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Crystal Structure, Spectroscopy and Photocatalytic Properties of a Co(II) Complex Based on 5-(1,2,4-triazol-1-yl)pyridine-3-carboxylic Acid

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Abstract: A novel cobalt(II) complex, namely $[\text{Co}(\text{tpa})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (**1**) (Htpa = 5-(1,2,4-triazol-1-yl)pyridine-3-carboxylic acid) has been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Complex **1** was further characterized by elemental analysis, FTIR spectrum, electronic spectrum, X-ray powder diffraction and thermal gravimetric analysis. Structural analysis shows that complex **1** was stabilized via $\pi \cdots \pi$ stacking and hydrogen bonding interactions to give a 3D supramolecular framework. Hirshfeld surface analysis showed that $\text{O} \cdots \text{H}$ (29.5%), $\text{H} \cdots \text{H}$ (23.8%), $\text{N} \cdots \text{H}$ (21.5%) and $\pi \cdots \pi$ (8.6%) intermolecular contacts are the most important interactions in the crystal of **1**. In addition, the synthesized Co(II) complex showed favorable photocatalytic activity for the degradation of methyl orange (MO) under UV light at room temperature. The degradation process of MO was in accordance with the first-order reaction kinetics, and the $t_{1/2}$ for the reaction is 27.3 min, and the apparent rate constant is $k = 2.54 \times 10^{-2} \text{ min}^{-1}$.

Keywords: Co(II) complex; Hirshfeld surface analysis; photocatalysis; organic dye

1. Introduction

In the last few years, many metal–organic coordination compounds constructed by triazole ligands have been reported; some of them not only have charming molecular structures, but also promising physical properties [1–3]. In addition, the structure of coordination complexes will be influenced by the position of substituent groups in the ligands [4]. Recently, we have reported the structures, physical properties and intermolecular interaction analyses of several transition metal complexes derived from a series of rigid triazole-benzoic acid ligands [5,6].

Synthetic dyes used in the textile, leather and printing industry are difficult to degrade due to their stable molecular structure, and some of them are known to be toxic to the human body [7,8]. Common organic dyes, such as methylene blue (MB), congo red (CR), and methyl orange (MO) are widely used in textile, printing and packaging industries and have caused serious natural water pollution. Although different water treatment techniques have been developed to deal with dye pollution, photocatalytic degradation seemed to be the most promising method [8]. Therefore, the synthesis of efficient and environmentally friendly photocatalysts has attracted ever-increasing attention [9,10]. TiO_2 and ZnO-based semiconductor materials are the most widely used photocatalysts in recent decades [11,12]. However, the main drawback for these materials is the fast recombination of electrons and hole pairs generated by irradiation [13]. In recent years, a new

emerging application of metal–organic complexes as photocatalysts for the degradation of organic dyes has been established [14,15]. For instance, cobalt complexes with different structures have been used to degrade organic dyes in water medium under UV or visible irradiation [16,17].

In continuation of our work, herein we describe the solvothermal synthesis, supramolecular structure, spectroscopic, thermal stability and photocatalytic activity of complex $[\text{Co}(\text{tpa})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$, starting with a triazole ligand 5-(1,2,4-triazol-1-yl)pyridine-3-carboxylic acid (Htpa).

2. Experimental

2.1. Materials and Methods

All starting materials were purchased from commercial sources and used as received. All the organic solvents used in synthesis and analysis were analytical grade and purchased from commercial sources. Methyl orange (MO) was purchased from Sinopharm Chemical Reagent co., Ltd, China. C, H and N elemental analyses were tested on a Vario EL III organic elemental analyzer (Elementar, Langensfeld, Hesse, Germany). FTIR spectrum was obtained from KBr pellet on a Varian 640-IR spectrometer (Varian, Palo Alto, CA, USA) in the range of 400–4000 cm^{-1} . Powder X-ray diffraction patterns were performed on a Rigaku TTR(III) diffractometer (Rigaku, Takatsuki, Osaka, Japan), Cu $k\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$. Thermal analysis was performed on a Mettler Toledo TGA/DSC 1/1600 (Mettler Toledo, Zurich, Switzerland) thermal analyzer from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. UV–Vis absorption spectra were measured on a Persee TU-1901 (Persee, Beijing, China) spectrometer.

2.2. Synthesis of $[\text{Co}(\text{tpa})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (1)

A mixture of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (43.5 mg, 0.15 mmol) and Htpa (19 mg, 0.1 mmol) was dissolved in 6 mL deionized water, and the mixed solution was stirred for 10 minutes at room temperature. Then, the solution was sealed into a 25 mL Teflon-linear autoclave and heated at 150 $^{\circ}\text{C}$ for 48 h. The reactant mixture was cooled to room temperature at 10 $^{\circ}\text{C per hour}$. The solution was filtered and left undisturbed for 3 days, and red block crystals of complex **1** were obtained (yield: 55%, based on Htpa ligand). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{CoN}_8\text{O}_{10}$ (%): C 35.24, H 4.07, N 20.55; Found (%): C 35.28, H 4.04, N 20.58.

2.3. X-ray Crystallography

Single-crystal X-ray diffraction data for complex **1** was collected on a Bruker Smart Apex II CCD (Bruker, Munich, Bavaria, Germany) area detector using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The crystal structure was solved by the direct method procedure and refined by full-matrix least squares on F^2 with the use of the SHELXTL-2014 program [18]. The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were added theoretically. The crystallographic and refinement data of complex **1** are summarized in Table 1. CCDC deposition number 1947682 contains the supplementary crystallographic data for **1**, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for complex **1**.

Complex 1	
Empirical formula	C ₁₆ H ₂₂ CoN ₈ O ₁₀
Formula weight	545.34
Temperature/K	293(2)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	6.8212(9)
<i>b</i> /Å	9.0225(12)
<i>c</i> /Å	10.1018(13)
α /°	63.8650(10)
β /°	83.2140(10)
γ /°	76.5600(10)
Volume/Å ³	542.77(12)
<i>Z</i>	1
ρ_{calc} /g/cm ³	1.668
<i>F</i> (000)	281.0
Crystal size/mm ³	0.34 × 0.23 × 0.14
Radiation	MoK α (λ = 0.71073)
Independent reflections	1880, <i>R</i> _{int} = 0.0149
restraints/parameters	0/165
Goodness-of-fit on <i>F</i> ²	1.087
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0296, <i>wR</i> ₂ = 0.0781
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0788
L. diff. peak/hole /e Å ^{−3}	0.36/−0.34

2.4. Hirshfeld Surface Analysis

Hirshfeld surface analysis is a powerful technique used to understand the intermolecular interactions within crystals. Hirshfeld surface analyses for complex **1** were carried out using Crystal Explorer 3.1 computer programs, with bond lengths to hydrogen atoms set to standard values. For each point on the Hirshfeld surface, *de* is the distance from the point to the nearest nucleus external to the surface, and *di* is the distance to the nearest nucleus internal to the surface [19]. The normalized contact distance (*d*_{norm}) is defined as [19,20]

$$d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdw}})}{r_i^{\text{vdw}}} + \frac{(d_e - r_e^{\text{vdw}})}{r_e^{\text{vdw}}} \quad (1)$$

where *r*_i^{vdw} and *r*_e^{vdw} are the van der Waals radii of the atoms.

2.5. Photocatalytic Experiments

The photocatalytic behavior of [Co(tpa)₂(H₂O)₄].2H₂O (**1**) was tested for the degradation of methyl orange (MO) under UV irradiation at room temperature. A sample of 30 mg powder crystals of complex **1** was immersed in 25 mL of MO solution (10 mg/L). The solution was kept in the dark for 1 h to ensure adsorption equilibrium. Then, the mixed solution was magnetically stirred and exposed to UV irradiation from a 400 W, high-pressure mercury lamp. The mercury lamp was put in the chamber of the annular hollow quartz tube, then the circulating cold water flowed in the hollow quartz tube to ensure that the emitted light was cold. The distance between the lamp and the reaction solution was about 20 cm. At given time intervals, about 3 mL of analytical samples were withdrawn and analyzed by the UV–Vis spectrometer. The control experiment was performed under the same conditions but without catalysts.

3. Results

3.1. Crystal Structure of $[Co(tpa)_2(H_2O)_4] \cdot 2H_2O$

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetry unit of **1** contains one central Co(II) ion, one deprotonated tpa^- ligand, two coordinated water molecules, and one lattice water molecule. As shown in Figure 1a, the Co(II) ion is six-coordinated with an N_2O_4 coordination environment. The Co–O distances are 2.0757(15) and 2.0933(16) Å, and the Co–N bond length is 2.1821(17) Å (Table 2). The carboxylate group of tpa^- ligand is deprotonated but not coordinated with the Co(II) ion.

Figure 1. (a) Coordination environment of Co(II) atom in complex **1**, (b) $\pi \cdots \pi$ stacking interactions between the adjacent benzene rings, (c) intermolecular H bonds for complex **1**, (d) supramolecular framework of complex **1** formed by H bonds and $\pi \cdots \pi$ interactions (viewed along a axis).

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for complex **1**.

Complex 1			
Co1–N1	2.1821(17)	O1W1–Co1–N11	89.62(6)
Co1–O1W	2.0933(16)	O1W–Co1–N11	90.38(6)
Co1–O2W	2.0757(15)	O2W–Co1–O1W	89.98(7)
O1W–Co1–O1W1	180.0	O2W1–Co1–O1W	90.02(7)

¹ Symmetry code: $-x, 1-y, -z$.

As shown in Figure 1b, face-to-face $\pi \cdots \pi$ stacking interactions between the adjacent benzene rings can be obviously observed. The centroid to centroid distances between the two adjacent benzene rings are 3.589 and 4.183 Å, respectively. It can be concluded that the $\pi \cdots \pi$ interactions play an important role in stabilizing the crystal structure of **1**.

Six groups of classical O–H $\cdots$ O and O–H $\cdots$ N hydrogen bonds are found in the packing structure of complex **1**. The intermolecular hydrogen bonds are shown in Figure 1c, and the structural parameters of these hydrogen bonds are listed in Table 3. The coordinated water molecules act as H donors to form

O–H...N hydrogen bonds with triazole groups (O1W–H1WA...N3), and form O–H...O hydrogen bonds with carboxylate oxygen atoms (O1W–H1WB...O1). However, another coordinated water molecule acts as an H donor to form an O–H...N hydrogen bond with N2 atom of triazole group (O2W–H2WA...N2), and form an O–H...O hydrogen bond with lattice water (O2W–H2WB...O3W). In addition, as the H donor, the lattice water also forms two O–H...O hydrogen bonds with carboxylate oxygen atoms (O3W–H3WA...O1, O3W–H3WB...O2). Moreover, based on intermolecular hydrogen bonds and $\pi\cdots\pi$ interactions, complex **1** further forms a stable 3D supramolecular framework (Figure 1d).

Table 3. Geometrical parameters for the hydrogen bonds in complex **1**.

D–H...A	d(D–H)/Å	d(H...A)/Å	d(D...A)/Å	<DHA/°	Symmetry Code ¹
O1W–H1WA...N3A	0.881	1.970	2.818	161.31	–x, –y, –z + 1
O1W–H1WB...O1	0.880	1.953	2.778	155.63	–x, –y, –z
O2W–H2WA...N2A	0.858	2.200	2.892	137.61	–x, –y, –z
O2W–H2WB...O3W	0.858	1.905	2.651	144.42	–x, –y + 1, –z
O3W–H3WA...O1	0.850	1.914	2.733	161.22	–x + 1, –y, –z
O3W–H3WB...O2	0.850	1.846	2.691	172.85	x, y, z + 1

¹ The symmetry codes were obtained based on A atoms in the packing structure of complex **1** (D donor atom, A acceptor atom).

3.2. Hirshfeld Surface of [Co(tpa)₂(H₂O)₄] $\cdot$ 2H₂O (**1**)

The 3D Hirshfeld surfaces of complex **1** are illustrated in Figure 2, which maps d_{norm} , shape index and curvedness [21]. The d_{norm} Hirshfeld surfaces displayed using a red–white–blue color scheme, where the red spots indicate the close contact interactions, white color indicate contacts around the van der Waals radius distance, and blue color is for longer contacts [19]. As shown in Figure 2a, the deep red spots on the d_{norm} Hirshfeld surface indicate the close contact interactions, which are mainly responsible for the significant intermolecular O–H...O and O–H...N hydrogen bonds, created by carboxyl groups (spot A), coordinated water (spot B), triazole nitrogen atoms (spot C) and lattice water (spot D). For the shape index plot (Figure 2b), the orange–red areas represent concave regions, indicating that there are hydrogen bonding or $\pi\cdots\pi$ stacking interactions in these areas. For the curvedness plot (Figure 2c), the flat areas of the surface indicate interactions between neighboring molecules. In addition, the flat regions above the benzene and triazole rings refer to the strong $\pi\cdots\pi$ stacking interactions between the aromatic rings of adjacent molecules.

Figure 2. Hirshfeld surfaces of complex **1** mapped with (a) d_{norm} , (b) shape index and (c) curvedness.

As shown in Figure 3, a 2D fingerprint plot was performed to identify important intermolecular interactions, which was further decomposed to highlight particular atom pairs' close contacts. It is found that there are five kinds of intermolecular interactions, including O...H, N...H, H...H, C...H and C...C ($\pi\cdots\pi$) interactions. The O...H/H...O intermolecular interactions comprise 29.5% of the total Hirshfeld surface, which appear as two distinct spikes in the 2D fingerprint plot (Figure 3b). It can be inferred from the strongest spike that the O...H interaction is the shortest contact, with a minimum value of ($d_e + d_i$) around 1.7 Å [22]. The N...H/H...N interactions also appear as two sharp spikes,

which comprise 21.5% of the total Hirshfeld surface (Figure 3c). Apart from those mentioned above, the H $\cdots$ H interactions also have a large contribution to the total Hirshfeld surface, comprising 23.8%. It is interesting that C $\cdots$ C interactions are found in the 2D fingerprint plot, which comprised 8.6% of the total Hirshfeld surface (Figure 3f). The C $\cdots$ C interactions are mainly caused by the strong $\pi\cdots\pi$ stacking interactions between adjacent aromatic rings. From the 2D fingerprint plots, we can also find that the $\pi\cdots\pi$ stacking interactions have much longer contact distances when compared with hydrogen bonding interactions. The H bonding and $\pi\cdots\pi$ stacking information conveyed by Hirshfeld surface analyses are consistent with the crystal structure analyses.

Figure 3. Fingerprint plots of complex **1**: full (a) and resolved into O $\cdots$ H (b), N $\cdots$ H (c), H $\cdots$ H (d), C $\cdots$ H (e) and C $\cdots$ C (f) contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

3.3. XRD and Thermal Stability

As shown in Supplementary Materials Figure S1, the experimental XRD pattern agrees well with the simulated pattern generated on the basis of the single-crystal analysis for complex **1**, which suggests good phase purity and homogeneity of the synthesized sample. The thermal behavior of complex **1** was studied by gravimetric analysis (TGA). In the TGA curve (Figure S2), the first step takes place in the range of 60–147 °C with a weight loss of 13.0%, which can be attributed to the gradual release of four coordinated H₂O (calcd. 13.2%). After that, the skeleton of the complex begins to decompose and a significant weight loss of 22.1% is observed in the range of 264–425 °C, which could be assigned to the decomposition of the triazole group (calcd. 24.9%). Keeping the heat at 900 °C, consecutive decompositions suggest the total destruction of the framework, and at last a residue of CoO remained (obsd. 16.6%, calcd. 13.7%).

3.4. FT-IR and UV-Vis Absorption Spectra

In the FT-IR spectrum of complex **1** (Figure S3), the broad absorption band at about 3300–3500 cm^{−1} can be assigned to the -OH stretching vibrations of water, including water ligands, lattice water and

absorbed water molecules. The bands at 1582 and 1385 cm^{-1} are attributed to the stretching vibrations of C=C and C=N bonds from benzene and triazole rings [23]. As shown in Figure S4, the UV-Vis absorption spectrum of complex **1** was measured in methanol solution at room temperature (concentrations ca. 10^{-5} M). Complex **1** has three absorption bands with different intensities, where the two strong absorption bands at 212 and 239 nm can be attributed to the $\pi \rightarrow \pi^*$ transition absorption of aromatic rings (C=C), while the weak band at 276 nm can be assigned to the $n \rightarrow \pi^*$ transition of the triazole group (C=N) [24].

3.5. Photocatalytic Activity

The removal of toxic organic dyes from contaminated water is very important from the perspective of environmental protection. The photocatalytic degradation of methyl orange (MO) in aqueous solution by complex **1** under UV irradiation is shown in Figure 4a. It can be found from the absorption spectra that the absorption intensity of MO solution decreased gradually with the reaction time under the catalysis of complex **1**, and the MO is almost completely degraded after 90 min of light irradiation. Degradation efficiencies (D) for MO dye was calculated as $D = (A_0 - A_t)/A_0 \times 100\%$ [25], where A_0 is the initial absorbance of MO solution at $\lambda_{\text{max}} = 464$ nm, and A_t is the absorbance obtained at t min. As shown in Figure 4b, the degradation efficiency of MO is about 51.9% after reacting for 30 min, and is up to 89.2% after irradiating for 90 min, which indicates the high catalytic efficiency of complex **1**. In contrast, the degradation efficiency of MO is only 14.9% after irradiating for 90 min in the absence of complex **1**. In addition, we measured the XRD pattern of **1** after the photocatalytic experiment, which was identical to the corresponding one of the original compound (Figure S1), indicating that the crystal structure of complex **1** was stable after photocatalytic reactions. The catalyst was reused to study its reusable performance, as shown in Figure 5a. The catalyst retained favorable photocatalytic efficiencies after reused for two cycles, with the degradation efficiency of MO decreased from 89.3% to 80.5%. However, after being reused for three cycles, the degradation efficiency of MO decreased to 65.2%.

Figure 4. (a) The UV-Vis absorption spectra of methyl orange (MO) solution during the decomposition reaction under UV irradiation; (b) Degradation efficiencies of MO under UV light.

Figure 5. (a) Reusable degradation activity of complex 1 (irradiation time 90 min, the catalyst was centrifuged, filtered and dried for the next experiment); (b) pseudo-first-order kinetics for the degradation of MO under UV light.

Reaction kinetics studies have shown that the degradation process of MO was in accordance with the pseudo-first-order model, $\ln(C_0/C_t) = k \cdot t$, where C_0 and C_t were the concentrations of MO solution at irradiation time t_0 and t [26]. As shown in Figure 5b, the $\ln(C_0/C_t)$ versus t showed a linear relationship, with the correlation coefficient $R = 0.9985$ ($p < 0.0001$), and the apparent rate constant $k = 2.54 \times 10^{-2} \text{ min}^{-1}$. As an important parameter of the pseudo-first-order reaction, the half-life time $t_{1/2}$ (calculated as $t_{1/2} = \ln 2/k$) means the time at which $C = 0.5 C_0$ [27,28]. The $t_{1/2}$ for the photocatalytic reaction of MO is 27.3 min, implying that complex 1 is an effective photocatalyst.

The mechanism of photocatalytic degradation of organic dyes by metal–organic complexes has been described in detail in much of the literature, which proved that these reactions were mainly based on the advanced oxidation of hydroxyl radicals ($\cdot\text{OH}$) [29]. In aqueous solution, under the excitation of UV light, N–Co charge transfer occurs between the ligands and the metal center of complex 1, promoting electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, the highest occupied molecular orbital strongly needs an electron to return to its stable state. The electrons are captured from aqueous solution to generate $\cdot\text{OH}$ radicals. At the same time, the electrons excited to the LUMO are captured by water to generate $\cdot\text{OH}$ radicals [14,29,30]. Finally, the oxidizing $\cdot\text{OH}$ radicals decomposed MO dye to complete the photocatalytic process. Wang and co-workers studied the photocatalytic activity of six different complexes [30]. They observed that the Co(II) complexes show much better photocatalytic activity than that of the Cu(II), Ni(II), Zn(II) and Cd(II) complexes in the degradation of different types of organic dyes. They also pointed out that the different structures and central metal ions of complexes might affect the photocatalytic activity, but the reasons are still unclear. For the synthesized Co(II) complex 1, the N atom of pyridine ring on the ligand coordinate with the cobalt atoms. The pyridine ring is a stable aromatic structure; when the Co(II) complex is excited by UV light, the charges can be distributed over the entire pyridine ring, which promotes the separation of photogenerated electrons and positive charges, making the excited state more stable [30,31]. Besides, in aqueous solution, the presence of four coordination water molecules may contribute to the production of hydroxyl radicals (Figure S5). Moreover, Lin et al. point out that the charge-carrier mobility of materials is affected by π conjugation and $\pi \cdots \pi$ stacking [32]. We can infer from the single-crystal structure of complex 1 that the $\pi \cdots \pi$ stacking structure makes the photogenerated electrons more stable, which will facilitate the transfer of photogenerated electrons to water to produce hydroxyl radicals.

4. Conclusions

In summary, a novel Co(II) complex $[\text{Co}(\text{tpa})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (1) has been synthesized using multifunctional triazole derivative as an organic ligand. Hirshfeld surface analysis was used to study

the intermolecular interactions, which revealed that the O $\cdots$ H, H $\cdots$ H, N $\cdots$ H and $\pi\cdots\pi$ contacts were the most significant interactions in the crystal of complex **1**. The hydrogen bonding and $\pi\cdots\pi$ stacking information conveyed by Hirshfeld surface analyses were consistent with the crystal structure analyses. Photocatalytic studies revealed that complex **1** could effectively catalyze the degradation of MO dye under UV irradiation, and the degradation process was in accordance with the pseudo-first-order kinetics model.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/2/98/s1>, Figure S1: XRD patterns of complex **1**, Figure S2: TGA curve of complex **1**, Figure S3: FT-IR spectrum of complex **1**, Figure S4: UV absorption spectrum of complex **1** in methanol solution at room temperature, Figure S5: Possible photocatalytic mechanisms showing the two excited states of Co(II) catalyst under UV excitation.

Author Contributions: D.W. and B.Y. conceived and designed the experiments; T.W. and Y.W. performed X-ray structure determination and analyzed the results; D.W., N.Z. and C.Z. carried out the synthetic and photocatalytic experiments. All authors took part in writing and discussion processes. All authors have read and agreed to the published version of the manuscript.

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