Original article

Temperature-triggered phase transition in pyridazine hexafluorophosphate

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ABSTRACT

The pyridazine hexafluorophosphate $[C_4H_5N_2]^+[PF_6]^-$ (**1**) undergoes a reversible phase transition around 140 K, which was confirmed by the DSC measurement. Variable-temperature crystal structures determined at 293 K and 93 K show that the compound crystallizes in the same space group $P2_1/c$, indicating that **1** undergoes an iso-structural phase transition. As the temperature decreases, dielectric measurement of the title compound shows no significant change around the phase transition temperature. Classic hydrogen bonds are found between molecules at 293 K and 93 K with similar packing arrangement. The most distinct difference between the low temperature and room temperature structures is the order–disorder transition of the hexafluorophosphate anion, which is probably the driving force of the phase transition.

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1. Introduction

For the prospect of applications as molecular sensors, switches, and data storage devices, a large number of temperature-triggered solid-to-solid phase transition materials (SSPTMs) have been found and studied [1–17]. Among of them, phase transition materials of molecular–ionic crystals are of great importance and they are also hotspots that chemists are researching. To design such materials, one of the most efficient strategies is to introduce moieties that can easily undergo the order–disorder transitions. Cases for organic cations including pyridinium and imidazolium are flexible cations. While cases for inorganic anions are mainly the tetrahedral ones such as ClO_4^-, BF_4^- and IO_4^-. The common features of these anions are that they all have small volumes and high symmetries. When changing the temperature, the moieties may undergo an order–disorder transformation, thus leading to phase transitions, as depicted in imidazolium perchlorate [18]. In contrast, octahedral anions like hexafluorophosphate, which can also reorient, have been rarely explored comparing with the tetrahedral ones.

For the above-mentioned reasons, numerous imidazolium and pyridinium have been explored and their tetrafluoroborate and perchlorate compounds have been found to exhibit ferroelectric properties [19–21]. Moreover, we found that pyridazine cation can also undergo the order–disorder transition triggered by the temperature. However, the pyridazine compounds have not been studied as thorough as imidazolium and pyridinium. According to the literatures, Czapla *et al.* have reported the structural phase transitions of first order in pyridazine fluoroborate and perchlorate [22,23]. Interestingly, the phase transitions of these two compounds are coupled with the crystal symmetry changing from the monoclinic $P2_1/n$ to trigonal $R\bar{3}m$ on heating. The driving force of the phase transitions can be attributed to the dynamics of the constituent cationic and anionic units. In addition, the existence of intermolecular hydrogen bonds plays an important role in the stabilization of the structures.

In order to check whether hexafluorophosphate compounds have different mechanism of phase transition from the perchlorate and tetrafluoroborate salts, we have successfully synthesized the pyridazine hexafluorophosphate and study its physical properties by X-ray diffraction, dielectric measurement and differential scanning calorimetry (DSC). It turns out that pyridazine hexafluorophosphate undergoes a solid–solid phase transition around 140 K, accompanying by the order–disorder changing of the hexafluorophosphate anion. During the phase transition progress, the pyridazine moiety shows no observable disorder. As far as we know, this is the first low temperature phase transition for pyridazine compounds, and probably will be beneficial for the research of molecular–ionic crystals.

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2. Experimental

2.1. Materials and measurements

All reagents and solvents were commercially available and used as received without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The X-ray powder diffraction data was obtained by a Rigaku X-ray powder diffractometer D/MAX 2000/PC. Dielectric measurements were performed on pure crystalline powder of title compound using automatic impedance TongHui 2828 Analyzer.

Single-crystal X-ray diffraction measurements: Single-crystal data were collected at 93 K and 293 K on a Rigaku SCXmini CCD diffractometer equipped with graphite-monochromated MoK$_\alpha$ radiation. The structures were solved using direct methods and successive Fourier difference syntheses (SHELXS-97) [24], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters (SHELXL-97) [25]. Differential scanning calorimetry (DSC) was undertaken by a NETZSCH DSC 200 F3 instrument under nitrogen atmosphere in aluminum crucibles with heating and cooling rates of 10 K min^{-1} (Fig. 1).

2.2. Synthesis

The title compound, pyridazine hexafluorophosphate can be readily obtained by slow evaporation of mixed solution containing pyridazine and fluorophosphoric acid with stoichiometric proportion of 1:1. Several days later, colorless needle crystals were collected. Anal. Calcd. (%) for $C_4H_5N_2PF_6$: C, 21.25; H, 2.23; N, 12.39. Found (%): C, 20.87; H, 2.60; N, 12.23. The IR spectrum of **1** clearly shows the existence of typical strong vibration peaks of hexafluorophosphate anion around 827 cm^{-1} and 561 cm^{-1} (Fig. S1 in Supporting information). The powder XRD pattern of **1** at room temperature matches well with the pattern simulated from the single-crystal structure (Fig. S2 in Supporting information).

3. Results and discussion

Thermal analysis such as DSC measurement is an effective method of detecting phase transitions that occur in response to the changing temperature. The DSC curves of pyridazine hexafluorophosphate are shown in Fig. 1. Upon heating and cooling, compound **1** undergoes a single phase transition at approximately T_c = 140 K, showing an endothermic peak at 142.5 K and an exothermic peak at 137.5 K. These observed heat anomalies
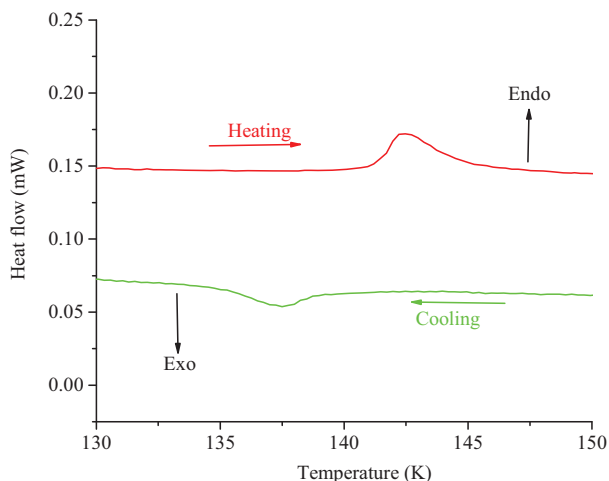
represent a reversible phase transition with a 5 K hysteresis. The wide heat hysteresis and the shape of the peaks indicate a first-order feature.

Crystal structures of **1** have been characterized at different temperatures by X-ray diffraction to confirm whether the phase transition is associated with structural changes. At room temperature (293 K) and low temperature (93 K), the crystals are in the monoclinic space group $P2_1/c$, with a = 5.8349(12) Å, b = 18.0020 (4) Å, c = 7.7103(15) Å, β = 104.840(3)°, V = 782.9(3) Å^3 and Z = 4 at 293 K, and a = 10.6640(11) Å, b = 18.0740(19) Å, c = 11.9210(13) Å, β = 99.650(18)°, V = 2265(4) Å^3 and Z = 12 at 93 K respectively. It shows that compound **1** undergoes a phase transition with two of the axes (a and c) and β angle changing significantly. Moreover, the cell volume of the low temperature structure is almost triple of that in room temperature, increasing from 782.9(3) Å^3 to 2265(4) Å^3 in the monoclinic cell. Although the temperature changes, the space group retains unchanged, meaning that there is no structurally symmetry-breaking occurrence in this phase transition. Crystallographic data and details of collection are listed in Table 1.

In the room temperature (RTP), an asymmetric unit contains one $[C_4H_5N_2]^+$ cation and one $[PF_6]^-$ anion as shown in Fig. 2a. All of the eleven atoms of the pyridazine cation are co-planar. Although two nitrogen atoms in pyridazine molecule have the same ability of getting the proton, only one of them could be protonated in the reaction due to the charge-effect. Further studies show that the protonation has a slight effect on the bond lengths of the pyridazine moiety, with the difference in the C4–N1 and C1–N2 lengths is only 0.021 Å (Table S1 in Supporting information). However, the intraring bond angle at the protonated nitrogen is opened by about 10°, corresponding to that found in the structure investigation of pyridazine hydrochloride [26]. It is worth noting that each F atom is orientationally disordered over two positions with occupation factors of 0.672(11) and 0.328(11). The P–F bond lengths range from 1.528 to 1.580 Å, leading to a distorted octahedral geometry. Classic hydrogen bonds are found between a couple of adjacent pyridazine cations and between anions and cations as N(1)–H(1A)···N(2), N(1)–H(1A)···F(2), N(1)–H(1A)···F(2′), N(1)–H(1A)···F(1′), N(1)–H(1A)···F(1) (Table 2).

In the low temperature (LTP) crystal structure, an asymmetric unit contains three $[C_4N_2H_5]^+$ cations and three $[PF_6]^-$ anions as shown in Fig. 2b. Also, the pyridazine molecule was monoprotonated.

Fig. 1. DSC curves of **1**.

Table 1
Crystal data and structure refinement parameters.

	RTP	LTP
Moiety formula	$C_4H_5N_2PF_6$	$C_4H_5N_2PF_6$
Formula weight	226.07	226.07
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	293	93
a (Å)	5.8349(12)	10.664(11)
b (Å)	18.002(4)	18.074(19)
c (Å)	7.7103(15)	11.921(13)
α (deg)	90.00	90.00
β (deg)	104.84(3)	99.650(18)
γ (deg)	90.00	90.00
Volume (Å^3)	782.9(3)	2265(4)
Z	4	12
Range of hkl	$-7 \le h \le 7$	$-13 \le h \le 11$
	$-23 \le k \le 23$	$-23 \le k \le 23$
	$-10 \le l \le 10$	$-15 \le l \le 15$
Radiation type	Mo-K$_\alpha$	Mo-K$_\alpha$
Absorption correction	Multi-scan	Multi-scan
Crystal size/mm	$0.20 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.20$
$F(000)$	448	1344
S	1.062	1.222
R_1 [$I > 2\sigma(I)$]	0.0680	0.0759
wR_2 [$I > 2\sigma(I)$]	0.1878	0.1444