

含八齿苦味酸根的超分子苦味酸钾的合成和结构

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Synthesis and Crystal Structure of Supramolecular Potassium Picrate Bearing Octadentate μ -Picrate Bridges

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Abstract: A supramolecular complex, $[\text{Kpic}]_n$ (pic^- is picratol, $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{O}^-$), has been synthesized unexpectedly in acetone solution, and characterized by elemental analysis, IR and X-ray crystallography. In the complex, the $\text{K}^+:\text{pic}^-$ is 1:1, and one K(I) ion is surrounded by six picrate anions, one picrate anion can coordinate to six K(I) ions. The coordination number of every potassium atom is eight. Interestingly, the picratol adopts an eight-coordinated ideal mode unreported. CCDC: 630627.

Key words: potassium(I) complex; synthesis; crystal structure

Crown ether compounds have been well known for their coordination ability to alkali, alkaline earth, transition metal and rare earth metal ions to form various types of structures^[1]. Benzo-15-crown-5 with five oxygen atoms on its cycle and suitable diameter of cavity reacting with potassium ions affords very usually the sandwiched structure $[\text{K}(\text{benzo-15-crown-5})_2]^+[\text{pic}]^-$ ^[2,3]. In a few cases the mono crown cycle-capped potassium cation $[\text{K}(\text{benzo-15-crown-5})]^+$ with remaining coordination positions that can accept other donor were detected^[4]. Of this type of structure is sole example of $[\text{K}(\text{benzo-15-crown-5})_2\text{OC}_6\text{H}_2(\text{NO}_2)_3]_n$ ^[5]. It is possible for one to use $[\text{K}(\text{15-crown-5})_2]^+$ as building blocks to construct low dimensional coordination complex. Therefore,

$[\text{K}(\text{15-crown-5})\text{OC}_6\text{H}_2(\text{NO}_2)_3]_n$ can be expected to obtained from reaction of 15-crown-5 with potassium picrate. However only one picrate ligand in this reaction is coordinated to potassium cation and in consideration of the interactions this compound has in fact a three-dimensional supramolecular structure, which is different from the reported results of structure of potassium picrate^[6,7].

1 Experimental

1.1 Chemicals and instruments

Solvents and starting materials were purchased commercially and used without further purification unless otherwise stated. Elemental analysis for K was

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performed by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra in the range of 400~4 000 cm^{-1} were recorded on a VERTEX70 FTIR spectrophotometer using KBr pellets. X-ray single crystal structure was obtained on a Rapid Auto Version 3.0 Rigaku RAXIS-RAPID detector.

1.2 Synthesis of $[\text{Kpic}]_n$

$\text{Kpic} \cdot 4\text{H}_2\text{O}$ was synthesized according to our previous work^[8]. A solution of 15-crown-5 (0.219 3 g, 1.0 mmol) in acetone (30 mL) was added dropwise to a solution of potassium picrate tetrahydrate (0.340 6 g, 1.0 mmol) in acetone (120 mL) at room temperature. The color of the mixing solution turns to brilliant yellow immediately, and then continuing stirring for 12 h at room temperature. The solution was filtered and the filtrate was allowed to stand at room temperature for about three weeks, the solvent was partially evaporated and obtained the single crystals suitable for X-ray crystal structure analysis. Anal. Calc. for $\text{C}_6\text{H}_2\text{KN}_3\text{O}_7$ (%): C, 26.97; H, 0.75; N, 15.73; K, 14.63. Found (%): C, 26.88; H, 0.79; N, 15.65; K, 14.48. IR spectrum of $[\text{Kpic}]_n$ exhibits Ar-O stretching bands at 1 272 cm^{-1} (Fig.1).

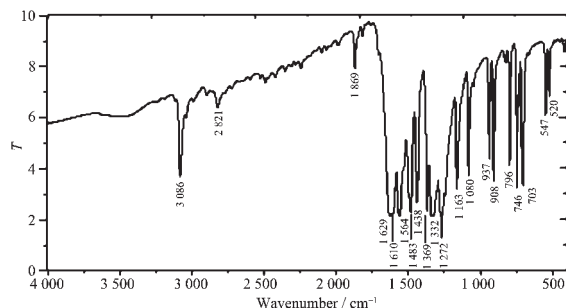


Fig.1 IR spectrum of $[\text{Kpic}]_n$

1.3 Crystal structure determination of $[\text{Kpic}]_n$

The yellow crystal with an approximate dimensions of 0.54 mm \times 0.38 mm \times 0.34 mm was selected for the structure analysis. Intensity data were collected on a Rapid Auto Version 3.0 Rigaku RAXIS-RAPID detector diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) at 163 (2) K. The structure was solved by direct methods (SHELXS 97) and refined by full matrix least squares on F^2 using the

program SHELXL 97. All hydrogen atoms were added theoretically. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1, and the final positional and thermal parameters are available as supplementary material.

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Table 1 Crystal data and structure refinement for $[\text{Kpic}]_n$

Empirical formula	$\text{C}_6\text{H}_2\text{KN}_3\text{O}_7$
Formula weight	267.21
Temperature / K	153(2)
Wavelength / nm	0.071 073
Crystal size / mm	0.54 \times 0.38 \times 0.34
Crystal system	Orthorhombic
Space group	<i>Ibca</i>
<i>a</i> / nm	0.697 4(1)
<i>b</i> / nm	1.334 2(3)
<i>c</i> / nm	1.912 5(4)
<i>V</i> / nm ³	1.779 6(6)
<i>Z</i>	8
<i>D</i> _{calc} / (g·cm ⁻³)	1.995
μ / mm ⁻¹	0.632
<i>F</i> (000)	1072
θ range / (°)	3.06~27.50
<i>hkl</i> ranges	-9~-9, -17~-17, -24~-24
Total number of reflections	8089
Number of unique data (<i>R</i> _{int})	8 063 (0.015 9)
Number of parameters	81
<i>R</i> (<i>F</i>)	0.023 3
<i>wR</i> (<i>F</i> ²)	0.065 2
Goodness-of-fit on <i>F</i> ²	1.002
Largest diff. peak and hole / (e·nm ⁻³)	361, -203

2 Results and discussion

The crystal structure of $[\text{Kpic}]_n$ reveals that the K(I) ions in the complex are eight-coordinated (Fig.2a) by four oxygen atoms from two chelate picrates which act as a bidentate donor fashion attached to the K(I) ion through the phenolic oxygen (O1 or O1A) and one of the o-nitro oxygen atoms (O2 or O2A), two oxygen atoms from one of the o-nitro oxygen atoms (O2D or O2E) of two picrates, and two oxygen atoms from one of the p-nitro oxygen atoms (O4B or O4C) of two picrates,

respectively. Therefore, one K(I) ion is surrounded by six picrate anions. The coordination polyhedron is a triangular dodecahedral arrangement.

The picrate anions in the $[\text{Kpic}]_n$ are all octadentate ligand (Fig.2b), not reported tridentate ligand^[6]. The phenolic oxygen (O1) and the two oxygen atoms (O2 or O2G) from one of the two o-nitroes are all bridged oxygen atoms which coordinate to four K(I) ions (K1, K1G, K1E and K1J), and the two oxygen atoms (O4 or O4G) from p-nitro which coordinate to two K(I) ions (K1H, K1I) respectively. Therefore, one picrate anion can coordinate to six K(I) ions. Furthermore, it is noteworthy that the octadentate picrate anions in the complex are interesting, which is different from the usual coordinate modes of picrate, such as monodentate^[8], bidentate^[9] and tridentate^[5].

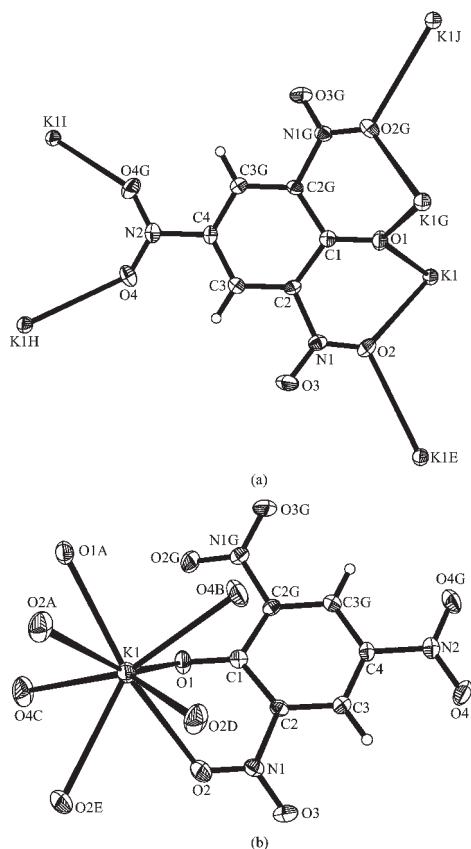


Fig.2 Molecular structure of $[\text{Kpic}]_n$

The crystal structure of $[\text{Kpic}]_n$ shows it is an infinite three-dimension complex with Kpic moieties bridged by the picrate groups (Fig.3). The K(I) ion is surrounded by six picrate anions, similarly, there are

six K(I) ions around the picrate anion. Therefore, the rate of K(I) and picrate anion is 1:1 in the complex, and the empirical formula is Kpic in the $[\text{Kpic}]_n$. This is similar to the structure of NaCl. It's very rare for the large anion picrate to form this structure.

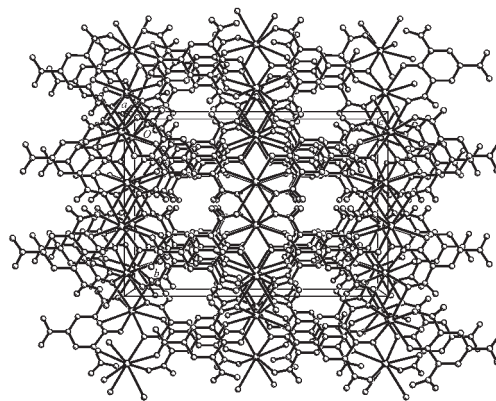


Fig.3 Packing diagram of $[\text{Kpic}]_n$ along a -axis, H atoms are omitted for clarity

In conclusion, the picrate anions can form stable complex with potassium ions. The picrate is octadentate ligand unreported. It, therefore, shows high coordination ability, which could make it a useful agent in organic reaction. Further studies of the complex are under way.

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