

## Synthesis and characterization of tetraacetonitrilolithiumhexafluorophosphate crystal



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### HIGHLIGHTS

- Green synthesis of  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  crystal.
- X-ray powder diffraction and different spectroscopic characterizations were applied.
- Solid-state NMR spectra and GAUSSIAN 09 program were used in determining structure.

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### ABSTRACT

Tetraacetonitrilolithiumhexafluorophosphate ( $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$ ) crystal is an important intermediate in the preparation of high purity lithium hexafluorophosphate electrolyte via a simple transformation method. In this study, the crystal parameters were determined by X-ray powder diffraction analysis, which showed that it belongs to the triclinic system with space group P1. FTIR spectral studies identified the characteristic absorption bands of  $\text{C}\equiv\text{N}$  and  $\text{PF}_6^-$  in the synthesized complex. Chemical analysis, gas chromatography, and ICP-AES results showed that the elementary ratio of  $\text{Li}:\text{P}:\text{F}:\text{CH}_3\text{CN}$  in the complex is approximately: 1:1:6:4. Furthermore, the geometric optimization structure of  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  was obtained using GAUSSIAN 09 program on a B3LYP/6-31+G(d, p) level. In this structure, two acetonitrile ligands bind strongly with the  $\text{Li}^+$  ion, whereas the other two are weakly-coordinated with lithium. The results of solid-state  $^{13}\text{C}$ -,  $^{31}\text{P}$ -, and  $^{19}\text{F}$ -NMR spectra confirmed that this configuration is reasonable.

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### Introduction

At present, most of the methods used for the industrial production of high-purity lithium hexafluorophosphate ( $\text{LiPF}_6$ ) electrolyte involve the highly hazardous hydrogen fluoride (HF), which makes them unsafe and  $\text{LiHF}_2$  may also occur as an impurity in the final product. Lithium hexafluorophosphate has poor thermal stability, and it can react to release corrosive HF gas in the presence of trace water (environmental water  $>10$  ppm) [1,2]. By contrast, the  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  complex has relatively stable properties. For example, when  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  samples are dissolved in acetonitrile, the solution can be heated to  $80^\circ\text{C}$ . Thus, our lab proposed a promising transformation method to replace the HF solvent method, which can proceed at ambient temperature and pressure [3]. The reaction equation in the solvent can be expressed as:  $\text{KPF}_6 + \text{LiCl} \rightarrow \text{LiPF}_6 + \text{KCl}$ . The KCl and LiF impurities are insoluble in acetonitrile

which facilitates the crystallization and purification of  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$ . The acetonitrile can be removed from the synthetic  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  crystals by vacuum decomposition to produce highly surface active electrolyte lithium hexafluorophosphate which dissolves rapidly in solvent.  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  crystals can also be prepared by combination of lithium fluoride in excess acetonitrile, with subsequent addition of phosphorus pentafluoride or via the action of excess acetonitrile on even impure  $\text{LiPF}_6$  because its solubility increases with temperature. Another use for  $\text{Li}(\text{CH}_3\text{CN})_4\text{PF}_6$  is as a polymerization catalyst for cyclic ethers or unsaturated hydrocarbons [4].

The complex was first proposed in patent US3594402 in 1969, but its structural characteristics and the mechanism of vacuum decomposition have never been studied in detail. Thus, we used different methods to characterize the complex and to determine its structure. The results of our study provide new insights into the complex and they help to elucidate the mechanism of vacuum decomposition.

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## Experimental

### Crystal preparation

KPF<sub>6</sub> (purity ≥ 99.5%) and LiCl (purity ≥ 97.0%) were predried at 120 °C for 2 h. The following procedures were carried out in an argon-purified glove box (the water content was less than 10 ppm by volume). A magnetically stirred suspension of 18.4 g of KPF<sub>6</sub> was prepared in 140 ml CH<sub>3</sub>CN (purity ≥ 99.9%, water 30 ppm) and 4.7 g of LiCl was added, which had been previously dissolved in 35 ml organic solvent. The reaction suspension was then filtered off with suction over a G3 frit after the KCl had precipitated completely for 2 h. The filtrate was then distilled at 45 °C to remove part of the organic solvent and the slightly soluble LiCl, KCl salts would also precipitate out, before adding 70 ml CH<sub>3</sub>CN for the next vacuum distillation stage. The remaining super-saturated solution was mixed with 80 ml CH<sub>3</sub>CN and cooled at –30 to –10 °C for 6–8 h, where a needle-like white crystal precipitate of Li(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> was formed. The solid was collected by rapid filtration and dried at 34 °C for about 1 h. The yield was 8 g (purity > 99.9%), which depended on the losses during crystallization.

### Characterization methods

The PF<sub>6</sub><sup>–</sup> content in the complex was determined using the gravimetric method [5] with Nitron reagent (Tokyo Kasei Kogyo Co. Ltd; purity ≥ 98.0%). The amount of elementary Li and P in the complex was analyzed using IRIS 1000 ICP-AES (Thermo Electron Corporation).

The CH<sub>3</sub>CN content of the complex dissolved in dimethylformamide was determined by reference to the external standard method using a GC-AED 6890A instrument.

X-ray powder diffraction analysis was performed with X'pert Pro MPD (Philips), which operated at 24 °C, using Cu Kα X-ray source. The 2θ value was set between 5° and 80° with a step size of 0.02° per second. The samples were first wrapped with a special membrane in the glove box.

The infrared spectra of acetonitrile, LiPF<sub>6</sub>, the compound and paraffin oil samples were recorded using a Nicolet 6700 (Thermo Scientific, USA) spectrophotometer at 4000–400 cm<sup>–1</sup> (KBr pellets). Solid samples of LiPF<sub>6</sub> and the complex were coated with paraffin oil to isolate moisture. Acetonitrile was also mixed with paraffin oil to eliminate solvent effect on samples.

Solid-state <sup>13</sup>C-, <sup>31</sup>P-, and <sup>19</sup>F-NMR analyses were performed on a Bruker Avance III 400 NMR spectrometer. Samples were packed in solid-state nuclear magnetic tubes inside the glove box.

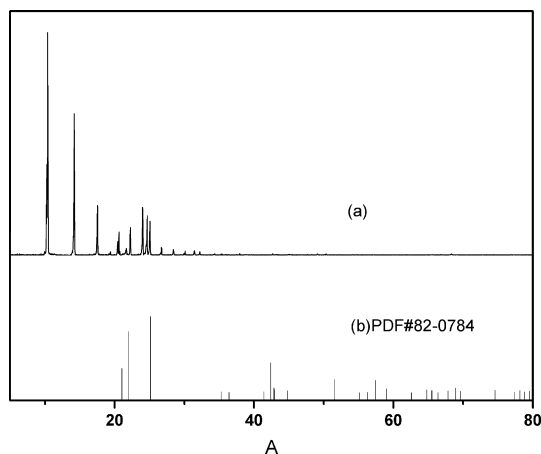


Fig. 1. XRD patterns of (a) Li(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub>; (b) PDF card of LiPF<sub>6</sub>.

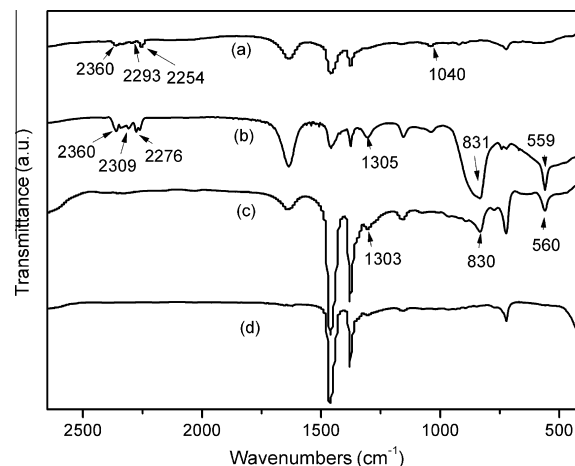


Fig. 2. FTIR spectra of acetonitrile (a), the complex (b) and LiPF<sub>6</sub> (c) dispersed in paraffin oil and the FTIR spectrum of paraffin oil (d).

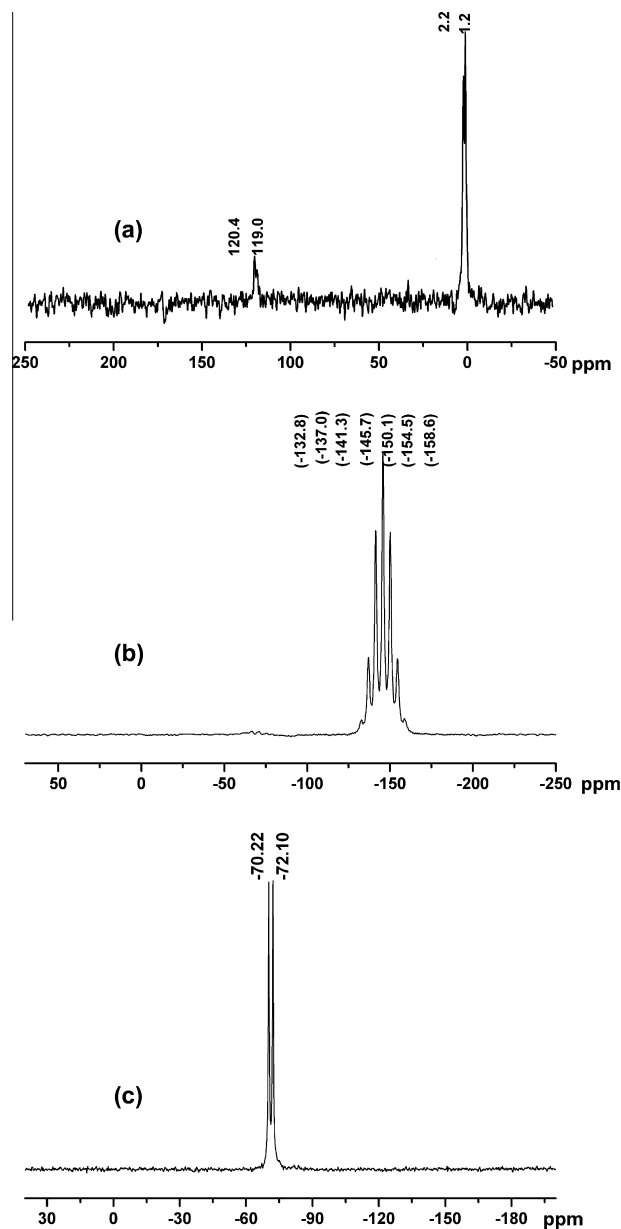


Fig. 3. NMR patterns of Li(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub>: (a) <sup>13</sup>C NMR; (b) <sup>31</sup>P NMR; (c) <sup>19</sup>F NMR.

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