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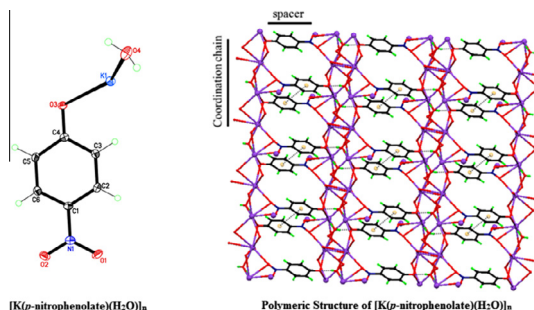
Structural characterization, electrochemical, photoluminescence and thermal properties of potassium ion-mediated coordination polymer

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HIGHLIGHTS

- A novel polymeric potassium complex of *p*-nitrophenol is reported.
- Molecular structure of the complex was determined by X-ray diffraction technique.
- Electrochemical and thermal properties of the complex were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A polymeric potassium complex of *p*-nitrophenol was synthesized and characterized by analytical and spectroscopic techniques. Molecular structure of the complex was determined by single crystal X-ray diffraction study. X-ray structural data show that crystals contain polymeric K⁺ complex of *p*-nitrophenol. Asymmetric unit consists of one *p*-nitrophenolate, one K⁺ ion and one water molecule. All bond lengths and angles in the phenyl rings have normal *Csp*²–*Csp*² values and are in the expected ranges. The *p*-nitrophenolate is close to planar with small distortions by some atoms. Each potassium ion in the polymeric structure is identical and eight-coordinate, bonded to four nitro, two phenolate oxygen atoms from five *p*-nitrophenolate ligands and two oxygen atoms from two water molecules. Electronic, electrochemical, photoluminescence and thermal properties of the complex were also investigated.

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Introduction

p-Nitrophenol is a product of the enzymatic cleavage of several substrates such as *p*-nitrophenyl acetate (used as a substrate for carbonic anhydrase) and *p*-nitrophenyl-β-D-glucopyranoside and other sugar derivatives which are used to assay various glycosidase enzymes. Amounts of *p*-nitrophenol produced by a particular enzyme (alkaline phosphatase) in the presence of its corresponding

substrate can be measured with a spectrophotometer at around 405 nm and used as a proxy measurement for the amount of the enzyme activity in the sample. *p*-Nitrophenol shows two polymorphs in the crystalline state. The alpha-form is colorless pillars and unstable at room temperature. The beta-form is yellow pillars and stable at room temperature, and gradually turns red upon irradiation of sunlight. Usually, *p*-nitrophenol exists as a mixture of these two forms [1]. Potassium complexes of *p*-nitrophenyl compounds have been reported in literature [2–6]. Molecular structure of potassium complex of *p*-nitrophenyl sulfate (PNPS) was structurally characterized by X-ray diffraction study. The crystal structure of the compound [K(PNPS)] contains

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p-nitrophenylsulphate anions and potassium cations. Each K⁺ ions is 8-coordinate with approximate square antiprism geometry [2].

In this study, polymeric potassium complex of *p*-nitrophenol (KNP) was prepared and characterized by spectroscopic and analytical methods. Molecular structure of the complex was determined by single crystal X-ray diffraction study. Electronic and electrochemical properties of the complex were also investigated.

Experimental

General methods

All starting materials and organic solvents were purchased from commercial sources and used as received, unless noted otherwise. IR spectrum was performed on a Perkin Elmer, Spectrum 400 (resolution; 0.5–4 cm⁻¹). CHN analysis was performed using a CE-440 Elemental analyzer. The ¹H- and ¹³C NMR were performed using a BrukerAvance 400. Mass spectrum was recorded on a Thermo Fisher Exactive Orbitrap mass spectrometer coupled to an Advion TriVersa Nanomate injection system.

X-ray structures solution and refinement for the polymeric complex

X-ray diffraction data for the complex was collected at 100(2) K on a Bruker ApexII CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction was performed using Bruker SAINT. SHELXTL was used to solve and refine the structures [7]. The structures were solved by direct methods and refined on F^2 using all the reflections [8]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Hydrogen atoms bonded to water oxygen atom (O4) were located from difference maps and refined with temperature factors riding on the carrier atom. Details of the crystal data and refinement are given Table 1. Hydrogen bond parameters are given in Table 2 and bond lengths and angles are given in Table 3.

Preparation of the polymeric complex (KNP)

p-Nitrophenol (1 mmol, 0.139 g) in acetone (10 ml) and K₂CO₃ (0.5 mmol, 0.069 g) in acetone (5 ml) were mixed and refluxed

Table 1
Crystallographic data.

Identification code	K1
Empirical formula	C ₆ H ₆ KNO ₄
Formula weight	195.22
T/K	100(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Unit cell</i>	
<i>a</i> (Å)	10.4828 (2)
<i>b</i> (Å)	7.2887 (1)
<i>c</i> (Å)	11.2186 (2)
α (°)	90
β (°)	117.682 (1)
γ (°)	90
Volume (Å ³)	759.06 (2)
<i>Z</i>	4
Calculated density (g/cm ³)	1.708
Crystal size (mm ³)	0.33 × 0.23 × 0.16
Abs. coeff. (mm ⁻¹)	0.670
Refl. collected	6878
Ind. Refl. [R_{int}]	1894 [0.0204]
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0245, 0.0637
R_1 , wR_2 (all data)	0.0274, 0.0655
Goodness-of-fit on F^2	1.064
CCDC number	987883

Table 2
Hydrogen-bond geometry for the complex (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O4–H4A...O3 ⁺	0.79 (2)	2.00 (2)	2.7863 (13)	172.7 (18)
O4–H4B...O3 ⁺	0.84 (2)	1.97 (2)	2.7781 (13)	160.1 (17)

Symmetry codes.

⁺ –*x*, –*y*, –*z*.

⁺ *x*, *y* – 1, *z*.

Table 3
Bond lengths and angles for the complex (Å, °).

K1–O4	2.6652 (10)	O2–K1 ^{vii}	2.8493 (9)
K1–O3	2.7683 (9)	O2–K1 ^{iv}	2.8972 (10)
K1–O4 ⁱ	2.7819 (10)	O2–N1	1.2484 (14)
K1–O1 ⁱⁱ	2.8308 (9)	O1–N1	1.2430 (14)
K1–O2 ⁱⁱⁱ	2.8493 (9)	O3–C4	1.2891 (14)
K1–O3 ^{iv}	2.8704 (9)	N1–C1	1.4187 (15)
K1–O2 ^v	2.8972 (10)	C1–C6	1.3983 (17)
K1–O1 ^v	2.9813 (10)	C1–C2	1.4006 (16)
O1–K1 ⁱⁱ	2.8309 (9)	C2–C3	1.3735 (17)
O1–K1 ^{iv}	2.9813 (10)	C3–C4	1.4293 (16)
O3–K1 ⁱ	2.8705 (9)	C4–C5	1.4292 (16)
O4–K1 ^{iv}	2.7819 (10)	C5–C6	1.3693 (17)
O4–K1–O3	146.88 (3)	O3 ^{iv} –K1–O1 ^v	72.43 (3)
O4–K1–O4 ⁱ	135.11 (3)	O2 ^v –K1–O1 ^v	43.26 (3)
O3–K1–O4 ⁱ	77.05 (3)	N1–O1–K1 ⁱⁱ	161.62 (8)
O4–K1–O1 ⁱⁱ	73.16 (3)	N1–O1–K1 ^{iv}	93.89 (7)
O3–K1–O1 ⁱⁱ	126.34 (3)	K1 ⁱⁱ –O1–K1 ^{vii}	88.22 (2)
O4 ⁱ –K1–O1 ⁱⁱ	85.21 (3)	N1–O2–K1 ^{vii}	149.50 (8)
O4–K1–O2 ⁱⁱⁱ	74.97 (3)	N1–O2–K1 ^{iv}	97.82 (7)
O3–K1–O2 ⁱⁱⁱ	76.12 (3)	K1 ^{vii} –O2–K1 ^{iv}	94.89 (3)
O4 ⁱ –K1–O2 ⁱⁱⁱ	147.90 (3)	C4–O3–K1	106.54 (7)
O1 ⁱⁱ –K1–O2 ⁱⁱⁱ	96.75 (3)	C4–O3–K1 ⁱ	122.55 (7)
O4–K1–O3 ^{iv}	77.20 (3)	K1–O3–K1 ⁱ	91.71 (2)
O3–K1–O3 ^{iv}	130.91 (3)	K1–O4–K1 ^{iv}	95.94 (3)
O4 ⁱ –K1–O3 ^{iv}	58.85 (3)	O1–N1–O2	120.96 (10)
O1 ⁱⁱ –K1–O3 ^{iv}	73.39 (3)	O1–N1–C1	119.66 (10)
O2 ⁱⁱⁱ –K1–O3 ^{iv}	152.11 (3)	O2–N1–C1	119.36 (10)
O4–K1–O2 ^v	72.63 (3)	C6–C1–C2	120.99 (11)
O3–K1–O2 ^v	89.17 (3)	C6–C1–N1	119.41 (10)
O4 ⁱ –K1–O2 ^v	111.82 (3)	C2–C1–N1	119.56 (11)
O1 ⁱⁱ –K1–O2 ^v	143.95 (3)	C3–C2–C1	119.46 (11)
O2 ⁱⁱⁱ –K1–O2 ^v	85.11 (3)	C2–C3–C4	121.43 (11)
O3 ^{iv} –K1–O2 ^v	88.25 (3)	O3–C4–C5	121.71 (11)
O4–K1–O1 ^v	107.77 (3)	O3–C4–C3	121.31 (10)
O3–K1–O1 ^v	72.57 (3)	C5–C4–C3	116.98 (10)
O4 ⁱ –K1–O1 ^v	69.23 (3)	C6–C5–C4	121.54 (11)
O1 ⁱⁱ –K1–O1 ^v	144.549 (14)	C5–C6–C1	119.60 (11)
O2 ⁱⁱⁱ –K1–O1 ^v	118.04 (3)		

Symmetry codes.

ⁱ –*x*, *y* + 1/2, –*z* + 1/2.

ⁱⁱ –*x* + 1, –*y*, –*z* + 1.

ⁱⁱⁱ –*x* + 1, *y* – 1/2, –*z* + 1/2.

^{iv} –*x*, *y* – 1/2, –*z* + 1/2.

^v *x* – 1, –*y* + 1/2, *z* – 1/2.

^{vi} *x* + 1, –*y* + 1/2, *z* + 1/2.

^{vii} –*x* + 1, *y* + 1/2, –*z* + 1/2.

for 4 h at 358 K. An intense light brown coloration appeared immediately. After one week, well-formed light brown crystals grew on the walls. A single crystal of dimensions 0.33 × 0.23 × 0.16 mm³ was selected from mother liquor and mounted for X-ray diffraction study at low temperature.

Yield: 88%, color: light brown, M.p.: 127 °C. Anal. (%) Found (Calculated for C₆H₆KNO₄): C 36.95(36.92), H 3.10(3.07), N 7.18(7.20). ¹H NMR (δ , ppm): 6.25–7.55 (4H, Ar–H). ¹³C NMR (δ , ppm): 115.20–149.10 (Ar–C). Mass Spectrum (LC/MS APCI): *m/z* 196 [M+1]⁺ (40%), 195 [M]⁺ (100%). FTIR (KBr, cm⁻¹): 2960 ν (C–H)_{aromatic}, 1455 ν (NO₂), 1345 ν (phenolic C–O). UV–vis (λ_{max} (ϵ_{max}), nm). EtOH; 344(0.42 × 10³), 459(0.36 × 10³), MeOH; 319(1.19 × 10³), 449(0.61 × 10³), DMF, 316(0.67 × 10³), 448(0.35 × 10³), Ethylacetate; 349(0.19 × 10³), 454(0.13 × 10³).

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