

## Article

# Synthesis, Structural Characterization, and Hirschfeld Surface Analysis of a New Cu(II) Complex and Its Role in Photocatalytic CO<sub>2</sub> Reduction

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**Abstract:** A new Cu(II) complex, [CuL<sub>1</sub>L<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O, was synthesized by the reaction of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, 6-phenylpyridine-2-carboxylic acid (HL<sub>1</sub>), and 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (L<sub>2</sub>) in ethanol-water (*v:v* = 1:1) solution. The Cu(II) complex was characterized using elemental analysis, IR, UV-vis, TG-DTA, and single-crystal X-ray analysis. The fluorescence properties of the copper complex were also evaluated. The structural analysis results show that the Cu(II) complex crystallizes in the triclinic system with space group *P*-1. The Cu(II) ion in the complex is five-coordinated with one O atom (O2) and one N atom (N1) from one 6-phenylpyridine-2-carboxylate ligand (L<sub>1</sub>), one N atom (N2) from 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ligand (L<sub>2</sub>), one O atom (O4) from acetate, and one O atom (O5) from a coordinated water molecule, and it adopts a distorted trigonal bipyramidal geometry. Cu(II) complex molecules form a two-dimensional layer structure through intramolecular and intermolecular O-H···O hydrogen bonding. The two-dimensional layer structures further form a three-dimensional network structure by  $\pi$ - $\pi$  stacking interactions of aromatic rings. The analysis of the Hirschfeld surface shows that the H···H contacts made the most significant contribution (46.6%) to the Hirschfeld surface, followed by O···H/H···O, N···H/H···N and C···H/H···C contacts with contributions of 14.2%, 13.8%, and 10.2%, respectively. In addition, the photocatalytic CO<sub>2</sub> reduction using Cu(II) complex as a catalyst is investigated under UV-vis light irradiation. The findings reveal that the main product is CO, with a yield of 10.34  $\mu$ mol/g and a selectivity of 89.4% after three hours.

**Keywords:** 6-phenylpyridine-2-carboxylic acid; 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine; Cu(II) complex; synthesis; crystal structure; Hirschfeld surface analysis; photocatalytic CO<sub>2</sub> reduction



**Citation:** Wang, L.-H.; Azam, M.; Yan, X.-H.; Tai, X.-S. Synthesis, Structural Characterization, and Hirschfeld Surface Analysis of a New Cu(II) Complex and Its Role in Photocatalytic CO<sub>2</sub> Reduction. *Molecules* **2024**, *29*, 1957. <https://doi.org/10.3390/molecules29091957>

Academic Editor: Jonathan Albo

Received: 14 March 2024

Revised: 10 April 2024

Accepted: 23 April 2024

Published: 24 April 2024

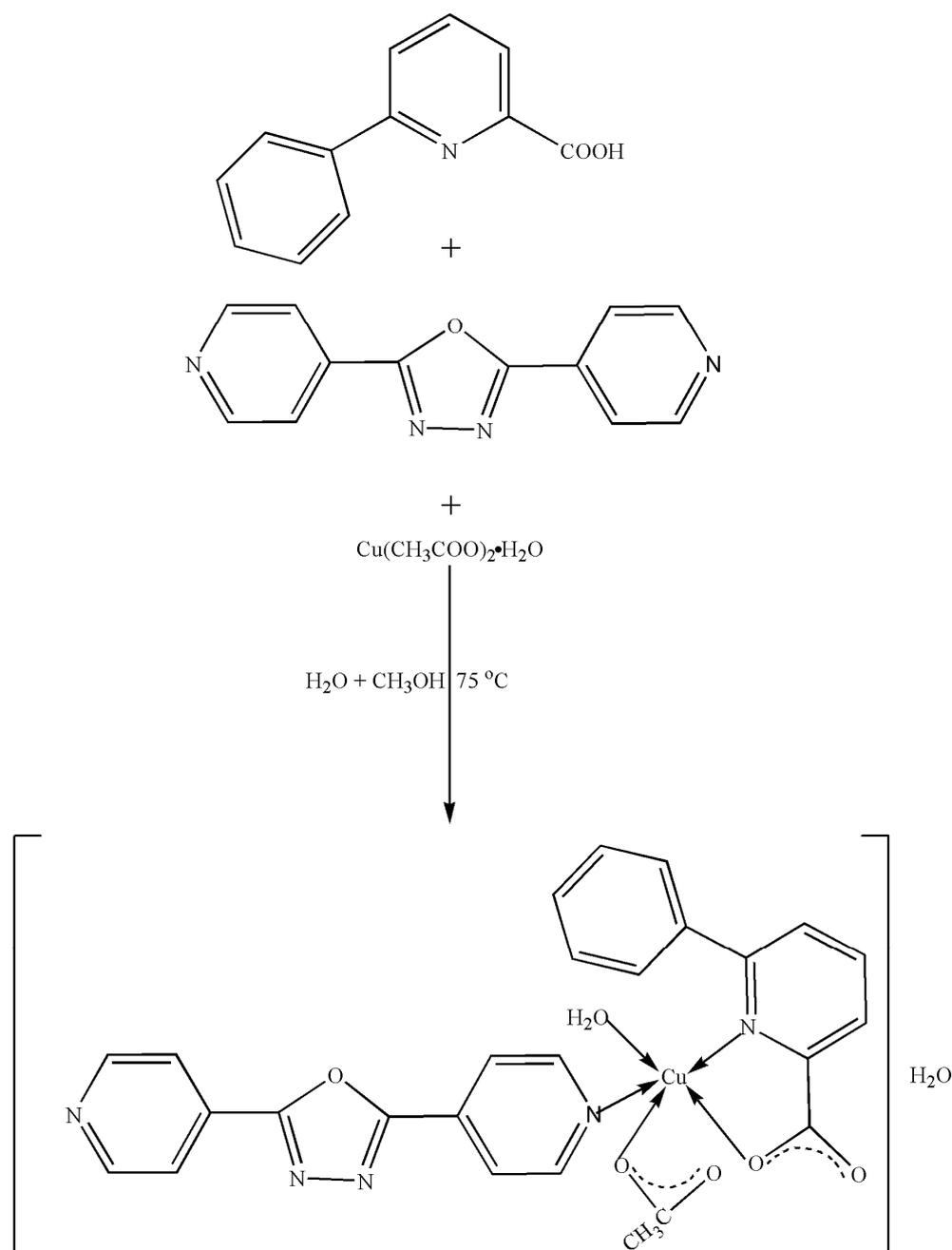


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## 1. Introduction

With the rapid development of the fossil fuel industry, large amounts of CO<sub>2</sub> have been excessively emitted, causing climate changes, such as droughts, typhoons, acid rains, cold waves, high-temperature heat waves, and dust storms [1]. Therefore, there is an urgent need to find highly efficient CO<sub>2</sub> conversion technologies. Reducing CO<sub>2</sub> by photocatalytic processes is a promising strategy for achieving sustainability, which not only diminishes CO<sub>2</sub> emissions but also produces valuable chemicals and fuels, making a substantial contribution to environmental remediation to address the urgent concerns regarding climate change and the ultimate exhaustion of fossil fuel reserves [2,3]. In addition, several technologies that transform CO<sub>2</sub> into high-value-added products, such as CO, CH<sub>4</sub>, CH<sub>3</sub>OH, ethylene, ethanol, and HCOOH, have been investigated. Various metal oxide composite catalysts are widely used in photocatalytic CO<sub>2</sub> reduction due to their unique properties, high stability, and low cost [4–8]. Cu catalysts for the synthesis of multi-carbon products exhibit a series of consistent motifs, such as oxidation, a high surface

area, nanostructuring, and specific faceting, which promote the production of ethylene and ethanol at consistently lower over-potentials, with Faradaic efficiencies approaching 50–60%. However, these catalysts have a short lifespan and limitations in terms of the current density of the substrate [9]. Metal-semiconductor catalysts have been proven to widen the light absorption range of light-driven catalyst materials, and the presence of metal particles not only enhances the optical absorption capability but also provides active sites for the activation of CO<sub>2</sub>; however, the cost of these catalysts is very high because many of them contain precious metals [10]. Despite their potential, these systems have not been widely used because of several limitations that greatly limit their practical applications, including their inefficiency in converting energy, high charge recombination, and limited capacity to absorb visible light [11]. Since the initial report on photocatalytic CO<sub>2</sub> reduction using fac-[ReICl(bpy)(CO)<sub>3</sub>] [12], researchers have constructed numerous effective systems for reducing CO<sub>2</sub> using noble metal complexes by finetuning the features of the catalytic systems, and they have developed molecular catalysts, such as dinuclear rhenium-bipyridine assemblies, trinuclear ruthenium polyazine-GOphen compounds and ruthenium trisphenanthroline assemblies, as photocatalysts for the conversion of CO<sub>2</sub> [13–15]. However, due to the high cost of these noble metal complexes, the use of earth-abundant metal complexes as catalysts for photocatalytic CO<sub>2</sub> reduction has attracted increasing attention from chemists and material scientists. Among these complexes, Co(II), Mn(II), Fe(II), Cu(I), and rare earth ions containing complexes have been used for photocatalytic CO<sub>2</sub> reduction [16–24]. However, to date, there are very few reports on the photocatalytic CO<sub>2</sub> reduction by Cu(II) complexes [25–27]. 6-Phenylpyridine-2-carboxylic acid is an excellent ligand and can form structurally stable, coordination-diverse complexes with many metal ions [28,29]. To further enhance the application of metal complexes in the photocatalytic reduction of CO<sub>2</sub>, and to explore the synergistic action of metal ions and ligands in metal complexes with photocatalytic CO<sub>2</sub> reduction (rather than the role of simple metal ions or the role of simple ligands), we have synthesized a new Cu(II) complex by one-pot method using Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, 6-phenylpyridine-2-carboxylic acid (HL<sub>1</sub>), and 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (L<sub>2</sub>) in an ethanol-water solution. The isolated Cu(II) complex was thoroughly characterized using elemental analysis, IR, UV-vis, TG-DTA, and single-crystal X-ray analysis. In addition, the fluorescence behavior of the complex was also investigated. Moreover, the Cu(II) ion in the complex is five-coordinated with one O atom and one N atom from one 6-phenylpyridine-2-carboxylate ligand (L<sub>1</sub>), one N atom from 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ligand (L<sub>2</sub>), one O atom from acetate, and one O atom from coordinated water molecule, and it adopts a distorted trigonal bipyramid geometry. Furthermore, the photocatalytic reduction of CO<sub>2</sub> by Cu(II) complex was investigated using UV-vis light irradiation, and the results indicated that the main product formed is CO, with a yield of 10.34 μmol/g and a selectivity of 89.4% after three hours. CO can be widely used in the metallurgical industry as a reducing agent, gas fuel, etc. The synthesis of the Cu(II) complex is shown in Figure 1.



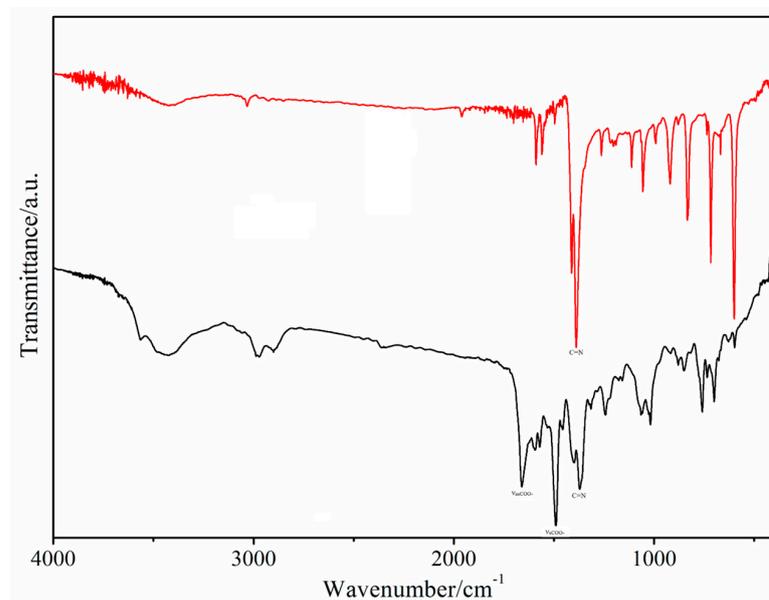
**Figure 1.** Synthesis of Cu(II) complex.

## 2. Results and Discussion

### 2.1. Infrared Spectra

The infrared spectra of the Cu(II) complex and 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand are shown in Figure 2. The free 6-phenylpyridine-2-carboxylic acid ( $HL_1$ ) ligand shows characteristic bands at 1646 ( $\nu_{\text{as}}\text{COO}^-$ ) and 1575 ( $\nu_{\text{s}}\text{COO}^-$ )  $\text{cm}^{-1}$  [30], while the free 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand shows an important band at 1388  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{N}}$ ). In Cu(II) complex, these bands are observed at ca. 1660, 1489, and 1371  $\text{cm}^{-1}$ , respectively, indicating the coordination of both the  $L_1$  ligand and  $L_2$  ligands with the Cu(II) ion. The difference between  $\nu_{\text{as}}\text{COO}^-$  and  $\nu_{\text{s}}\text{COO}^-$  |  $\nu_{\text{as}}\text{COO}^- - \nu_{\text{s}}\text{COO}^-$  | = 171  $\text{cm}^{-1}$  suggests that the  $\text{COO}^-$  group of 6-phenylpyridine-2-carboxylic acid ( $HL_1$ ) ligand in the Cu(II) complex adopts a monodentate coordinated mode. In addition, a broad absorption band at ca. 3481  $\text{cm}^{-1}$  is assigned to

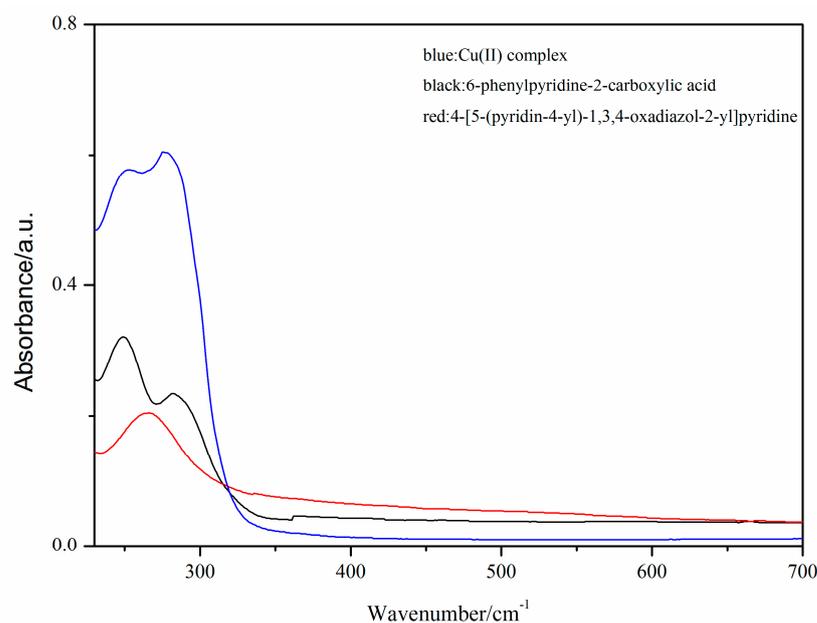
the  $\nu(\text{OH})$ , indicating the presence of water molecules in the Cu(II) complex. The IR results are consistent with the X-ray single-crystal diffraction data of the Cu(II) complex.



**Figure 2.** The infrared spectra of the Cu(II) complex (black) and 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand (red).

## 2.2. UV-Vis Spectrum

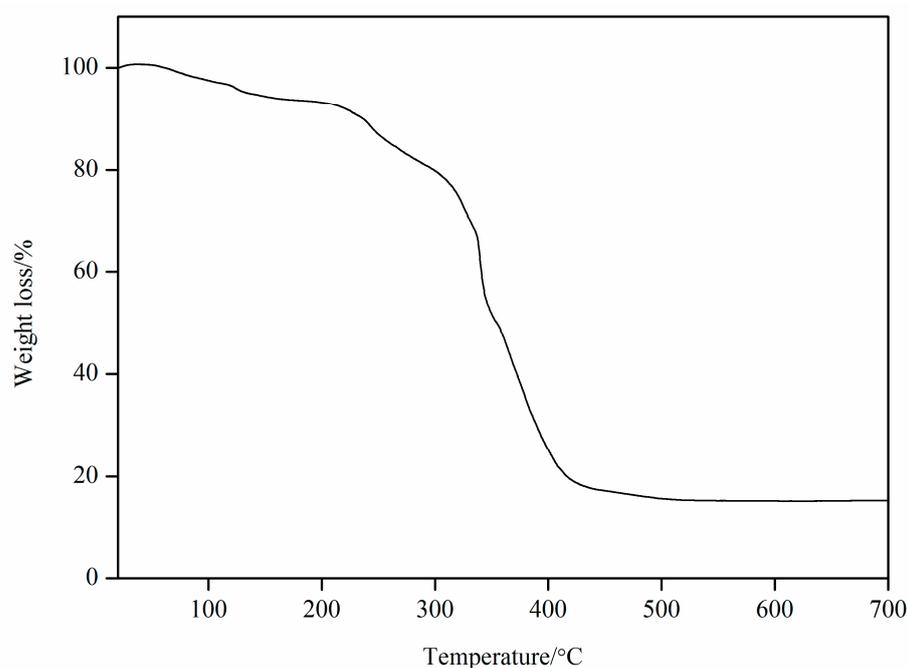
The UV-vis spectra of the free 6-phenylpyridine-2-carboxylic acid ( $HL_1$ ) ligand, the 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand and the Cu(II) complex are shown in Figure 3. The free 6-phenylpyridine-2-carboxylic acid ( $HL_1$ ) ligand exhibits two absorption bands at 249 and 282  $\text{cm}^{-1}$ , while the free 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand exhibits one absorption band at 266  $\text{cm}^{-1}$ . The Cu(II) complex shows bands at ca. 253 and 276  $\text{cm}^{-1}$ , which may be attributed to the  $\pi$ - $\pi^*$  transitions of  $L_1$  and  $L_2$  ligands. The variations in the UV absorption peaks between the Cu(II) complex and  $L_1$  and  $L_2$  ligands indicate the coordination of  $L_1$  and  $L_2$  ligands to the Cu(II) ion, which agrees well with the results of the infrared spectra.



**Figure 3.** The UV-vis absorption spectra of free ligands and Cu(II) complex.

### 2.3. Thermogravimetric Analysis

The thermogravimetric analysis of the Cu(II) complex was performed in the air atmosphere with a heating rate of 5 °C/min (room temperature to 700 °C). The thermal stability curve of the Cu(II) complex is shown in Figure 4, and it shows that its decomposition went through two distinct phases: The first stage occurs at 25–200 °C, corresponding to a weight loss of 6.20%, which is likely attributed to the loss of two water molecules (6.19%). The second stage occurs at 200–700 °C, corresponding to a weight loss of 15.30%, which may be due to the continuous decomposition of 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand, 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand, and acetate. The final residue identified was CuO (Found: 15.30%, Calculated: 13.77%).

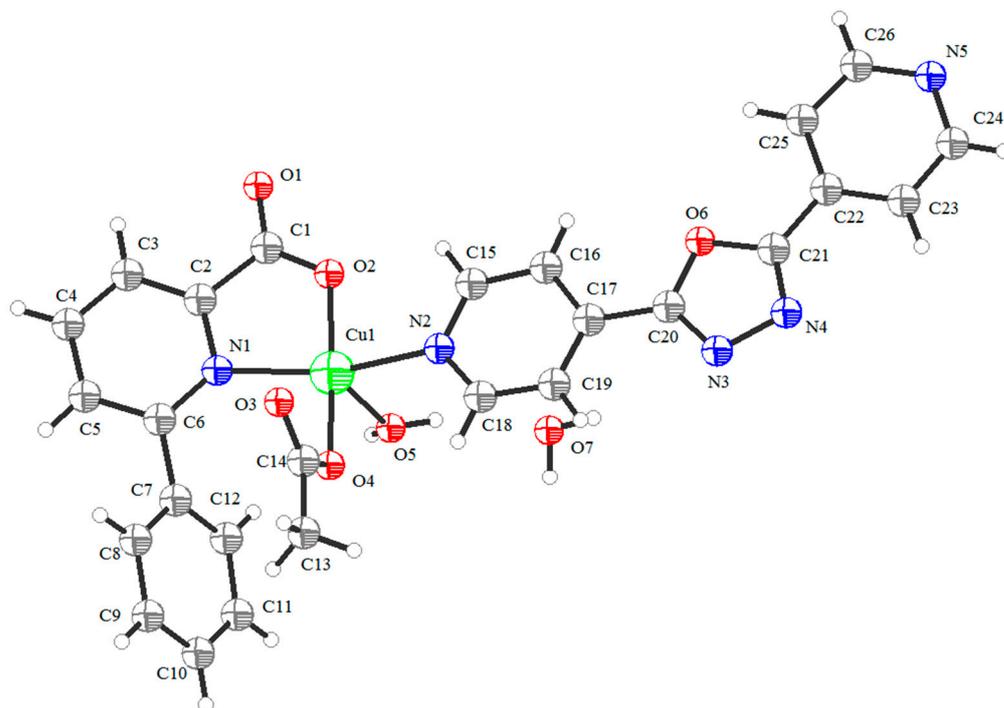


**Figure 4.** Thermal stability curve of Cu(II) complex.

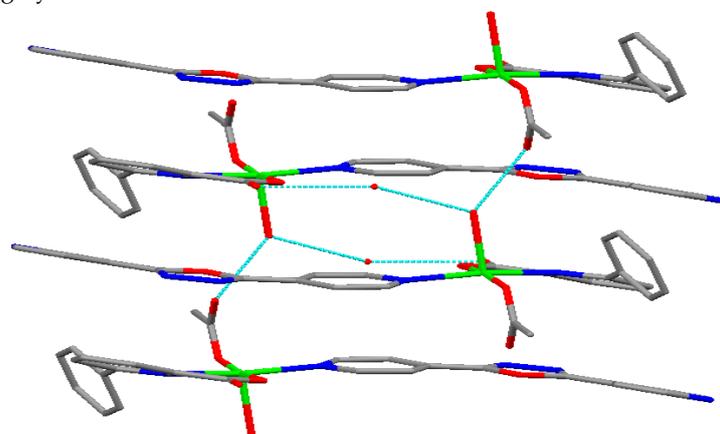
### 2.4. Structural Description of Cu(II) Complex

The Cu(II) complex crystallizes in a triclinic system with space group  $P-1$ . Its structure comprises one Cu(II) ion, one 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand, one 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand, one acetate, one coordinated water molecule, and one uncoordinated water molecule. The molecular structure of the Cu(II) complex is shown in Figure 5. The selected bond lengths (Å) and angles (°) for the Cu(II) complex are listed in Table 1. The two-dimensional layered structure of the Cu(II) complex formed by hydrogen bonds is shown in Figure 6. Additionally, a three-dimensional network structure of Cu(II) complex stacked by a two-dimensional layered structure is shown in Figure 7. As shown in Figure 5, the Cu(II) ion exhibits a five-coordinated geometry, surrounded by one N atom (N1) and one carboxylate O atom (O2) from the same 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand, one N atom (N2) from 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand, one O atom (O4) from one acetate, and one O atom (O5) from one coordinated water molecule, and they form a trigonal bipyramidal geometry with an O4-Cu1-O2 bond angle of 172.04(7)°. The bond angles around the Cu(II) ion are N1-Cu1-N2 (165.99(7)°), N1-Cu1-O5 (103.25(6)°), N2-Cu1-O5 (86.56(7)°), with a total sum of 355.8°, showing that the N1, N2 and O5 atoms are at the equatorial plane. The dihedral angle of ring 1 (N1-C2-C3-C4-C5-C6-N1) and ring 2 (C7-C8-C9-C10-C11-C12-C7) is 49.97°, indicating that the 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand is not coplanar, and that of ring 3 (N2-C15-C16-C17-C19-C18-N2) and ring 4 (O6-C20-N3-N4-C21-O6) is 5.05° while that of ring 5 (N5-C24-C23-C22-C25-C26-N5) and ring 4 (O6-C20-N3-N4-C21-O6) is 9.49°.

indicating that the 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine ( $L_2$ ) ligand is almost coplanar. The results of the dihedral angles show that the Cu(II) complex molecule is not coplanar. The bond distances of Cu1-N1, Cu1-N2, Cu1-O2, Cu1-O4, and Cu1-O5 are 2.1179(17), 2.0832(18), 1.9216(16), 1.9203(14), and 2.2628(16) Å, respectively, consistent with literature reports [29,31]. In the Cu(II) complex, both the 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand and acetate adopt a monodentate coordinated mode, which is in agreement with the infrared spectra results. The Cu(II) complex molecules form a two-dimensional layered structure by O-H $\cdots$ O through hydrogen bonds including uncoordinated water molecules, coordinated water molecules, carboxylate O atoms of 6-phenylpyridine-2-carboxylate ( $L_1$ ) ligand, and O atoms of acetate (Figure 6). These two-dimensional layer structures further form a three-dimensional network structure by  $\pi$ - $\pi$  stacking interactions of aromatic rings (Figure 7). The hydrogen bonds of the Cu(II) complex are listed in Table 2.



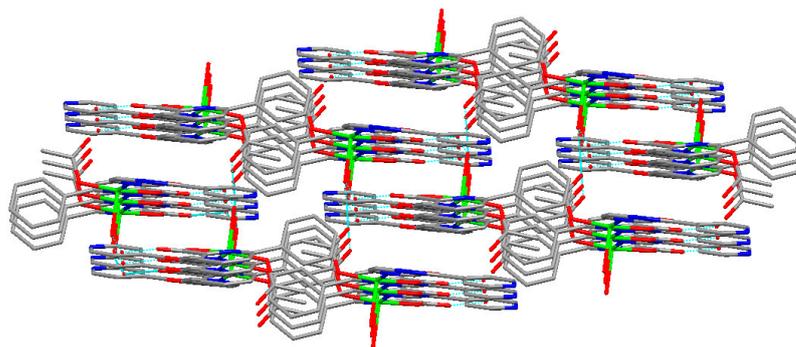
**Figure 5.** The molecular structure of Cu(II) complex. Red: O atoms, blue: N atoms, green: Cu atom, gray: C atoms.



**Figure 6.** The two-dimensional layered structure of Cu(II) complex formed by hydrogen bonds. Red: O atoms, blue: N atoms, green: Cu atom, gray: C atoms.

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

Bond	<i>d</i>	Angle	(°)
Cu1-O2	1.9216 (16)	O2-Cu1-O5	96.77 (8)
Cu1-O4	1.9203 (14)	O2-Cu1-N1	81.18 (7)
Cu1-O5	2.2628 (16)	O2-Cu1-N2	87.83 (7)
Cu1-N1	2.1179 (17)	O4-Cu1-O2	172.04 (7)
Cu1-N2	2.0832 (18)	O4-Cu1-O5	91.10 (7)
		O4-Cu1-N1	98.22 (6)
		O4-Cu1-N2	91.47 (6)
		N1-Cu1-O5	103.25 (6)
		N2-Cu1-O5	86.56 (7)
		N2-Cu1-N1	165.99 (7)
		C1-O2-Cu1	118.87 (16)
		C2-N1-Cu1	107.96 (14)
		C6-N1-Cu1	132.89 (13)
		O1-C1-O2	124.7 (2)
		C20-O6-C21	102.67 (16)
		C15-N2-Cu1	120.08 (15)
		C18-N2-Cu1	122.95 (15)
		C20-N3-N4	105.93 (18)
		C21-N4-N3	106.40 (18)
		C14-O4-Cu1	115.06 (12)

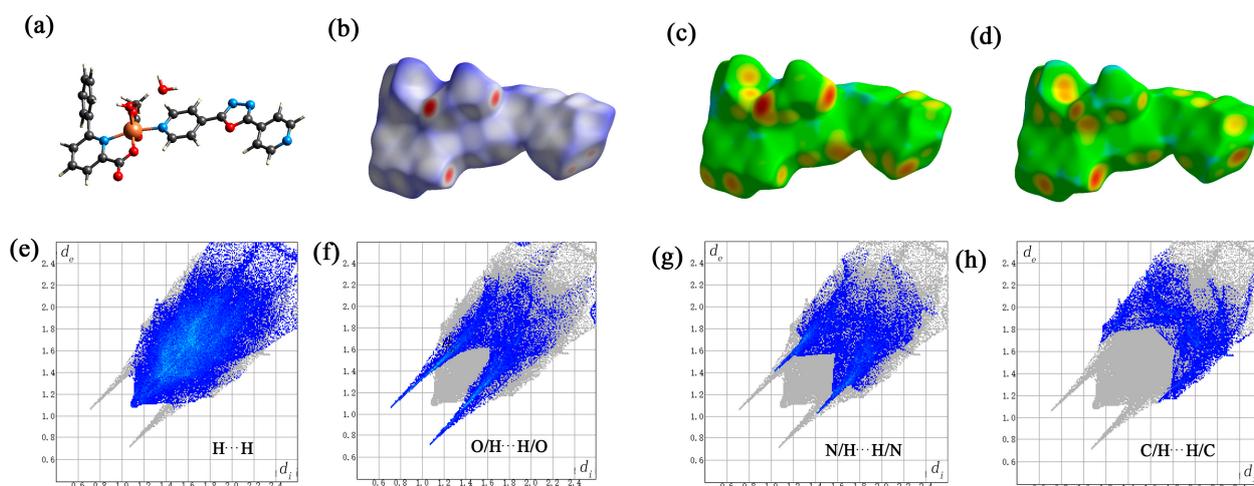
**Figure 7.** The three-dimensional network structure of Cu(II) complex stacked by two-dimensional layered structure. Red: O atoms, blue: N atoms, green: Cu atom, gray: C atoms.**Table 2.** Hydrogen bonds in Cu(II) complex.

Donor-H	Acceptor	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O5-H5A	O3 #1	0.84	1.92	2.7516 (1)	172
O5-H5B	O7 #1	0.85	2.02	2.8221 (1)	159
O7-H7A	O1 #2	0.85	2.18	2.9809 (1)	157

Symmetric operation code: #1:  $1 + x, 1 - y, 1 - z$ ; #2:  $1 + x, y, z$ .

### 2.5. Hirshfeld Surface Analysis of Cu(II) Complex

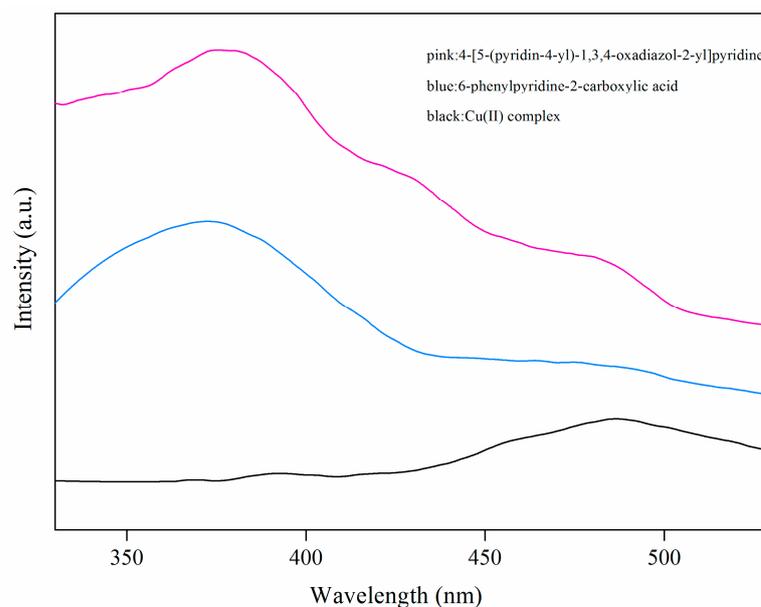
The Hirshfeld surface of the Cu(II) complex was analyzed using the Crystal Explorer software 21.5. Figure 8 displays the original crystal structure unit (a), the Hirshfeld surfaces mapped over  $d_{\text{norm}}$ ,  $d_i$  and  $d_e$  of the crystal (b–d), and the two-dimensional (2D) fingerprint plots representing the overall and top four interactions ( $\text{H}\cdots\text{H}$ ,  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ ,  $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$  and  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ ) (e–h). Based on the calculations, it can be concluded that the  $\text{H}\cdots\text{H}$  contacts represented the largest contribution (46.6%) to the Hirshfeld surface, followed by  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ ,  $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$  and  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$  contacts with contributions of 14.2%, 13.8% and 10.2%, respectively. It is worth noting that the  $\pi$ - $\pi$  stacking interactions play a minor role in the formation, representing 6.6% of the Hirshfeld surface contribution for the  $\text{C}\cdots\text{C}$  contacts.



**Figure 8.** The Hirschfeld surface of the Cu(II) complex. the original crystal structure unit (a)  $d_{\text{norm}}$  (b),  $d_i$  (c),  $d_e$  (d); and the top three interactions (H··H (e), O/H··H/O (f), N/H··H/N (g) and C/H··H/C (h)).

### 2.6. Fluorescence Studies

The fluorescence behavior of the Cu(II) complex, along with the ligands 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine and 6-phenylpyridine-2-carboxylic acid, were explored in ethanol. The excitation and emission slit widths were 2.5 nm. The emission spectra for each compound are illustrated in Figure 9. In the case of the Cu(II) complex, a weak luminescent emission peak was observed at 486 nm upon excitation at 296 nm. Meanwhile, the ligands 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine and 6-phenylpyridine-2-carboxylic acid exhibited luminescent emission peaks at 384 nm and 365 nm, respectively, under the same excitation conditions. It is worth mentioning that the maximum emission peak for each compound was observed to be red-shifted in comparison to the free ligands.

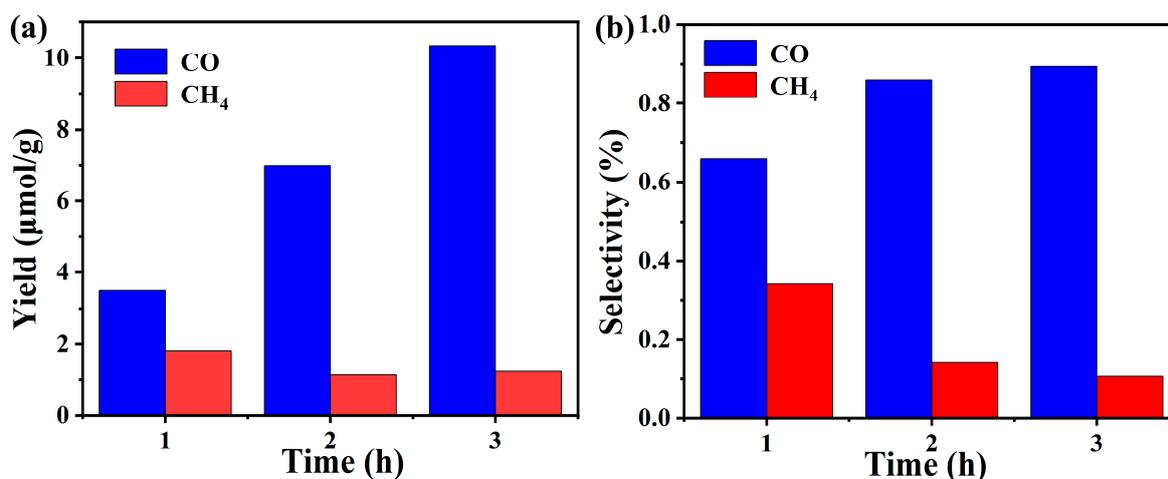


**Figure 9.** The emission spectra of the Cu(II) complex and the ligands 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine and 6-phenylpyridine-2-carboxylic acid in ethanol.

### 2.7. Photocatalytic CO<sub>2</sub> Reduction Activity of Cu(II) Complex

We are concerned here with exploring the potential application of the Cu(II) complex as a catalyst in the photocatalytic reduction of CO<sub>2</sub>. The experimental findings shown in

Figure 10 clearly exhibit the performance of the Cu(II) complex as a catalyst ((a) photocatalytic CO<sub>2</sub> reduction performance and (b) product selectivity of Cu(II) complex catalyst). The main product is CO, and as the reaction period extended, the yield gradually increased. Specifically, after three hours of UV-Vis light irradiation, the yield reached 10.34 μmol (CO)/g (catalyst). Moreover, methane products have been detected in trace amounts, with an approximate output of 1.22 μmol (CH<sub>4</sub>)/g (catalyst) after three hours of UV-vis light irradiation. The CO selectivity is high, at 89.4%. To prove whether the Cu(II) complex catalyst changed before and after the catalysis, we also tested the elemental analysis of the Cu(II) complex catalyst after the catalytic reaction, and the results showed that the catalyst did not change (Found: C, 53.49%, H, 4.12%, N, 11.71%). Our investigation involved the use of two metal complexes as catalysts for the photocatalytic CO<sub>2</sub> reduction: one is a dinuclear Gd(III) complex constructed by 6-phenylpyridine-2-carboxylic acid (L) and 1,10-phenanthroline ligands, [Gd<sub>2</sub>(L)<sub>4</sub>(Phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(DMF)<sub>2</sub>·2H<sub>2</sub>O·2Cl (1) [24], and the other is a Gd(III) coordination polymer constructed using 6-phenylpyridine-2-carboxylic acid (L<sub>1</sub>) and 4,4'-bipyridine ligands, {[Gd(L<sub>1</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]·L<sub>2</sub>]<sub>n</sub> (2) [29]. The results indicate that the primary catalytic products using complex (1) and complex (2) as catalysts were all CO, with yields and a selectivity of 22.1 μmol/g and 78.5% and of 60.3 μmol/g and 100%, respectively. A comparison of the catalytic activity among the three complexes reveals that the yield follows the following order: complex (2) > complex (1) > Cu(II) complex (this work); meanwhile, the selectivity follows the following order: complex (2) > Cu(II) complex (this work) > complex (1). This suggests that both the central metal ion and the ligand play crucial roles in influencing the catalytic activity of the complex.



**Figure 10.** (a) Photocatalytic CO<sub>2</sub> reduction performance and (b) product selectivity of Cu(II) complex catalyst.

### 3. Experimental Section

#### 3.1. Materials and Measurements

Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, 6-phenylpyridine-2-carboxylic acid (HL<sub>1</sub>), 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (L<sub>2</sub>), and NaOH were purchased commercially from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. (Jilin, China) and used as received without further purification. C, H and N analyses were performed using a Vario III EL elemental analyzer (Elementar, Hanau, Germany). IR spectra were recorded on a Tianjin Gangdong FTIR-850 spectrophotometer (Tianjin, China) (KBr discs, 4000–400 cm<sup>-1</sup>). UV-vis spectra in the 190–700 nm region were carried out with a PERSEE T9 spectrophotometer (Beijing, China) in water with quartz cuvettes of 1 cm path length. TG–DTA was recorded by a HENVEN HCT-2 thermal analyzer (Beijing, China). The Hirschfeld surface of the Cu(II) complex was calculated by the Crystal Explorer software [32]. Fluorescence measurements were made on a PE LS-55 fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length (PerkinElmer, Waltham, MA, USA). The excitation and emission slit

widths were 2.5 nm. X-ray diffractions of the Cu(II) complex were collected on a Bruker CCD area detector (SuperNova, Billerica, MA, USA, Dual, Cu at zero, 296.15 K, multi-scan). Samples of the compounds are available from the authors.

### 3.2. Synthesis of Cu(II) Complex

A mixture of 6-phenylpyridine-2-carboxylic acid (HL<sub>1</sub>) (0.0996 g, 0.5 mmol), 4-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (L<sub>2</sub>) (0.1000 g, 0.5 mmol), NaOH (0.020 g, 0.5 mmol), and Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.0998 g, 0.5 mmol) was added to the solution of 20 mL water-ethanol (*v:v* = 1:1) with stirring. The mixture was heated at 76 °C for 4 h and stirred continuously for 2 h at room temperature. The blue block crystals of the Cu(II) complex grew out from the filtrate after 10 days by evaporation. Elemental analysis calcd for [CuL<sub>1</sub>L<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O: C, 53.70%, H, 3.96%, N, 12.05%; Found: C, 53.46%, H, 4.19%, N, 11.76%.

### 3.3. Crystal Structure Determination

X-ray diffraction data for the single crystal (dimensions of 0.15 mm × 0.13 mm × 0.11 mm) of the Cu(II) complex were collected and mounted on a SuperNova, Dual, Cu at zero Bruker Smart CCD diffractometer. Data were collected at 296.10(10) K by using a graphite-monochromator with MoK $\alpha$  radiation. Data collection and absorption correction were carried out by the Olex2 [33]. The structure was solved by the SHELXS program [34] and refined by the Least-Squares minimization techniques SHELXL [35] program. The crystal structural parameters for the Cu(II) complex are listed in Table 3.

**Table 3.** The crystal structural parameters for Cu(II) complex.

Empirical Formula	C <sub>26</sub> H <sub>23</sub> CuN <sub>5</sub> O <sub>7</sub>
Formula weight	581.03
Temperature/K	296.10 (10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	7.11322 (11)
<i>b</i> /Å	11.62617 (17)
<i>c</i> /Å	16.2290 (3)
$\alpha$ /°	96.8735 (13)
$\beta$ /°	98.3307 (13)
$\gamma$ /°	92.0443 (12)
Volume/Å <sup>3</sup>	1316.50 (4)
<i>Z</i>	2
$\rho_{\text{calc}}$ , mg/mm <sup>3</sup>	1.466
$\mu$ /mm <sup>-1</sup>	1.643
<i>S</i>	1.058
<i>F</i> (000)	598
Index ranges	$-8 \leq h \leq 7$ , $-14 \leq k \leq 14$ , $-20 \leq l \leq 20$
Reflections collected	37,707
Independent reflections	5238 [R (int) = 0.0485]
Data/restraints/parameters	5238/4/363
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.058
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0410, <i>wR</i> <sub>2</sub> = 0.1218
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0463, <i>wR</i> <sub>2</sub> = 0.1158

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2333570. The CIF file can be obtained conveniently from the website: <https://www.ccdc.cam.ac.uk/structures> (accessed on 19 February 2024).

### 3.4. Photocatalytic CO<sub>2</sub> Reduction Test

A total of 7 mg of Cu(II) complex catalyst and 50 mL deionized water were mixed into a quartz reactor. Then, the high-purity CO<sub>2</sub> gas was passed into the suspension and maintained at a temperature of 20 °C. After 15 min, the reactor was sealed, and a xenon lamp was turned on (Beijing Trusttech Co., Ltd., Beijing, China). The gas analysis was conducted using a gas chromatograph equipped with a FID detector and Propark Q column (Shandong Huifen Instrument Co., Ltd., Zaozhuang, China).

## 4. Conclusions

A newly designed Cu(II) complex has been successfully synthesized and thoroughly characterized using various analytical techniques, including elemental analysis, infrared spectroscopy (IR), UV-visible spectroscopy (UV-vis), thermogravimetric–differential thermal analysis (TG–DTA), and single-crystal X-ray analysis. The fluorescence properties of the copper complex were also studied. Additionally, Hirschfeld surface analyses have been conducted on the Cu(II) complex. Furthermore, the photocatalytic activity of the Cu(II) complex in CO<sub>2</sub> reduction under UV-visible light irradiation was investigated. The results revealed that CO is the primary product, with yields of 10.34 μmol/g and a selectivity of 89.4% after three hours. The findings presented here serve as a valuable reference for the potential design and synthesis of metal complex catalysts for photocatalytic CO<sub>2</sub> reduction applications.

**Author Contributions:** X.-S.T.: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing, Review and Editing; L.-H.W. and X.-H.Y.: Investigation, Resources, Writing, Review and Editing, Validation; M.A.: Data Curation, Writing, Review and Editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This project was supported by the National Natural Science Foundation of China (No. 21171132), Science Foundation of Weifang (2020ZJ1054) and Science Foundation of Weiyuan Scholars Innovation Team. The authors acknowledge the financial support provided through the Researchers Supporting Project number (RSP2024R147), King Saud University, Riyadh, Saudi Arabia.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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