

Magnetic field induced proton transfer of 18-crown-6-ether/fluoroboric acid/water system: Crystal structure and Hirshfeld surfaces

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ABSTRACT

A new complex of the title system ($[2(\text{H}_3\text{O}^+)\cdot 18\text{-crown-6}]\cdot 2[\text{BF}_4^-]$), which was induced by external magnetic field, has been prepared and characterized. When compared with other two members of the same system, the proton transfer induced by magnetic field from HBF_4 to H_2O has leads to the co-plane of six oxygen atoms in the crown and stronger H–F and O–F intermolecular interactions, which can be attributed to the closer contacts between 18-crown-6, oxonium ion H_3O^+ and counterion BF_4^- . In addition, a compression effect of crystals stacking has been observed. These results are of importance for the evaluation the effect of magnetic field on the host–guest systems.

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1. Introduction

Because of their significant importance in the fields such as supramolecular chemistry [1,2], analytical chemistry [3], host–guest interaction [4], extraction techniques [5], catalysts inorganic synthesis, and so on, the crown ethers have received intensive attention since they were discovered by Pedersen in 1967 [6]. Among the whole crown ethers system, the 18-crown-6 (1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane) molecule is the most ordinarily characteristic compound because it is the prototype of synthetic macrocyclic polyether and prominent compound in supramolecular chemistry [7]. Crown ethers can complex with water and acids (organic and inorganic) by in either of two ways as $\text{H}_2\text{O}/\text{HX}$ or $[\text{H}_3\text{O}^+][\text{X}^-]$. Within this context, there were several examples of 1:1:1 and 2:2:1 water: acid: crown ether complexes have been reported since 1972 [8,9]. The studies of this system is of significant importance because water plays a key role in the stability of 18-crown-6 complexes, this is why such a considerable number of studies have been devoted to the water-acids-18-crown-6 system.

Among the water-acids-18-crown-6 system, the water- HBF_4 -18-crown-6 system has attracted special attention. It has been shown to exist as ionized 1:1:1 species (I) $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}][\text{BF}_4^-]$ [10] and unionized 2:2:1 species (II) $[(18\text{-crown-6})\cdot 2(\text{H}_2\text{O}\cdot \text{HBF}_4)]$ [11]. In this work, we report the third ionized 2:2:1

species (III) $[2(\text{H}_3\text{O}^+)\cdot 18\text{-crown-6}]\cdot 2[\text{BF}_4^-]$, the proton transfer from HBF_4 to water was induced by magnetic field.

It is well-known that external physical stimulus during crystallization process can influence selectivity of polymorphs growth, for instance, magnetic field [12], light [13], pressure, etc., which can change the structures and some special properties like magnetic and redox properties [14]. It has proven that crystal growth with an external magnetic field is efficacious in the melt texturing of alloys [15] or in the cases where controlled convection of the crystallizing solution is required, for example, in the growth of high-quality protein crystals [16], chiral aggregates [17] or in the alignment of liquid crystal [18] and block copolymer arrays [19]. A magnetic field has even been demonstrated to be able to separate polymorphs of crystals post-synthetically [20]. Magnetic forces can influence solidification and subsequent physical behaviour in crystals [21,22]. A high and homogeneous or steep-gradient magnetic field has also been applied to improve growth and quality of crystal [23]. It has been proved that the product of vertical magnetic flux density and its gradient correlates to the strength of the magnetic force acting on substances [24]. Jason Potticary group showed that by crystallizing the polycyclic aromatic hydrocarbons coronene in the presence of a magnetic field, a new β -herringbone polymorph instead of the universal γ -herringbone can be formed, with a change as large as 35° to the herringbone nearest neighbour angle [25]. Many researches magnetic field on nanoscales and semiconductor have been done. However, there were few examples of novel polymorphs induced by magnetic field, and the magnetic-induced proton transfer is rare.

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Currently, our group has reported the effects on cocrystallization with different strengths of magnetic fields, based on our previous works, the stretching mechanism of a magnetic field have been proposed. Meanwhile, the concept is discovered that a multi-step reversible transformation between cocrystals in the solution state can be achieved by properly adjusting the magnetic field strength. To the best of our knowledge, the present work is an interesting example of magnetic-induced proton transfer.

2. Experimental

2.1. Materials

18-Crown-6 ether was obtained from ChemFuture PharmaTech, Ltd (Nanjing, Jiangsu) commercially, and used as received without further purification. All the solvents (reagent grade) used were commercially available from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification.

2.2 Preparation of $[2(\text{H}_3\text{O}^+)\cdot 18\text{-crown-6}]\cdot 2[\text{BF}_4^-]$ (III)

Colourless prisms crystals of $[2(\text{H}_3\text{O}^+)\cdot 18\text{-crown-6}]\cdot 2[\text{BF}_4^-]$ (III) suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution containing 1:1 (mol) stoichiometry 18-crown-6: HBF_4 under 1 T magnetic field after approximately 15 days at the room temperature. Elemental analysis. *Anal. Calc.* (%): C, 30.28; H, 6.35. Found: C, 30.24; H, 6.38.

2.3 X-ray crystallographic study

The single-crystal X-ray diffraction data of the complex III were collected at 293 K with graphite-monochromated Mo K α radiation ($\lambda = 0.071073$ nm), using a Rigaku SCXmini diffractometer with the ω -scan technique [26]. The lattice parameters were integrated by using vector analysis and refined from the diffraction matrix, the absorption correction were performed with multi-scan method by using Bruker SADABS program. The structures of them were solved by full-matrix least-squares methods on all F^2 data, and using SHELXS-97 and SHELXL-97 programs [27] for structure analysis and structure refinement, respectively. Reliability factors were defined as $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and the function minimized was $R_w = [\Sigma_w(F_o^2 - F_c^2)^2/w(F_o)^4]^{1/2}$, where in the least-squares calculation the unit weight was used. All non-hydrogen atoms were refined anisotropically [28,29]. Molecular graphics were prepared by using the mercury.

3. Results and discussion

3.1. Comparison of the three forms

The crystallographic data for I and II were reported in 1982 and 1992 by Chenevert et al. [9] and Atwood et al. [11], respectively.

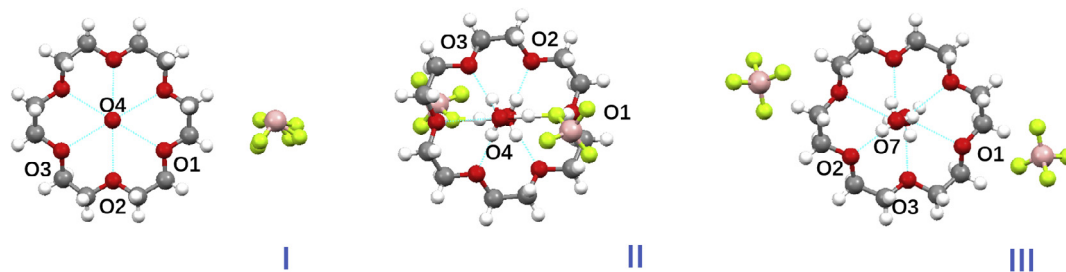


Fig. 1. Molecular structure of complexes I, II and III, hydrogen bonds were shown in dotted lines.

Table 1
Unit cells of complexes I, II and III.

Complex	I	II	III
Space group	$P4_12_12$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.575(3)	7.341(2)	7.3420(15)
b (Å)	10.575(3)	8.364(2)	8.3560(17)
c (Å)	16.471(3)	10.631(3)	10.378(2)
α (°)	90	71.48(2)	93.36(3)
β (°)	90	67.91(2)	108.64(3)
γ (°)	90	67.94(2)	112.15(3)
V (Å ³)	1842(1)	549	547.0(3)
Z	4	1	1

The molecular structures and unit cell parameters for complexes I, II and III were shown in Fig. 1 and Table 1. Though complex III were adjusted with magnetic field that different from complex II, both of them shown similar space group and a , b , c values but completely different unit cell angles. That's to say that the proton transfer from HBF_4 to water just change the unit cell angles and decrease the unit cell volume with the presence of magnetic field.

In complex I, the 18-crown-6 adopts the most commonly encountered “round” “ D_{3d} like” conformation [30], which shows lowest energy. The torsion angles of the crown involving O1, O2 and O2, O3 were found to be 62.28 (4)° and 52.36 (4)°, respectively. The oxonium ion H_3O^+ (O4) located in the centre “cavity” of the macrocycle exhibits practically equidistant (2.68–2.73 Å) from the six macrocyclic ethereal oxygens. The BF_4^- counterion is positioned 7.3 Å away from the oxonium ion in the same general plane of the crown ether (Fig. 1), and it is not involved in any direct intermolecular contacts. The adjacent crown molecules packed in face to face (cavity to cavity) motif into a double-crown unit with BF_4^- counterions act as cap for the crown. The different double-crown units then further stacked along a axis in $\cdots A(-A)A(-A)\cdots$ fashion (Fig. 2).

In complex II, the macrocyclic ring of the crown ether exhibits as the “round” “ D_{3d} like” conformation in a similar, yet not identical, conformation to the 18-Crown-6 ring of I. The torsion angles of the crown involving O1, O2 and O2, O3 were found to be 65.75 (6)° and 72.44 (6)°, respectively. These torsion angles in complex II are larger than that in I. The crystallographic asymmetric unit consisting of only one half of the complex (Fig. 1), the centre of the macrocyclic acts as crystallographic centre of inversion despite the fact that there is no ion or molecule in the “cavity” of the macrocycle. The six oxygen atoms of the crown ether are planar to 0.23 Å, and the two $\text{H}_2\text{O}\cdot\text{HBF}_4$ systems were lie above and below the plane with water oxygen atom resides 1.59 (5) Å out of the plane. The water oxygen atoms contact with four of the six oxygen atoms of the crown through $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonding interactions, while the other two oxygen atoms contact with F atoms through $\text{F}\cdots\text{H}\cdots\text{O}$ hydrogen bonding interactions. The complex further stacked vertical to a axis with the crown display centrosymmetric dodecagon (Fig. 2).

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