A uranium (VI) complex: Synthesis, structural and thermal kinetic analysis

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A B S T R A C T

A new complex $[UO_2(2,6-DNP)_2phen]$ (**1**) $(2,6-DNP = 2,6-dinitrophenol, phen = 1,10-phenanthroline)$ was synthesized, and identified by elemental analysis, IR, Powder XRD and single crystal X-ray crystallography. Crystal structure provides the abundant information's about the bonding and geometry around the U(VI) metal center. The thermal decomposition was studied by TG—DSC, and the kinetics of thermolysis was investigated by applying model fitting as well as isoconversional methods. Explosion delay measurement (D_e) was also evaluated to determine the response of this complex under the condition of rapid heating.

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1. Introduction

Due to participation in bonding with high coordination number and offer better reactivity modes, actinide coordination chemistry has received much attention in the recent years [1—4]. Uranium(VI) is the most stable oxidation state of uranium, and form linear dioxo cation $[O=U=O]^{2+}$ with two double bonded oxygen atoms, which is present in the majority of known uranium compounds [5,6]. UO_2^{2+} ion is typically coordinated by other −O and −N containing organic ligands and give the complexes with variety of coordination numbers [7]. In past, some uranyl-organic coordination complexes have been discovered because of their kinetic and thermodynamic stability [8], but the uranium complexes with polynitro aromatic compounds and their explosive behavior are not reported in literature yet now. It is well established that the aromatic compounds undergo rapid thermal decomposition in presence of nitro groups because of oxidizing tendency of nitrates, and give oxygen as one of the major product on decomposition at elevated temperature [9,10]. Metal salts with nitro phenols as high energetic materials have been the subject of fairly extensive investigation of various aspects [11—15]. Presence of two nitro groups in 2,6−dinitrophenol (2,6−DNP) makes it an energetic compound. 2,6−DNP coordinates in different ways, and its coordination behavior changes in presence of secondary ligand in same solution. N−heterocyclic compounds are selected as one of the secondary components because they have higher heat of formation, density, and oxygen balance. Due to these interesting features, 2,6−DNP and 1,10−phenanthroline are used for the preparation of uranium complex [16]. Such high energetic complexes may be further used for the variety of defense, security, civilian and peaceful applications [17]. In the present work, I synthesized a new U(VI) complex with 2,6−dinitrophenol and 1,10−phenanthroline, its structural characterization, and mechanism of thermolysis. The purpose of this work is to see the coordination behaviour of these ligands around the uranium metal centre, and also see the effect on thermal and explosive properties of the complex.

2. Experimental

2.1. Materials

The reaction was performed under aerobic condition using commercial grade solvent. 1,10-phenanthroline was commercially available from SD Fine Chem. Pvt. Limited, Bangalore, whereas 2,6-dinitrophenol and $UO_2(NO_3)_2.6H_2O$ of the highest grade were purchased from Aldrich Chem. Co. USA.

2.2. Synthesis of complex (**1**)

10.0 ml methanolic solution of $UO_2(NO_3)_2.6H_2O$ (0.25 g, 0.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) was added

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dropwise to the 5.0 ml methanolic solution of 2,6-DNP (0.09 g, 0.5 mmol), whose pH was adjusted at 6–7 (1.0 M NaOH solution). The reaction mixture was further stirred for 24 h at room temperature. The precipitates were filtered, and washed with methanol several times. Square shaped yellow crystals were obtained from slow evaporation of solvent in 73.7% (0.60 g, 0.73 mmol) yield. Elemental analysis for $C_{24}H_{14}N_6O_{12}U$ (816.44), Calculated (%): C, 35.30; H, 1.73; N, 10.29. Found (%): C, 34.93; H, 1.64; N, 10.11. IR (KBr, cm^{-1}): 1631 (C=C str, Ar), 1587 (C=N str, phen), 1537, 1490, 1384 and 1334 (N=O str, Ar–NO_2), 904 (N–O str, NO_2), 839 and 731 (C–H def, phen).

2.3. Instrumentation

Crystallized complex was carefully dried under vacuum for several hours prior to elemental analysis on Elementar Vario EL III analyzer. For the IR analysis, a transparent pellet was prepared by mixing the complex **1** with KBr, and the spectrum was recorded on a Varian 3100 FT–IR spectrometer as percentage transmittance against wavenumber (4000-500 cm^{-1}). Powder X-ray diffraction (PXRD) data was recorded on Rigaku MiniFlex 600 XRD diffractometer using Cu Kα_1 radiation ($\lambda = 1.5406$ Å) for the scan range of 5–50° (2θ) with a scan speed of 5 deg/min.

2.4. X-ray crystallographic study

The diffraction data was collected on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71070$ Å). Lorentz-Polarization correction was executed by SMART/SAINT program [18], while the empirical absorption correction was implemented through SADABS program [19]. SHELXTL program was accomplished for structure solution, refinement and data output [20,21]. All non-hydrogen atoms were refined by anisotropic displacement coefficients, while hydrogen atoms were placed in geometrically calculated positions with riding model. DIAMOND and MERCURY software's were adopted for draw

Table 1
Crystal data and structure refinement parameters of complex **(1)**.

Complex	$[UO_2(2,6-DNP)_2phen]$
formula	$C_{24}H_{14}N_6 O_{12}U$
Crystal habit	Square
Crystal color	Yellow
Formula weight	816.44
Crystal System	Triclinic
Space Group	P-1
a (Å)	8.989(16)
b (Å)	11.003(2)
c (Å)	13.935(3)
α (°)	101.454(11)
β (°)	98.032(10)
γ (°)	106.119(9)
V(Å^3)	1269.6(4)
Z	2
Temperature	296(2)
D_{Calc} (g/cm^3)	2.136
μ(Mo K$_\alpha$) (cm^{-1})	6.473
F(000)	776
Crystal size	0.23 × 0.22 × 0.18
Theta for data collection(°)	1.99-33.02
No. of measured reflections	9377
No. of observed reflections	7219
Data/restraints/parameters	9377/0/388
Goodness-of-fit	0.933
Final R indices[$I > 2(I)$ R$_1^a$	0.0300
wR$_2^b$	0.0611

$^a R_1 = \sum ||F_o|-|F_c|| / \sum |F_o|$, $^b wR_2 = \{\sum [w (F_o^2 - F_c^2)^2]/\sum w (F_o^2)^2$.

the images and elaborate the hydrogen bonding interactions [22,23]. The crystallographic data, elected bond lengths and bond angles are indexed in Tables 1 and 2.

2.5. Thermal analysis

2.5.1. TG-DSC and isothermal TG
Thermogravimetry and differential scanning calorimetry (TG-DSC) were performed on Perkin Elmer's Pyris Diamond at 10 °C/min (mass 55.0 mg) in air. The isothermal TG studies (mass 33.0 mg) were carried out at appropriate temperatures 250–290 °C for complex **1** in static air using indigenously fabricated TG apparatus [24].

2.5.2. Explosion delay measurements and percent oxygen balance
Tube furnace technique was used to record the explosion delay (D_e) data of complex **1** (mass 20.0 mg) in the temperature range 430–470 °C (±1 °C). Each run was repeated five times to calculate the mean D_e value. The D_e data can be used in the following equation [16,25,26].

$$D_e = A\, e^{Ea^*/RT} \tag{1}$$

Where E_a^* is the activation energy for thermal explosion, A is the pre-exponential factor and T is the absolute temperature. E_a^* was calculated from the slope of a plot of ln (D_e) vs. $1/T$.

The percent oxygen balance (OB) was determined by following equation [27].

$$OB = -1600(2x + y/2 + M - z)/\text{molecular weight} \tag{2}$$

Where x, y and z are the respective number of atoms of C, H, O, respectively, and M is the number of metal atom.

2.6. Kinetics analysis of isothermal TG data

It is based on a single step kinetic equation [28].

$$d\alpha/dt = k(T)\, f(\alpha) \tag{3}$$

Where t, T,α, $k(T)$ and $f(\alpha)$ represent time, temperature, extent of conversion ($0 < \alpha < 1$), rate constant and the reaction model, respectively [29]. It illustrates that the reaction rate depends upon the extent of conversion, which is experimentally calculated from the weight loss in TG experiments. The temperature dependence of $k(T)$ may be explained by the Arrhenius equation, whose substitution into Eq. (3) gives

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **(1)**.

Bond length			
U1—N1	2.556(15)	U1—O3	2.306(14)
U1—N2	2.582(9)	U1—O4	2.490(12)
U1—O1	1.763(9)	U1—O5	2.255(13)
U1—O2	1.766(9)		
Bond Angle			
N1—U1—N2	63.45(9)	O1—U1—N1	91.32(11)
O1—U1—O2	177.14(12)	O1—U1—N2	84.18(11)
O1—U1—O3	91.20(12)	O2—U1—N1	85.84(10)
O1—U1—O4	88.89(11)	O2—U1—N2	94.85(11)
O1—U1—O5	95.19(12)	O3—U1—N1	85.33(8)
O2—U1—O3	88.22(10)	O4—U1—N1	152.64(9)
O2—U1—O4	93.47(11)	O3—U1—N2	148.22(9)
O2—U1—O5	87.17(9)	O4—U1—N2	143.61(9)
O3—U1—O4	67.32(9)	O5—U1—N1	138.07(8)
O5—U1—O3	135.70(8)	O5—U1—N2	76.07(7)
O5—U1—O4	69.04(8)		