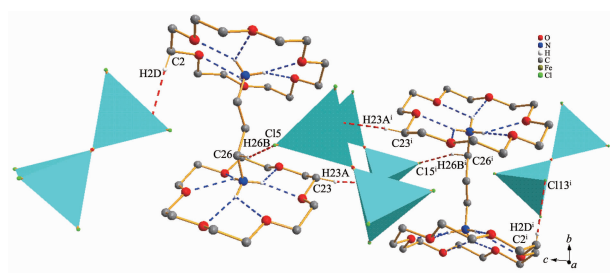
D–H \cdots A	D–H / nm	H \cdots A / nm	D \cdots A / nm	D–H \cdots A / ($^\circ$)
N(1)–H(1A) \cdots O(8)	0.089 00	0.209	0.292 4(5)	155.2
N(1)–H(1A) \cdots O(9)	0.089 00	0.221	0.281 9(5)	125.3
N(1)–H(1B) \cdots O(10)	0.088 99	0.215	0.293 4(5)	146.9
N(1)–H(1B) \cdots O(11)	0.088 99	0.218	0.281 6(5)	128.4
N(1)–H(1C) \cdots O(7)	0.088 99	0.224	0.289 2(5)	130.2
N(1)–H(1C) \cdots O(12)	0.088 99	0.214	0.292 2(5)	146.9
N(2)–H(2A) \cdots O(3)	0.089 00	0.228	0.296 6(5)	134.1
N(2)–H(2A) \cdots O(4)	0.089 00	0.204	0.281 3(5)	145.0
N(2)–H(2B) \cdots O(5)	0.089 00	0.228	0.293 6(6)	129.9
N(2)–H(2B) \cdots O(6)	0.089 00	0.208	0.282 7(6)	141.0
N(2)–H(2C) \cdots O(1)	0.088 99	0.233	0.295 2(5)	127.0
N(2)–H(2C) \cdots O(2)	0.088 99	0.210	0.291 1(5)	151.5
C(2)–H(2D) \cdots Cl(3)	0.097 00	0.281 68	0.378 18	173.21
C(12)–H(12B) \cdots O(8) ⁱⁱ	0.097 00	0.249 01	0.339 65	155.41
C(23)–H(23A) \cdots Cl(6) ⁱ	0.097 00	0.282 78	0.364 61	142.58
C(26)–H(26B) \cdots Cl(5)	0.097 00	0.281 03	0.374 61	161.35

Symmetry codes: ⁱ $-x+2, -y+1, -z+1$; ⁱⁱ $-x+2, -y+1, -z+2$.

The oxide anion, as a bridging ligand, exhibits a good binding ability in the formation of coordination complexes. In Fig.3, dinuclear iron complex contains two $\text{Fe}_2\text{OCl}_6^{2-}$ tetrahedral structures, Fe(III) atoms is linked by a bridging O atom. Fe(III) has a flattened tetrahedral coordination by three Cl^- ions and one oxygen atom (range of *cis*-bond angles: $105.01(7)^\circ \sim 112.53(8)^\circ$; $d(\text{Fe}-\text{Cl})=0.219\ 75(19)\sim 0.223\ 1(2)$ nm; $d(\text{Fe}-\text{O})=0.173\ 38(10)\sim 0.173\ 88(10)$ nm). The Fe(1)-O(13) and Fe(2)-O(14) bond distances in **1** indicate

relatively some distortion from a regular tetrahedron. It is rarely to see $\text{Fe}_2\text{OCl}_6^{2-}$ anion while most compounds form simple FeCl_4^- tetrahedral structure. Compared to $\text{Fe}_2\text{OCl}_6^{2-}$, the FeCl_4^- anion is relatively small for embedding large and structurally diverse supramolecular cations in the crystal lattice.

It has been shown that Cl atoms coordinated to metal-atom centre are good hydrogen-bonding acceptors^[35]. The stacks are fused into *bc* pseudo-sheets by way of the intermolecular C–H \cdots Cl hydrogen bonds,



Dotted lines indicate hydrogen bonding; Symmetry codes: i $1-x$, $1-y$, $1-z$

Fig.3 Structure of the compound **1** are stabilized by intramolecular N-H...O, C-H...Cl and intermolecular C-H...Cl hydrogen bonding

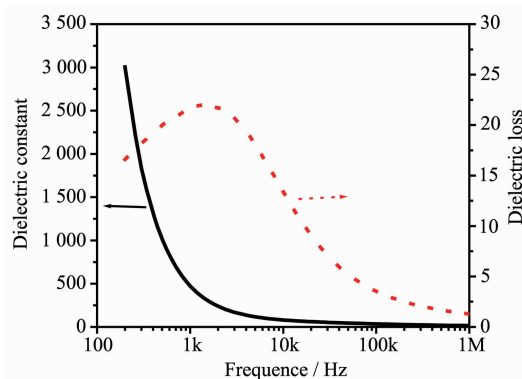
which are established between discrete $\text{Fe}_2\text{OCl}_6^{2-}$ anions and $[(\text{C}_3\text{N}_2\text{H}_{12}) \cdot (18\text{-Crown-6})_2]^{2+}$ groups, resulting in a novel structure.

The two $-\text{NH}_2$ sites of the 1,3-propane-diamine molecule have the potential to form two kinds of cations of $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^+$ and $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$ via a proton-accepting process according to the reaction in solution. It will prefer to form dication, $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$, when the hydrochloric acid is excessive. Because the crown ether moiety has a much higher affinity for the cationic $-\text{NH}_3^+$ group than the neutral $-\text{NH}_2$ group, the size and shape of the supramolecular assemblies between $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$ and crown ethers are strongly affected by the proton-transfer state (sandwich-type $[(\text{C}_3\text{N}_2\text{H}_{12}) \cdot (18\text{-Crown-6})_2]^{2+}$ structures for **1**).

2.4 Dielectric constants analysis

Dielectric results are shown in Fig.4 and Fig.5, respectively. The observations are made in the frequency range 200 Hz to 1 MHz at room temperature and in the measured temperature ranges at different frequencies. From the curves, it is seen that the dielectric constant decreases smoothly with increasing frequency and attains saturation at higher frequencies. It is worth noting that the ϵ_1 of **1** at low frequencies reaches a maximum value (3005 at 20.0 °C and 200 Hz), which rapidly drops to 15 at a relatively high frequency of 1 MHz. The high dielectric constant value of the sample at low frequency is attributed to space charge polarization while in the higher frequencies, the dipole reversal of space charge polarization can not keep up the AC (alternating current) field reversal, so the ϵ_1 is becoming gradually stabilized^[36-37]. In accor-

dance with Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient^[38]. The temperature dependence of the dielectric constant real part (ϵ_1) as estimated from the gradient at a frequency of 1 MHz indicates that ϵ_1 remains small changed; it decreases smoothly from 17 to 6 for **1** only within the measured temperature range, which could be due to the low dielectric loss (ϵ_2/ϵ_1) behavior. Again, such a feature would support the presence of a space charge polarization relaxation process rather than a temperature process. The dielectric constant as a function of temperature goes smoothly, and there is no distinct dielectric anomaly observed. The dielectric constant of compound **1** as a function of temperature indicates that the permittivity is basically temperature-independent, suggesting that this compound should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range.



Frequency range of 200 Hz to 1 MHz at ca. 20.0 °C

Fig.4 Frequency dependence of the dielectric constant for compound **1**

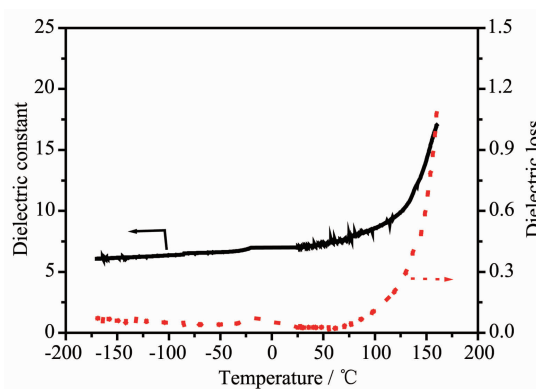


Fig.5 Temperature dependence of the dielectric constant for compound **1** at 1 MHz

In this context, we have shown the supramolecular cation structures between organic amine cation and 18-crown-6 ether as the counter cations of $[\text{Fe}_2\text{OCl}_6]^{2-}$. This approach allows us to modify and modulate the assembled molecule structures in the crystal and thus to modify many kinds of properties. By using this approach, relatively large and complex cations, which consist of an organic ammonium cation such as biprotonated 1,3-propane-diamine $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$, with the introduction of crown ethers into the crystal, give rise to a combination of metal chloride. The supramolecular cations are comprised of the $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$ moiety via H-bonded interactions to the cavity of the 18-crown-6. Hydrogen-bonding between the protons of the $-\text{NH}_3^+$ moieties of $(\text{NH}_3\text{-C}_3\text{H}_6\text{-NH}_3)^{2+}$ and the oxygen atoms of the crown ethers yield a sandwich-type supramolecular structure. Dielectric measurements reveal that the dielectric constant of the compound **1** increase with the increase of temperature, decrease with the increase of frequency, suggesting that there is no distinct dielectric anomaly observed.

References:

- [1] Izatt R M, Bradshaw J C, Nielsen S A, et al. *Chem. Rev.*, **1985**,**85**:271-339
- [2] Kirsh M, Lehn J M. *Angew. Chem.*, **1975**,**87**:542-543
- [3] Westley J W. *Polyether Antibiotics*, **1982**,**1**:1-20
- [4] Wu Y, An H, Tao J, et al. *J. Inclusion Phenom.*, **1990**,**9**:267-274
- [5] Zhang X X, Bradshaw J S, Izatt R M. *Chem. Rev.*, **1997**,**97**:3313-3361
- [6] Tsubaki K, Tanaka K, Furuta T, et al. *Tetrahedron Lett.*, **2000**,**41**:6089-6093
- [7] Suzuki I, Obata K, Anzai J, et al. *J. Chem. Soc., Perkin Trans.*, **2000**,**2**:1705-1710
- [8] Bang E, Jung L W, Lee W, et al. *J. Chem. Soc., Perkin Trans.*, **2001**,**2**:1685-1692
- [9] Beer P D, Gale P A. *Angew. Chem. Int. Ed.*, **2001**,**40**:486-516
- [10] Kryatova P, Kolchinski A G, Rybak-Akimova E V. *Tetrahedron*, **2003**,**59**:231-239
- [11] Ashton P R, Baxter I, Cantrill S J, et al. *Angew. Chem. Int. Ed.*, **1998**,**37**:1294-1297
- [12] Cantrill S J, Youn G J, Stoddart J F, et al. *J. Org. Chem.*, **2001**,**66**:6857-6872
- [13] Gibson H W, Yamaguchi N, Hamilton L, et al. *J. Am. Chem. Soc.*, **2002**,**124**:4653-4665
- [14] Chiu S H, Rowan S J, Cantrill S J, et al. *Chem. Commun.*, **2002**,**24**:2948-2949
- [15] Kryatova O P, Kryatov S V, Staples R J, et al. *Chem. Commun.*, **2002**,**24**:3014-3015
- [16] Kryatova O P, Korendovych I V, Rybak-Akimova E V. *Tetrahedron Lett.*, **2003**,**44**:4251-4255
- [17] Akutagawa T, Hasegawa T, Nakamura T, et al. *J. Am. Chem. Soc.*, **2002**,**124**:8903-8911
- [18] Akutagawa T, Hashimoto A, Nishihara S, et al. *J. Phys. Chem. B*, **2003**,**107**:66-74
- [19] Sharghi H, Nasser M A, Niknam K. *J. Org. Chem.*, **2001**,**66**:7287-7293
- [20] Lehn J M. *J. Supramol. Chem.*, **1995**,**5**:139-147
- [21] Gokel G W. *Crown Ethers & Cryptands*. Cambridge: Royal Society of Chemistry, **1991**:76-78
- [22] Akutagawa T, Hashimoto A, Nishihara S, et al. *J. Supramol. Chem.*, **2002**,**2**:175-186
- [23] Akutagawa T, Endo D, Imai H, et al. *Inorg. Chem.*, **2006**,**45**:8628-8637
- [24] Akutagawa T, Sato D, Koshinaka H, et al. *Inorg. Chem.*, **2008**,**47**:5951-5962
- [25] Fende N S, Kahwa I A. *J. Solid State Chem.*, **2002**,**163**:286-293
- [26] Izatt R M, Pawlak K, Bradshaw J S. *Chem. Rev.*, **1991**,**91**:1721-2085
- [27] Metzger A, Gloe K, Stephan H, et al. *J. Org. Chem.*, **1996**,**61**:2051-2055
- [28] Johnson B F M, Judkins C M G, Matters J M, et al. *Chem. Commun.*, **2000**,**16**:1549-1550
- [29] Kryatova O P, Korendovych I V, Rybak-Akimova E V. *Tetrahedron*, **2004**,**60**:4579-4588
- [30] Vanderah T A. *Nature*, **2002**,**298**:1182-1184
- [31] (a) Rijnders G, Blank D H V. *Nature*, **2005**,**433**:369-370
(b) Lee H N, Christen H M, Chisholm M F. *Nature*, **2005**,**433**:395-399
- [32] (a) Qu Z R, Zhao H, Wang Y P, et al. *Chem. Eur. J.*, **2004**,**10**:53-60
(b) Zhao H, Qu Z R, Ye Q, et al. *Chem. Mater.*, **2003**,**15**:4166-4168
(c) Xiong R G, You X Z, Abrahams B F, et al. *Angew. Chem. Int. Ed.*, **2001**,**40**:4422-4425
(d) Zhang W, Xiong R G, Huang S P. *J. Am. Chem. Soc.*, **2008**,**130**:10486-10469
(e) Zhang W, Chen L Z, Xiong R G, et al. *J. Am. Chem. Soc.*, **2009**,**131**:12544-12545
- [33] Sheldrick G M. *US Patent*, 5631250. 1997-05-20.
- [34] Altomare A, Burla M C, Camalli M, et al. *J. Appl. Crystallogr.*, **1994**,**27**:435-436
- [35] Aullon G, Bellamy D, Brammer L. *Chem. Commun.*, **1998**,**6**:653-654
- [36] Narasimha B, Choudhary R N, Roa K V. *Mater. Sci.*, **1988**,**23**:1416-1418
- [37] Roa K V, Samakula C. *J. Appl. Phys.*, **1965**,**36**:2031-2038
- [38] von Hundelshausen U. *Phys. Lett.*, **1971**,**34A**:405-406