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SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF A NEW PADDLE-WHEEL Cu(II) COMPLEX: AN INTEGRATED EXPERIMENTAL AND THEORETICAL INVESTIGATION

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ABSTRACT. A new paddle-wheel Cu(II) complex having formula $[Cu(L)_2(DMF)]$ (**1**) (HL = 2-fluorobenzoic acid) has been synthesized and characterized using FTIR and single crystal X-ray diffraction. The single crystal X-ray diffraction study indicates that the carboxylic acid ligand adopt bridging bidentate modes to coordinate Cu(II) centers thereby forming a binuclear copper(II)carboxylate type structure. The complex has been utilized as photocatalyst to photodegrade model aromatic dyes *viz.* methyl violet (MV) and rhodamine B (Rh B) in UV light. The photocatalytic results indicated that**1** offered moderate photocatalytic activity and offers good stability after performing photocatalysis. The plausible mechanism through which **1** exerted photcatalytic property had been proposed by using density of states (DOS) and partial DOS calculations.

KEY WORDS: Photocatalysis, Aromatic dyes, 2-Fluorobenzoic acid, Calculation

INTRODUCTION

The photocatalytic materials which are based on coordination complexes and metal-organic frameworks (MOFs) are gradually becoming a promising area of investigation as this class of materials offers good photocatalytic efficiency [1-2]. In such materials, varied interactions operating between inorganic/clusters and organic linkers led to variety of charge transfer transitions which is responsible for inducing better photocatalytic activities [3-4]. In view of these peculiar features associated with coordination complexes and MOFs, the photocatalytic performances of such materials have been explored extensively. For example, a 3D anionic framework was constructed using O-donor ligand, which exhibited good photocatalytic effects for degrading methyl orange (MO) [5]. Hou *et al.* have explored the polynuclear MOF based materials and tested them as photocatalyst for degradation of organic dyes [6]. These results indicated that the coordination complexes have high photocatalytic activities towards dye degradation due to different kinds of nuclei which form the cluster units [6]. Hence, in view of these pertinent findings the photocatalytic activities of MOF shaving varied type of frameworks should be explored further [7-8].

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As an important class of ligand, carboxylates can adopt diverse coordination modes, *viz.* monodentate, monodentate bridging, bidentate chelating and bidentate bridging and hence can lead to the formation of different two- and three-dimensional structures in the resulting complexes and MOFs. With these aspects in mind, we had made an attempt to explore the coordination properties of 2-fluorobenzoic acid [9] with copper(II) cation. In the present investigation, we report the synthesis and structure of a new Cu(II) based carboxylate complex having formula$[Cu(L)_2(DMF)]$ (**1**) (HL = 2-fluorobenzoic acid). Further, the complex **1** had been used as photocatalytic materials for the degradation of aromatic dyes. The results of these investigations are presented herewith.

EXPERIMENTAL

General considerations

All reagents were commercially available and used without further purification. The powder X-ray diffraction (PXRD) data for the complex was collected on Bruker Advance X-ray diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. FTIR spectrum for the complex as KBr pellet was recorded using Nicolet Impact 750 FTIR in the range of 4000-400 cm^{-1}. The photocatalytic activity studies were carried out in a Shimadzu UV-Vis 2501PC spectrophotometer.

X-ray crystallography

The single crystal X-ray diffraction data was collected using Bruker SMART APEX diffractometer having graphite monochromated MoKα radiation (λ = 0.71073 Å) by using ω-scan technique. The intensities were corrected for absorption effects by using SADABS. The crystal structure of the complex was solved by direct method (SHLEXS-2014) and was refined using full-matrix least-squares procedures based on F^2 (SHELXL-2014) [10]. All the hydrogen atoms were generated geometrically and refined isotropically using a riding model. All non-hydrogen atoms were refined by applying anisotropic displacement parameters. CCDC number: 1898139.

Synthesis of $[Cu(L)_2(DMF)]$

A mixture of HL (0.010 g), *N,N'*-dioxide-3,3'-benzocinnoline (0.019 g), $Cu(NO_3)_2·6H_2O$ (0.036 g) and 10 mL DMF in a 25 mL Teflon-lined stainless steel container was heated to 80 °C for 72 h. After that, container was cooled to room temperature with cooling rate of 5 °C/h to obtain blue crystals of **1** in 58% yield which is based on Cu. Calcd (%) for $C_{34}H_{30}Cu_2F_4N_2O_{10}$, C, 49.21; H, 3.64; N, 3.37. Found C, 49.01; H, 3.44; N, 3.19. IR (cm^{-1}): 2305 (m); 1633 (vs); 1589 (m); 1467 (v); 1302 (m); 1223 (m); 890 (m); 755 (m); 659 (m).

Photocatalytic method

The photocatalytic reactions were performed as follows: The binuclear Cu(II) complex **1** (80 mg) was dispersed in 50 mL aqueous solution containing methyl violet (MV)or rhodamine B (Rh B) (10 mg/L). The mixture was stirred in dark for 30 min to ensure the establishment of adsorption-desorption equilibrium. The photocatalytic degradation of MV/Rh B was conducted on an XPA-7 type photochemical reactor equipped with a 100W mercury lamp (mean wavelength 365 nm) with light intensities at quartz tube positions of 12.7 mW/cm^2. During experiment, aliquots of 5.0 mL was taken out at specified time intervals and the clear solution was separated through centrifugation and then subsequently analyzed by using a UV–visible spectrophotometer. Additionally, control experiments were also conducted under similar reaction conditions in the absence of complex **1**.

Computational details

The probable mechanism dealing with the photocatalytic properties of **1** has been addressed using theoretical calculations. For this the gas phase geometry of the binuclear Cu(II) complex was fully optimized using the B3LYP functional [11-12] using 6-31G** basis set. All the calculations were performed using Gaussian 09 program [13]. After achieving global minimum the density of states (DOS) plot and partial DOS plots for the complex **1** was obtained using GaussSum 3.1 [14].

RESULTS AND DISCUSSION

Synthesis and spectroscopy

If the N,N'-dioxide-3,3'-benzocinnoline was absentin the reaction medium the desired complex was not obtained. Thus, the N,N'-dioxide-3,3'-benzocinnoline behave as template during the reaction between HL and Cu(II) salt. The IR spectra of **1** exhibits the main characteristic absorption bands in the range of 1462–1633 cm^{-1} which is mainly attributed to the asymmetric and symmetric stretching vibrations of the carboxylate groups. Also, the $\Delta\nu$ [ν_{as}(COO)–ν_s(COO)] value of 150 cm^{-1} indicates the coordination of carboxylate groups to the central Cu(II) center.

Crystal structure description

The complex crystallizes in orthorhombic system with *P*cab space group. The asymmetric unit in complex **1** possess Cu(II)cation, two 2-fluorobenzoates, and a DMF molecule. It contains the commonly occurring paddle-wheel unit Cu(II) dinuclear structure constructed by four bridging 2-fluorobenzoates and two DMF ligands (coordination through the DMF oxygen atom). The two halves of the dimeric species are related by an inversion centre at the mid-point of the Cu–Cu bond. This arrangement means that the two DMF molecules are oriented in a linear fashion but pointing in opposite directions. Each Cu atom shows distorted octahedral coordination geometry with four carboxyl O-centers in the basal plane [mean Cu–O(carboxyl) = 1.951(3) Å] and the O-centers of the DMF ligands in the axial positions with a significantly longer Cu–O distance [2.143(3) Å]. All the Cu–O bond distances in the basal plane are in agreement with the bond lengths found in similar complexes [15-16]. The Cu···Cu distance in dinuclear core is 2.630(5) Å, and the Cu–Cu distance between adjacent metal-complexes within each hydrogen-bonded chain is 9.6 Å. The shortest separation through space inter-chain distance between Cu(II) ions is 6.2 Å. The Cu···Cu separation in $Cu_2X_4L_2$ type systems is usually longer when the axial ligand is nitrogen instead of an oxygen atom. The Cu···Cu distances vary from 2.576-2.886 Å, for CuO_4N chromophores, and from 2.563-2.666 Å for CuO_5 chromophores. Hence, the Cu···Cu distance in **1** agrees well the distances reported for CuO_5 chromophores [17]. The carboxylate groups of 2-fluorobenoate have similar coordination, *i.e.* bridging bidentate to Cu(II). Additionally, the four adjoining binuclear units form a 1-D structure by intermolecular hydrogen-bonding with *d*(C-H•••O) = 2.66Å and <(C-H•••O) = 133° (Figure 1b).

Photocatalysis

The complex **1** was used as photocatalyst to photo-decompose model organic dyes pollutants *viz.* methyl violet (MV) and rhodamine B (Rh B). This had previously been established that in due course of degradation, MV and Rh B can be broken down into non-polluting compounds under light irradiation [18]. To monitor the photocatalytic degradation of MV and Rh B, the characteristic UV-Vis absorption band maxima of MV and Rh B observed at ~550 nm were selected. As presented in Figure 2, the band intensity of both the dyes decreases with time when these dyeswere irradiated with UV in presence of **1**. The change in concentration of MV and Rh

B solutions under UV irradiation had been plotted versus irradiation time. The results indicated that approximately 18% of MV and 13% Rh B decomposed during the starting 15 min of irradiation. The photocatalytic performance of the binuclear Cu(II) complex **1** had been compared to the highly connected framework [Ag_7(4,4'-tmbpt)$(HL)_2$(L)(H_2O)] (4,4'-tmbpt = 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole and H_3L = 5-(4-carboxy-benzyloxy)-isophthalic acid) [19]. When **1** was employed as photocatalyst to decompose MV and Rh B, approximately 58% of MV and merely 23% Rh B was decomposed after 45 min. For the sake of comparison, the total catalytic degradation efficiency of the control experiment (without any catalysts)only reached11.7% and 13.6% after 45 min, which indicated that small photo-degradation reaction going on between the **1** and dye solutions. The results indicate that **1** possess low capacity to induce photocatalytic decomposition of Rh B under UV irradiation. The observed variation in the photocatalytic activities can be ascribed to the nature of central metal centers, extent of the conjugation of organic ligands, the final framework structures of the complex and several other aspects [20-23]. When, $[Cu_2(L1)\cdot 5DMF]_n$ (H_4L1 = 3,5-di(3,5-dicarboxyphenyl)nitrobenzene) has been used as photocatalyst for the photodegradation of MV and Rh B. The results indicated that approximately 70% of MV and 41% of Rh B have been decomposed after 45 min irradiation [22]. A3D polymer based on $[Cu_2(COO)_4]$ unit with the paddle wheel structure is a good photocatalyst for degradation of Rh B. The degradation efficiencies of RhB can increase to 90.3% after 165 min in the presence of catalyst [23]. It had been demonstrated that central Cu(II) center and the coordinated ligands may get involved in the photocatalytic degradation of aromatic dyes [21].

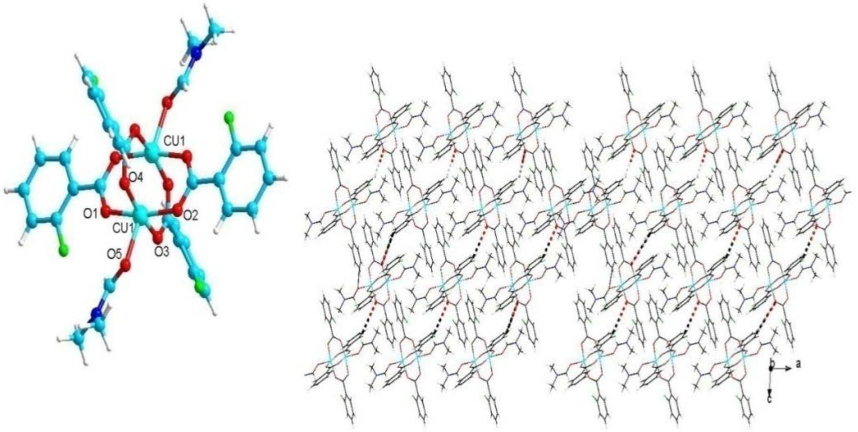

Figure 1. (a) Perspective view of coordination geometries around Cu(II) center; (b) 1-D chains connected by hydrogen bonds (dash line represented the H-bonded interactions).

The powder X-ray diffractogram (PXRD) for **1** was recorded after performing photocatalytic experiments. The obtained diffractogram indicated resemblance of diffraction pattern with that of simulated and as-synthesized **1**. This indicates that **1** maintains its crystalline nature after photocatalysis which further proves stability and reusability (Figure 3a). As confirmed by PXRD and SEM, the structure integrity and surface morphology of **1** are well preserved which indicates its potential as a robust photocatalyst for photodegrading the organic dyes in wastewater (Figure 3b-3c).

To establish the plausible photocatalytic mechanism through which the photo-degradation of the aromatic dyes have been executed by **1**, band structure calculations of the binuclear Cu(II) complex which is based on density functional theory (DFT) method has been performed. The band structure which is precisely represented in terms of density of states (DOS) and partial

DOS plots have been presented in Figure 4. The DOS and partial DOS plots for the complex indicates that the valence band present just below the Fermi level is having contributions from aromatic carbonsand the carboxylate oxygens of the L ligand with small contribution from the Cu(II) center. Also, the conduction band in the case of **1**, lying just above the Fermi level in the range of -1.2 to -0.5 eV have been derived from aromatic carbons with small contributions from oxygen and metal centers. Hence, in **1**, the electronic transitions are mainly operating from aromatic center to another aromatic region (ligand-to-ligand) some mixing from Cu(II) and carboxylate oxygen centers.

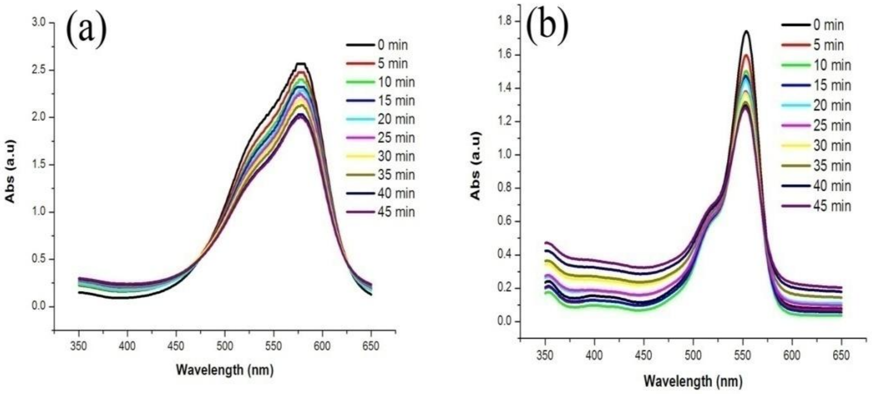

Figure 2. (a) Absorption spectra of the MV solution during the decomposition reaction under the light irradiation with the presence of complex **1**; (b) (a) Absorption spectra of the Rh B solution during the decomposition reaction under the light irradiation with the presence of complex **1**.

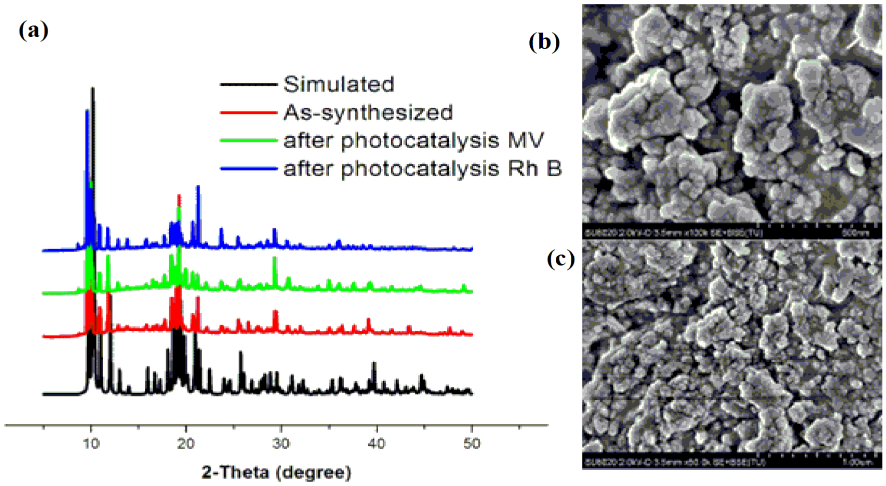

Figure 3. (a) The simulated and experimental PXRD patterns of **1** before and after performing photocatalytic experiments; (b) SEM image of 1 before photocatalysis; (c) SEM image of **1** after photocatalysis.

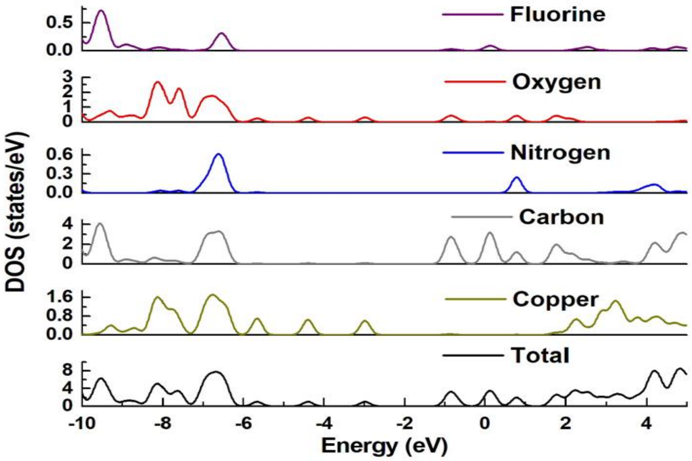

Figure 4. The density of states as well as partial density of states plots for the binuclear Cu(II) complex **1**.

During photoexcitation of **1**, charge transfer transitions from HOMO→LUMO takes place. After charge transfer, the electron deficient HOMO requires an electron to revert back to its stable state. Hence, an electron is captured from water molecule, which gets oxygenated into ·OH active species. These ·OH radicals decomposes the dye effectively to complete the photocatalytic process.The mechanistic scheme suggested to operate during the photocatalytic decomposition of dyes with the aid of binuclear complex **1** can be summarised as follows [24]:

$$1 \xrightarrow{h\nu} 1^{*} \text{ i.e. } 1(h^{+} + e^{-}) \tag{1}$$

$$1(h^{+} + e^{-}) + H_2O \xrightarrow{h\nu} 1(e^{-}) + HO^{\cdot} + H^{+} \tag{2}$$

$$HO^{\cdot} + MV \xrightarrow{h\nu} \text{oxidation products} \rightarrow CO_2 + H_2O \tag{3}$$

$$1\,(e^{-}) + O_2 \xrightarrow{h\nu} 1(O_2^{\cdot -}) \tag{4}$$

$$O_2^{\cdot -}/HO_2^{\cdot} + S \xrightarrow{h\nu} \text{oxidation products} \tag{5}$$

The complex **1** gets photo-excited to produce electron-hole pair (equation 1). This photo-excited molecule undergo reaction with H_2O (i.e. oxidative hole trapping) to produce hydroxyl ($OH^{\cdot}$) radical (equation 2). The hydroxyl radical reacts subsequently with aromatic dyes in variety of ways to produce oxidized products [23]. The dioxygen molecule (O_2) behave as very effective oxidant for the reduced **1(e⁻)** and its main action is to regenerate the reduced photocatalyst **1**. The formation of superoxide radical anion $O_2^{\cdot -}$($O_2^{\cdot -} + H^{+} \leftrightarrow HO_2^{\cdot}$) may participate further in oxidative process [25-26].

CONCLUSION

In summary, s a new copper(II) complex with paddle-wheel unit has been presented. The complex behaved like a photocatalyst to photo-degrade organic dyes of MV and Rh B. However, the photocatalytic results were modest, but using precise carboxylate ligands having pre-tuned electronic functions can develop suitable Cu(II) based complexes, which can offer better catalytic properties.

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