Research Article

Investigation on the Synthesis and Photocatalytic Property of Uranyl Complexes of the β -Diketonates Biscatecholamide Ligand

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A series of uranyl complexes have been synthesized by reacting hexadentate ligands $\text{CH}_2[\text{COO}(\text{CH}_2)_n\text{CAM}]_2$ [$\text{CAM} = 2,3\text{-Ph}(\text{OH})_2\text{CONH}$] containing the catecholamide (CAM) group and β -diketonates framework with uranyl nitrate. They were characterized by FTIR, UV-vis, ^1H NMR, XPS, TGA, and elemental analysis. The analysis revealed that oxygen atom of β -diketonate did not bind to uranyl ion in complexes 1–3. The photocatalytic degradation properties of the target complexes for degradation of rhodamine B (RhB) were investigated. The result indicated that approximately 74%, 71%, and 67% RhB were degraded in the presence of complexes 1–3 after about 210 min, respectively. Consequently, complexes 1–3 have excellent photocatalytic degradation property.

1. Introduction

In recent years, uranyl complexes have attracted much attention for exploring reactivity and coordination behavior of 5f-elements, developing suitable trivalent actinide (An(III)) extractants for nuclear remediation [1], screening highly effective chelators structure for decorporation of trivalent actinide (An(III)) [2], and investigating applications in the fields of catalysis, ion exchange, sensors, and photochemistry [3–5].

At present, a large number of uranyl complexes have been synthesized due to their diversified property. Nevertheless, the characteristics of organic ligands play a key role in formation process of the uranyl complexes. Multidentate β -diketonates biscatecholamide ligands [6] have six binding sites due to the O-donor of catechol aromatic ring and β -diketonates [7, 8]. As an important chelator for decorporation of uranyl ion, catechol has the favorable stability constant [9,

10]. The β -diketonates compounds were adequate sensitizers to luminescent lanthanide complexes in which either visible or NIR emission is consecutive with photoinduced energy transfer from the sensitizing ligand [11]. The β -diketonates catecholamide ligands (H_4L^{1-3}) have been reported as efficient uranyl sequestration agents in neutral pH aqueous media [6], but the detailed functional properties of their uranyl complexes have not been studied.

Since early 1800s, the photocatalytic behavior of uranyl complexes has attracted considerable attention. In general, the equatorial plane can be formed between the coordinated atom and the uranyl ion, which appeared to be bulky conjugate system surrounding the rigid rings of ligands centered in uranyl [12]. Then excitation of these species can result in $^*\text{UO}_2^{2+}$, which is very active and can trigger a variety of redox reactions to decompose the dye molecules [13, 14]. As compared to TiO_2 , the excited electrons of dye molecules are injected into TiO_2 to decompose the dye molecules [15, 16].

It is generally accepted that, in the photocatalytic reaction, the excitation of uranyl complexes is much more efficient than that of the dye molecules. So, we design the new uranyl- β -diketonates biscatecholamide complexes ($\text{UO}_2\text{L}^{1-3} \cdot 2\text{H}_2\text{O}$), which may have efficient photocatalytic property. In this paper, three complexes $\text{UO}_2\text{L}^{1-3} \cdot 2\text{H}_2\text{O}$ have been successfully synthesized in the presence of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and β -diketonates biscatecholamide ligand. These complexes were characterized by FTIR spectra, UV-vis spectra, ^1H NMR, XPS spectra, and elemental analysis. Then photocatalytic degradation properties of the complexes were also investigated by RhB as model compound of organic pollutant.

2. Experimental

2.1. Materials and Methods. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%) was purchased from commercial products from HuBei ChuShengWei Chemistry Co., Ltd. All the organic reagents were pure commercial products from Aladdin. The solvents were purchased from Chengdu Kelong Chemical Reagents Co. The 300–400 mesh silica gel was purchased from Qingdao Hailang. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 600 spectrometer. The FTIR spectra were obtained from Thermo Scientific Nicolet 380 FTIR spectrophotometer. The UV-vis spectra were obtained from Thermo Scientific Evolution 300 spectrophotometer. The XPS spectra were obtained from Thermo ESCALAB 250 electron spectrometer. Mass spectral analyses were conducted using Varian 1200 LC/MS. Elemental analyses of the complexes were carried out on a Vario EL III CHNS analyzer.

2.2. Synthesis of the Ligands. A solution of malonyl dichloride (1.0 mmol) in CH_2Cl_2 (20 mL) was dropped in the solution of 2,3-bis(benzyloxy)-*N*-(hydroxyalkyl)benzamide (2.0 mmol) and Et_3N (2.0 mL) in CH_2Cl_2 (20 mL) under ice bath and vigorous stirring conditions. After evaporation of the solvent, the residue was purified by flash column chromatography. Then deprotection of the hydroxyl groups under H_2 and Pd/C catalytic conditions in THF resulted in the β -diketonates biscatecholamide ligands H_4L^{1-3} [6].

Bis(2,3-bis(hydroxy)-N-(hydroxyethyl)benzamide)malonate (H_4L^1). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.90 (br s, 2H, CO-NH), 7.25 (dd, J = 7.8, 1.2 Hz, 2H, Ar-H), 6.91 (dd, J = 7.8, 1.2 Hz, 2H, Ar-H), 6.67 (t, J = 7.8 Hz, 2H, Ar-H), 4.20 (t, J = 5.7 Hz, 4H, $-\text{CH}_2-$), 3.52 (m, 6H, CO- CH_2 -CO and $-\text{CH}_2-$). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ = 170.4 (C=O), 166.9 (C=O), 150.0 (ArC), 146.7 (ArC), 119.2 (ArCH), 118.4 (ArCH), 117.8 (ArCH), 115.3 (ArC), 63.6 ($-\text{CH}_2-$), 41.5 ($-\text{CH}_2-$), 38.3 ($-\text{CH}_2-$). FTIR (KBr, cm^{-1}): 3398, 2957, 2929, 1750, 1731, 1642, 1590, 1546, 1459. UV-vis (DMSO, nm): 248, 319. APCI-MS (m/z): 463.2 [$\text{M}+\text{H}$] $^+$.

Bis(2,3-bis(hydroxy)-N-(3-hydroxypropyl)benzamide)malonate (H_4L^2). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 12.74 (br s, 2H, Ar-OH), 9.17 (br s, 2H, Ar-OH), 8.84 (br s, 2H, CO-NH), 7.26 (dd, J = 7.8, 1.2 Hz, 2H, Ar-H), 6.90 (dd, J =

7.8, 1.2 Hz, 2H, Ar-H), 6.67 (t, J = 7.8 Hz, 2H, Ar-H), 4.13 (t, J = 6.4 Hz, 4H, $-\text{CH}_2-$), 3.51 (s, 2H, CO- CH_2 -CO), 3.34 (m, 4H, $-\text{CH}_2-$), 1.87 (m, 4H, $-\text{CH}_2-$). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ = 169.8 (C=O), 166.5 (C=O), 149.6 (ArC), 146.2 (ArC), 118.8 (ArCH), 117.8 (ArCH), 117.1 (ArCH), 114.9 (ArC), 62.8 ($-\text{CH}_2-$), 41.2 ($-\text{CH}_2-$), 35.8 ($-\text{CH}_2-$), 27.9 ($-\text{CH}_2-$). FTIR (KBr, cm^{-1}): 3390, 2956, 1747, 1735, 1641, 1591, 1547, 1459. UV-vis (DMSO, nm): 246, 320. APCI-MS (m/z): 491.1 [$\text{M}+\text{H}$] $^+$.

Bis(2,3-bis(hydroxy)-N-(4-hydroxybutyl)benzamide)malonate (H_4L^3). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.80 (br s, 2H, CO-NH), 7.26 (dd, J = 7.8, 1.2 Hz, 2H, Ar-H), 6.99 (dd, J = 7.8, 1.2 Hz, 2H, Ar-H), 6.66 (t, J = 7.8 Hz, 2H, Ar-H), 4.09 (t, J = 6.3 Hz, 4H, $-\text{CH}_2-$), 3.50 (s, 2H, CO- CH_2 -CO), 3.29 (dd, J = 12.5, 6.3 Hz, 4H, $-\text{CH}_2-$), 1.59 (m, 8H, $-\text{CH}_2-\text{CH}_2-$). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ = 169.7 (C=O), 166.6 (C=O), 149.6 (ArC), 146.2 (ArC), 118.7 (ArCH), 117.8 (ArCH), 117.0 (ArCH), 114.9 (ArC), 64.5 ($-\text{CH}_2-$), 41.1 ($-\text{CH}_2-$), 38.3 ($-\text{CH}_2-$), 25.5 ($-\text{CH}_2-$), 25.2 ($-\text{CH}_2-$). FTIR (KBr, cm^{-1}): 3399, 2926, 1745, 1735, 1639, 1594, 1545, 1459. UV-vis (DMSO, nm): 248, 322. APCI-MS (m/z): 519.7 [$\text{M}+\text{H}$] $^+$.

2.3. Synthesis of Uranyl Complexes

Caution! Even though the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ used in this study contains depleted uranium, standard precautions for handling radioactive substances should be followed.

A solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (55.2 mg, 0.11 mmol) in methanol was added to a methanol solution of a β -diketonates biscatecholamide ligands H_4L^{1-3} (0.1 mmol) with stirring. The colorless ligand solution immediately turned orange and shown a strong acidic reaction to pH paper, indicating the formation of a uranyl complex. Following the addition of 1 or 2 drops of pyridine the transparent reaction mixture became turbid. The solution was then heated at reflux overnight, under nitrogen. The uranyl complexes deposited as orange precipitates, which were collected by centrifugation, washed with methanol, and dried in a vacuum oven and obtained orange power.

$\text{UO}_2\text{L}^1 \cdot 2\text{H}_2\text{O}$ Complex (1). Yield 72%. The ^1H NMR spectra of $\text{DMSO}-d_6$ at room temperature show that the complex contains the major and minor species (possibly isomers); the ratio was about 5.2 : 1. ^1H NMR (600 MHz, $\text{DMSO}-d_6$, major species): δ = 10.03 (d, J = 9.4 Hz, 2H, CO-NH), 7.13–7.03 (m, 2H, *ortho* cat-H), 6.98–6.88 (m, 4H, *meta* and *para* cat-H), 5.18 (dd, J = 23.8, 12.1 Hz, 2H, $-\text{CH}_2-$), 4.78 (d, J = 11.9 Hz, 2H, $-\text{CH}_2-$), 4.00 (t, J = 12.0 Hz, 2H, $-\text{CH}_2-$), 3.63 (d, J = 14.2 Hz, 2H, $-\text{CH}_2-$), 2.83 (d, J = 17.0 Hz, 1H, $0.5 \times -\text{COCH}_2\text{CO}-$), 1.71 (d, J = 17.0 Hz, 1H, $0.5 \times -\text{COCH}_2\text{CO}-$). ^1H NMR (600 MHz, $\text{DMSO}-d_6$, minor species): δ = 10.92 (s, 2H, CO-NH), 7.67 (d, J = 7.5 Hz, 2H, *ortho* cat-H), 7.44 (d, J = 7.7 Hz, 2H, *para* cat-H), 6.67 (t, J = 7.8 Hz, 2H, *meta* cat-H), 4.97 (b, 2H, $-\text{CH}_2-$), 4.55 (b, 2H, $-\text{CH}_2-$), 4.21 (b, 2H, $-\text{CH}_2-$), 3.93 (m, 2H, $-\text{CH}_2-$), 3.07 (d, J = 17.3 Hz, 1H, $0.5 \times -\text{COCH}_2\text{CO}-$), 2.83 (d, J = 17.3 Hz, 1H, $0.5 \times -\text{COCH}_2\text{CO}-$). FTIR (KBr, cm^{-1}): 3397, 1746, 1587, 1546, 1461, 1439, 1350, 1309, 1217, 927, 550. UV-vis (DMSO, nm): 258, 328. Anal. Calcd. for $\text{UO}_2\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_{11}$ (746.40): C, 33.76; H, 2.68; N, 3.75. Found: C, 34.76; H, 2.51; N, 3.69.

FIGURE 1: The UV-vis spectra of (a) the free ligands H_4L^{1-3} and (b) complexes 1–3.

$UO_2L^2 \cdot 2H_2O$ Complex (2). Yield 70%. The 1H NMR spectra of in $DMSO-d_6$ at room temperature show that the complex contains the major and minor species (possibly isomers); the minor species signals are too weak to assign. 1H NMR (600 MHz, $DMSO-d_6$, major species): δ = 10.07 (s, 2H, CO-NH), 7.04 (m, 2H, *ortho* cat-H), 6.93 (m, 4H, *meta* and *para* cat-H), 4.60–4.10 (m, 4H, $-CH_2-$), 4.04–3.78 (m, 4H, $-CH_2-$), 3.18 (d, J = 5.3 Hz, 2H, $-COCH_2CO-$), 2.29–1.97 (m, 4H, $-CH_2-$). FTIR (KBr, cm^{-1}): 3367, 1742, 1588, 1546, 1461, 1444, 1346, 1307, 1217, 929, 550. UV-vis ($DMSO$, nm): 259, 328. Anal. Calcd. for $UO_2C_{23}H_{24}N_2O_{11}$ (774.46): C, 35.64; H, 3.09; N, 3.62. Found: C, 36.71; H, 2.96; N, 3.59.

$UO_2L^3 \cdot 2H_2O$ Complex (3). Yield 74%. The 1H NMR spectra of in $DMSO-d_6$ at room temperature show that the complex contains the major and minor species (possibly isomers); the ratio was about 4.1 : 1. 1H NMR (600 MHz, $DMSO-d_6$, major species): δ = 10.04 (br s, 2H, CO-NH), 7.15–7.04 (m, 2H, *ortho* cat-H), 6.91 (m, 4H, *meta* and *para* cat-H), 4.10 (m, 4H, $-CH_2-$), 3.94 (m, 4H, $-CH_2-$), 3.19 (d, J = 16.0 Hz, 1H, $0.5 \times -COCH_2CO-$), 3.08 (d, J = 16.0 Hz, 1H, $0.5 \times -COCH_2CO-$), 1.78–1.56 (m, 8H, $-CH_2CH_2-$). 1H NMR (600 MHz, $DMSO-d_6$, minor species): δ = 10.54 (br s, 2H, CO-NH), 7.52 (dd, J = 7.6, 1.7 Hz, 2H, *ortho* cat-H), 7.49 (dd, J = 7.9, 1.7 Hz, 2H, *para* cat-H), 6.66 (t, J = 7.8 Hz, 2H, *meta* cat-H), 4.55 (m, 8H, $-CH_2-$), 2.61 (s, 1H, $0.5 \times -COCH_2CO-$), 2.38 (s, 1H, $0.5 \times -COCH_2CO-$), 1.91–1.79 (m, 8H, $-CH_2CH_2-$). FTIR (KBr, cm^{-1}): 3390, 1742, 1588, 1546, 1461, 1444, 1342, 1309, 1218, 927, 550. UV-vis ($DMSO$, nm): 259, 326. Anal. Calcd. for $UO_2C_{25}H_{28}N_2O_{11}$ (802.51): C, 37.38; H, 3.49; N, 3.49. Found: C, 38.45; H, 3.41; N, 3.43.

3. Results and Discussion

3.1. UV-Vis Spectra Analysis. The UV-vis spectra of the ligands H_4L^{1-3} and their corresponding target uranyl complexes 1–3 were recorded in $DMSO$ solution (Figure 1), and the data were summarized in Table 1. It was shown from Table 1

TABLE 1: UV-vis spectra data of the ligands and of target complexes.

Ligands	λ_{max} (nm)	Uranyl complex	λ_{max} (nm)
H_4L^1	248, 319	Complex 1	258, 328
H_4L^2	246, 320	Complex 2	259, 328
H_4L^3	248, 322	Complex 3	259, 326

that all free ligands $\pi \rightarrow \pi^*$ transitions absorption bands were in the range of 246–248 nm and $n \rightarrow \pi^*$ transitions absorption bands in the range of 319–322 nm. It was found that the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of complexes were slightly red-shifted as compared to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of ligands H_4L^{1-3} and had absorptions in the visible regions (380–450 nm), which was ascribed to charge transfer within the $U=O$ double bonds and the ligand to metal charge transfer (LMCT) between the oxygen atoms of the coordinating ligands and the empty orbital of the uranyl ion [17–19]. These results show that the H_4L^{1-3} take part in coordination with uranyl ion.

3.2. FTIR Spectra Analysis. The FTIR spectra of the ligands H_4L^{1-3} and their corresponding target uranyl complexes were recorded in the region 4000–400 cm^{-1} , which were studied to obtain information on the oxygen-to-uranyl coordination from the shift of the C–O stretching with respect to the nonbonded ligands. Since the FTIR spectra of all ligands have shown similar features, the FTIR spectra of ligands H_4L^1 as well as their corresponding complex 1 were selected for illustration for comparison reasons shown in Figure 2(a) and all complexes 1–3 are shown in Figure 2(b). The selected vibrations of the ligands H_4L^{1-3} and their corresponding complexes studied, together with the suggested assignments, were listed in Table 2.

As shown in Table 2, the bands at 1746–1750 cm^{-1} for the free ligands were assigned to the C=O stretching vibration of β -diketonate and the bands at 1742–1746 cm^{-1} for the

FIGURE 2: The FTIR spectra of (a) the free ligand H_4L^1 and complex 1 and (b) complexes 1–3.

TABLE 2: The FTIR spectral frequencies (cm^{-1}) and tentative assignments for the free ligands and uranyl complexes.

H_4L^1	Complex 1	H_4L^2	Complex 2	H_4L^3	Complex 3	Assignment of vibration
3398	3379	3397	3367	3400	3390	$\nu(OH)$
3104, 2957	3103, 2961	3094, 2956	3101, 2958	3083, 2927	3102, 2954	$\nu(C-H)$
1750	1746	1747	1742	1746	1742	$\nu(C=O)$ (β -diketonate)
1643	1588	1641	1587	1640	1587	$\nu(C=O)$
1547	1546	1547	1546	1546	1546	$\delta(C-N-H)$
1488	1461	1487	1461	1487	1461	$\delta(CH_2)$ s
1460	1439	1460	1444	1460	1444	$\delta(CH_2)$ s
1364	1367	1361	1384	1361	1384	$\delta(O-H)$
1337	1350	1337	1346	1334	1342	$\nu(C-N)$
—	1309	—	1307	—	1309	$\nu(C-N)$ and $\delta(N-H)$
1266	1260	1266	1256	1266	1256	$\nu(C-O)$
—	1217	—	1217	—	1218	$\nu(C-O-U)$
1178	1174	1177	1173	1171	1171	$\nu_{as}(C-O-C)$
1156	1157	1158	—	1157	—	$\delta(C-O)$
1073	1091	1072	1090	1069	1089	$\nu_s(C-O-C)$
1038	1039	1038	1052	1045	1053	$\delta(C-H)$
—	927	—	929	—	927	$\nu(U=O)$ as
845	856	834	847	842	853	$\delta(C-H)$
767, 743	783, 740	786, 743	793, 742	775, 742	788, 743	$\delta(C-H)$ (benzene ring)
—	550	—	550	—	550	$\nu(U=O)s$

corresponding complexes; there is hardly any red shifts to form enol tautomers in complexes [7, 20–22], which confirmed that oxygen atoms of carbonyl group of β -diketonate did not bind to uranyl ion. The bands at 1640–1643 cm^{-1} were assigned to the C=O stretching vibration of amide groups of free ligands, which shifted to 1588 cm^{-1} in its corresponding complexes; meanwhile, the peaks at 1266 cm^{-1} were attributed to the C-O stretching vibration of catechol units shifted to 1256–1260 cm^{-1} for their complexes, which indicated that oxygen atoms of phenolic hydroxyl take part in coordination with uranyl ion. In addition, the characteristic

absorption peaks of C-N groups at 1334–1337 cm^{-1} shifted to 1342–1350 cm^{-1} in their corresponding complexes, showing formation of strong hydrogen bond between hydrogen atoms of amide groups and oxygen atoms of phenolic hydroxyls [23, 24]. Frequencies of the stretching and deformation vibrations of the C=C, C-H groups of the benzene rings were also observed. The FTIR spectra of all complexes show strong absorption bands between 927 and 929 cm^{-1} and weak absorption bands in 550 cm^{-1} . The bands at 927 and 550 cm^{-1} were assigned to the asymmetric stretching modes of the uranyl moiety [25–27]. Therefore, analytical results of the

FIGURE 3: Possible geometric isomers of uranyl complexes with two asymmetrically substituted catecholate ligands and uranyl oxo atoms omitted for clarity.

FTIR spectra indicated uranyl ion complexes were to be obtained.

3.3. Proton NMR Spectra Analysis. The development of H_4L^{1-3} evolved from the following considerations. The dialkyl malonates spacer not only provides two coordination sites but also enhances the less rigidity and preorientation of the compound and should therefore favor the encapsulation of a uranyl ion unit. Furthermore, model studies show that steric strain in the predisposed ligand reduces the number of possible geometric isomers. For an octahedral linear uranyl complex of an asymmetrically substituted catecholamide ligand there are two conceivable geometrical isomers as shown in Figure 3. So the room-temperature 1H NMR spectra of complexes 1–3 compared with free H_4L^{1-3} have shown complex splitting.

The 1H NMR spectra of all ligands and corresponding uranyl complexes have shown similar features. The complexes in $DMSO-d_6$ at room temperature have shown that the complexes contain the major and minor species (possibly isomers a and b, resp.). The 1H NMR spectra of H_4L^1 as well as their corresponding complex 1 were selected for illustration and shown in Figure 4. The resonance signals of amide protons of the major species isomers shifted from 8.90 ppm to 10.02 ppm, since the downfield chemical shifts of amide protons are generally interpreted in terms of strong hydrogen bonding [23, 24], as shown in Figure 3. The resonance signals of catechol protons of the major species isomers of complex 1 showing two peaks at 7.13–7.03 (m, 2H, *ortho* cat-H) and 6.98–6.88 (m, 4H, *meta* and *para* cat-H), compared with the free ligand H_4L^1 , have appreciable changes and downfield shifts of the aromatic proton resonances of the catechol rings. Similarly, the changes in the level of the signals of the protons of the linker were also shift, turning into complex splitting due to the proximity of the uranyl ion nearby the altered protons. The resonance signals of the methylene protons of the major species isomers showed four peaks at 5.18 (dd, $J = 23.8, 12.1$ Hz, 2H, $-CH_2-$), 4.78 (d, $J = 11.9$ Hz, 2H, $-CH_2-$), 4.00 (t, $J = 12.0$ Hz, 2H, $-CH_2-$), and 3.63 (d, $J = 14.2$ Hz, 2H, $-CH_2-$). And the active methylene of β -diketonates shows

TABLE 3: Binding energy (eV) of complexes 1–3 and splitting value of U 4f.

Uranyl complex	O 1s	C 1s	N 1s	U 4f _{5/2}	U 4f _{7/2}	Splitting value
Complex 1	531.26	284.26	399.66	392.46	381.66	10.80
Complex 2	531.71	284.71	399.62	392.43	381.61	10.82
Complex 3	531.66	284.66	399.61	392.41	381.51	10.90

FIGURE 4: The 1H NMR spectra of ligand H_4L^1 and of complex 1.

two double peaks at 2.83 (d, $J = 17.0$ Hz, 1H) and 1.71 (d, $J = 17.0$ Hz, 1H), but generally, metal complexes present a singlet peak at 5.0–8.0 ppm for the enol tautomers of β -diketonates [20, 28–30]. It confirmed that oxygen atom of β -diketonate did not bind to uranyl ion, also indicated by the FTIR spectra analysis.

3.4. XPS Spectra Analysis. The XPS spectra of the samples were conducted at 10 KV and 5 mA under 10^{-8} Pa residual pressure. The peak energies were corrected with C 1s peak at 284.6 eV as a reference. The recorded lines (C 1s, O 1s, N 1s, and U 4f) were fitted using the XPSpeak program after the background subtraction.

To study the interaction of uranyl with ligands H_4L^{1-3} , XPS spectra were recorded for complexes 1–3. The O 1s, C 1s, N 1s, U 4d, and U 4f spectra were shown in Figure 5. Uranyl coordination reaction was observed in complexes evidenced by the appearance of doublet peaks of U 4f_{5/2} and U 4f_{7/2} with a splitting value of 10.80–10.90 eV. The values of the binding energies of O 1s, C 1s, N 1s, U 4f_{5/2}, and U 4f_{7/2} and the splitting values of the U 4f spectra were shown in Table 3. The O 1s and U 4f spectra of complexes 1–3 were shown in Figure 6. The peak fitting results of the O 1s and U 4f were shown in Table 4. Because XPS is not a quantitative analysis method, these data could be used for semiquantitative analysis of the distribution of multicomponent [31, 32].

TABLE 4: The peak fitting results of the O 1s, U 4f_{7/2} of complexes 1–3.

Core levels	Complex 1			Complex 2			Complex 3		
	Binding energy (eV)	FWHM (eV)	Area	Binding energy (eV)	FWHM (eV)	Area	Binding energy (eV)	FWHM (eV)	Area
O 1s	533.85	1.31	1468.15	533.98	2.13	7315.93	534.34	1.10	1318.23
	533.10	1.42	6015.89	533.50	1.3	5996.96	533.56	0.87	2983.22
	532.60	1.08	6718.25	532.70	1.06	6697.41	532.78	0.99	5832.76
	532.10	1.14	7356.14	532.30	1.13	7107.48	532.22	1.01	6766.91
	531.45	1.21	16239.1	531.60	1.20	15224.1	531.47	1.2	13254.9
	530.65	1.52	8646.69	530.69	1.49	8633.66	530.47	1.58	8728.48
U 4f _{7/2}	384.49	3.78	12770.3	384.79	4.33	17262.9	384.80	4.12	13500.5
	382.10	2.63	36018.1	382.22	2.84	45319.6	382.20	2.74	38513.2

FIGURE 5: XPS survey scans of complexes 1–3.

As shown in Figure 6(a), it was observed that complexes 1–3 presented six main components O 1s spectra for oxygen functionalities. The six peaks position at 530.50–530.69 eV (O=U=O) [33, 34], 531.40–531.55 eV (C–O–U), 532.20–532.33 eV (C=O of β -diketonate), 532.60–532.80 eV (C–O–C), 533.40–533.50 eV (C=O of benzamide), and 533.90–534.00 eV (adsorbed H₂O) [35] was observed. And the relative intensities of C–O–U were significantly higher than other oxygen functionalities; meanwhile, the presence of the U=O bonds was confirmed, as expected.

The U 4f_{7/2} spectra were deconvoluted into two components: the peak corresponding to the free uranyl ion that occurred at 381.05 eV and the peak of complexes 1–3 that occurred at 382.10–382.22 eV, as shown in Figure 6(b).

From the above discussion, it is clear that the ligands H₄L^{1–3} complexation of uranyl ion occurred with the catecholamide moieties.

3.5. Thermal Properties. To examine the thermal stability of complexes 1–3, thermal gravimetric analysis (TGA) was carried out at a heating rate of 10°C min^{–1} under the conditions of N₂ atmosphere with the temperature range from

25 to 1100°C (Figure 7). The TGA curves of complexes 1–3 show two steps to weight loss. The first weight loss in the range of 120–220°C should be attributed to the loss of two coordinated water molecules with a percentage weight loss (obs. 5.1%, 4.9%, and 4.8%; calcd. 4.82%, 4.65%, and 4.49%) of complexes 1–3, respectively. The second weight loss in the range of 250–1050°C is attributed to the loss of biscatecholamide ligands with a percentage weight loss (obs. 55.1%, 57.6%, and 60.0%; calcd. 56.86%, 58.42%, and 59.87%) of complexes 1–3, respectively. The percentage weight of final residue was in good agreement with the calculated value by the stoichiometric chemical formula UO₃.

3.6. Photocatalytic Activity. As we know, methyl blue, methyl orange, and RhB dyes have been widely used in textile, printing, paper, and pharmaceutical industries, causing serious pollution to the environment at the same time [35–38]. In this work, we selected RhB as model compound of organic pollutant to investigate the degradation efficiency using complexes 1–3 as catalysts. To rule out the possibility that the photocatalytic activity of the complex arises from molecular or oligomeric species formed through dissolution of the solid samples in the photocatalytic reaction systems, control experiments were conducted. We subjected the catalysts to UV light and continuous stirring in water for 3 h and tested the photocatalytic activity of the solution after filtering off the solid materials. No catalytic activity was observed for the solution. Then filtrates residue was added into fresh RhB for catalysis testing. During the degradation process, a 15 W Hg lamp was used as the UV light source. 10 mg of catalyst was dispersed in 100 mL of 10 mg L^{–1} RhB solution under ultrasonication for 15 min. A UV-vis spectrophotometer was used to monitor the reaction under the wavelength of 554 nm and continuously at 30 min intervals until the reaction reached steady state.

Figures 8(a)–8(c) show that the intensity characteristic absorption of RhB had obviously decreased in the presence of complexes 1–3 by the UV light irradiation. As it is shown in Figure 9(a), for comparison, the self-degradation of RhB was also assessed under the same experimental conditions. It obviously revealed that, without the solid catalyst in the reaction system, the RhB hardly degraded in 210 min of

FIGURE 6: Curves fitted high resolution scans of (a) O 1s and (b) U 4f of complexes 1–3.

FIGURE 7: The thermal gravimetric analysis curves of (a) complex 1, (b) complex 2, and (c) complex 3.

FIGURE 8: (a) The UV-vis absorption spectra of RhB solution during the photodegradation reaction when complex 1 was used as catalyst; (b) the UV-vis absorption spectra of RhB solution during the photodegradation reaction when complex 2 was used as catalyst; (c) the UV-vis absorption spectra of RhB solution during the photodegradation reaction when complex 3 was used as catalyst; (d) the standard curve of RhB solution.

FIGURE 9: (a) Photocatalytic degradation; (b) photocatalytic degradation reaction of RhB under UV light irradiation over complexes 1–3.

irradiation under UV light, suggesting that the solution contains no photocatalytically active species. However, in the presence of complexes 1–3, the RhB in the solution is degraded approximately 74%, 71%, and 67%, respectively. From the photodegradation constant k in Figure 9(b), we can see that the performance of complexes 1–3 ($k = 7.1 \times 10^{-3}$, 6.5×10^{-3} , and $6.0 \times 10^{-3} \text{ min}^{-1}$, resp.) is higher than commercially available TiO_2 ($k = 5.9 \times 10^{-3} \text{ min}^{-1}$) [39]. The result indicated that the degeneration process was efficient. Meanwhile, complex 1 is higher than other complexes. Because complexes 1–3 are similar in coordination environment with similar accessibility to active uranyl centers, the higher efficiency is presumably due to the higher content of active uranyl centers in complexes 1–3 (36.2%, 34.9%, and 33.6%, resp.)

It is well known that the uranyl complexes could degrade the organic pollutants mainly due to the active uranyl centers. At present, two photodegradation mechanisms, hydrogen abstraction and electron transfer, have been generally accepted for the photocatalytic reactions involving uranyl species (Figure 10) [12]. Upon photoexcitation, electrons may be promoted from the HOMO to the LUMO to generate excited $^*\text{UO}_2^{2+}$ species. And the HOMO and LUMO were ascribed to occupied 2p orbitals of oxygen and the empty uranium orbitals, respectively. The excited electron in the LUMO was not stable; it may return to the HOMO instantly. However, if the electrons from organic molecules (such as RhB) could be abstracted by the $^*\text{UO}_2^{2+}$ species, resulting in organic intermediates and protons, the excited electrons in the uranyl unit would remain in the LUMO until they were captured by electronegative substances, such as O_2 in the solution. Once O_2 captured excited electrons, highly active peroxide anions could be formed. The organic intermediates were decomposed; as a result, peroxide anions further oxidize in the solution.

4. Conclusions

The β -diketonates bis catecholamide ligands H_4L^{1-3} were obtained via the reported procedure; their complexes with UO_2^{2+} were also prepared successfully and determined by the means of UV-vis spectra, FTIR spectra, ^1H NMR, and elemental analyses. The complex ^1H NMR spectra show that the uranyl complexes have two conceivable geometrical isomers. The photodegradation property of the target complexes was investigated by the RhB which is a model compound of organic pollutant. The results show that complexes 1–3 exhibit good photocatalytic property, which will be used as the promising candidate photocatalytic materials for nuclear organic waste treatment in nuclear industry.

Competing Interests

The authors declare no conflict of interests.

Authors' Contributions

Bo Jin and Qingchun Zhang conceived and designed the experiments; Qingchun Zhang and Xiaofang Wang performed the experiments; Qingchun Zhang, Zhaotao Shi, Shan Lei, Hua Liang, and Qiangqiang Liu analyzed the data; Rufang Peng and Bo Jin contributed reagents/materials/analysis tools; Qingchun Zhang and Bo Jin wrote the paper.

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FIGURE 10: Proposed photocatalytic reaction mechanism of RhB in the presence of a uranyl complex.

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