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A novel copper(II) coordination polymer with carboxylate and isoindol backbones of a bifunctional ligand

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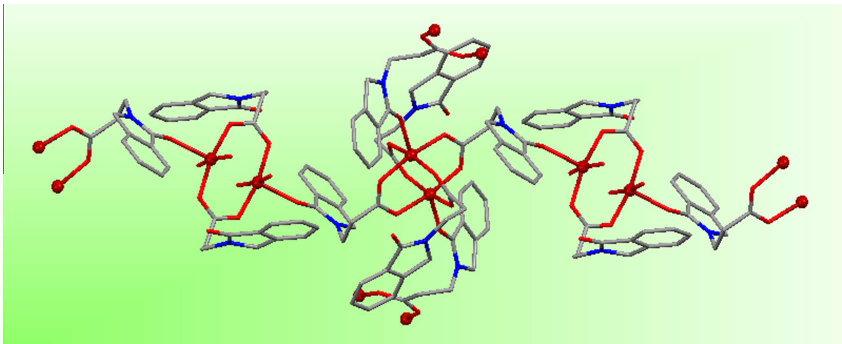
HIGHLIGHTS

- A novel copper(II) coordination polymer of a bifunctional ligand has been prepared.
- The complex consists of the square $Cu_2(O_2CR)_4$ paddlewheel secondary building unit.
- The complex shows axial binding of amide oxygen of the isoindol moiety with Cu(II) ions.

GRAPHICAL ABSTRACT



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ABSTRACT

The reaction of a bifunctional ligand, 3-(1-oxo-1,3-dihydro-isoindol-2-yl)-propionic acid (Hpda) with $Cu(NO_3)_2{\cdot}3H_2O$ in methanol–water in the presence of NaOH at room temperature produces a novel dinuclear copper(II) coordination polymer $[Cu_2(pda)_4]_n$. The complex is fully characterized in the solid state as well as in solution using various analytical techniques including single crystal X-ray diffraction study. The single crystal X-ray structure analysis reveals that the monomeric unit of complex consists of $Cu_2(O_2CR)_4$ paddlewheel building unit, where the two copper centers acquire a distorted square pyramidal geometry with amide oxygen of the isoindol ring of an adjacent Hpda ligand sitting on the axial positions.

1. Introduction

There has been an increasing interest in the design and synthesis of polymeric coordination networks containing paramagnetic metal ions. These class of complexes have potential applications in the fields of molecular magnetic materials, biological catalysis, and enhanced electrical conductivity, etc. [1–4]. One commonly used synthetic strategy in building metal complexes with extended structures is to employ appropriate bridging ligands which are capable of binding to several metal centers and promoting magnetic spin interactions. The self-assembly of the ligands with versatile coordination modes has lead to the formation of the coordination polymers [5,6]. A wide variety of diverse architectures with high structural stability have been prepared by connecting rigid metallic building blocks with appropriate organic linkers. In this context, the carboxylate ligands with their different coordi-

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nation modes have played very important roles in the formation of supramolecular assemblies [7–10]. Several complexes with multiple carboxylic acid groups have proven to be good synthons for supramolecular architectures and coordination polymers [11–15]. The use of polydentate carboxylate ligands, as the organic linkers, have been studied extensively and reported in the literature [16–18].

The focus here is on a bifunctional ligand, Hpda consisting of an isoindol and carboxylate functionalities (Fig. 1). Similar bifunctional carboxylate ligands have been used to assemble various metal ions into aggregates including the paddlewheel $Cu_2(O_2CR)_4$ units that show relevance in the area of supramolecular chemistry [19–22]. The dicopper tetracarboxylate system was of interest not just because of the appealing square architecture of the $Cu_2(O_2CR)_4$ core and the strong axial ligating properties provided by the copper(II) ions, but also because paddlewheel dicopper tetracarboxylates are known to exhibit very strong antiferromagnetic coupling between the unpaired electrons of the d^9 copper(II) ions [23–25]. Recently, we have reported a heptanuclear zinc complex of a carboxylate and amide rich polydentate ligand undergoing an intramolecular reaction between the N-alkylated amide and the benzoate functionality at the half-end of the symmetrical ligand to yield an unsymmetrical ligand with an isoindol moiety [26]. In this paper, we report synthesis, structure, and spectral properties of a new dinuclear copper(II) coordination polymer incorporating the isoindol functionality.

2. Experimental section

2.1. Materials

2-Carboxybenzaldehyde and β-alanine were purchased from Sigma–Aldrich Chemie GmbH, Germany. Copper(II) nitrate trihydrate was obtained from SRL, India. Zinc(II) perchlorate hexahydrate was prepared from zinc(II) carbonate and 1:1 perchloric acid. All other chemicals and solvents were reagent grade materials and were used as received from the commercial sources without further purification.

2.2. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNS/O Series II elemental analyzer. FTIR spectra were obtained on a Perkin–Elmer L120-000A spectrometer (200–4000 cm^{-1}). The solution electrical conductivity was measured with a Systronics digital conductivity meter 304 with a solute concentration of about 10^{-3} M. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 400 NMR spectrometer using TMS as the internal standard. UV–vis spectra were recorded on a Shimadzu UV 1800 (190–1100 nm) (1 cm quartz cell) spectrophotometer. Fluorescence spectroscopy was performed using a Perkin Elmer-LS55 Spectrofluorimeter equipped with FLWINLAB software with a rectangular quartz cuvette of path length 1 cm. The room temperature magnetic susceptibility in the solid state was measured using a home built Gouy balance fitted with a polytronic d.c. power supply. The experimental magnetic susceptibility was corrected for the diamagnetic response using Pascal's constants.

2.3. Synthesis of the ligand, Hpda

2.3.1. Synthesis of N-(2-carboxybenzomethyl)–alanine, H_2cbal

The precursor ligand, H_2cbal was prepared according to the previously published procedure [27]. The product was confirmed by elemental analysis, FTIR and ^{1}H NMR spectroscopy. Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.19%; H, 5.87%; N, 6.27%. Found: C, 59.08%; H, 5.93%; N, 6.20%. FTIR (KBr pellet, cm^{-1}): ν = 3106(b), 2967(b), 1697(s), 1597(s), 1454(s), 1391(s), 1305(s), 1281(s), 1160(s), 1080(s), 987(s), 935(s), 827(s), 718(s), 661(s). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 2.52 (t, 2H, ethylenic), 3.05 (t, 2H, ethylenic), 4.11 (s, 2H, ethylenic), 7.45 (t, 1H, aromatic), 7.48 (m, 2H, aromatic), 7.66 (d, 1H, aromatic).

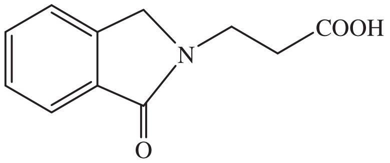


Fig. 1. Chemical structure of the ligand Hpda.

2.3.2. Synthesis of 3-(1-oxo-1,3-dihydro-isoindol-2-yl)-propionic acid, Hpda

The ligand, Hpda was prepared following our published procedure [28]. To a solution of the precursor ligand H_2cbal (0.500 g, 2.242 mmol) in 15 ml of water at room temperature was slowly added $Zn(ClO_4)_2{\cdot}6H_2O$ (0.417 g, 1.119 mmol) dissolved in 10 ml of water for a period of 15 min. After complete addition, a colorless clear solution was observed. The whole reaction mixture was stirred for 2 h at room temperature. The solvent was then rotary evaporated. The off-white precipitate isolated was washed with methanol followed by diethyl ether and hexane. The product was recrystallized from a concentrated water solution of the compound. The product was then dried in vacuo over anhydrous calcium sulfate. Yield: 0.207 g (90%). Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38%; H, 5.40%; N, 6.82%. Found: C, 64.14%; H, 5.57%; N, 6.64%. FTIR (KBr pellet, cm^{-1}): ν = 1695(s), 1595(s), 1371(s), 1339(s), 1220(s), 1173(s), 934(s), 826(s), 761(s). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 2.79 (t, 2H, ethylenic), 3.89 (t, 2H, ethylenic), 4.54 (s, 2H, methylenic protons of the isoindol ring), 7.51–7.73 (m, 4H, aromatic). ^{13}C NMR (400 MHz, D_2O, 25 °C): δ 35.31 (1C, CH_2), 42.88 (1C, CH_2), 49.17 (1C, CH_2 of the iosindol ring), 126.50 (1C, aromatic CH), 127.00 (1C, aromatic CH), 127.91 (1C, aromatic CH), 129.34 (1C, aromatic CH), 134.10 (1C, aromatic CH), 135.72 (1C, aromatic CH), 171.56 (1C, C=O of the isoindol ring), 177.21 (1C, aliphatic carboxylic).

2.4. Synthesis of the complex $[Cu_2(pda)_4]_n$

A water solution (15 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.294 g, 1.219 mmol) was slowly added dropwise at ambient temperature to a magnetically stirred solution of ligand Hpda (0.500 g, 2.437 mmol) and NaOH (0.097 g, 2.437 mmol) in 15 ml methanol during a period of 10 min. The whole reaction mixture was stirred at room temperature for 1 h. It was then filtered to discard any insoluble precipitate. The X-ray quality blue block shaped single crystals were grown by slow evaporation of the clear filtrate at room temperature after ~10 days. Yield: 0.8739 g (76%). Anal. Calcd for $C_{44}H_{40}N_4O_{12}Cu_2$: C, 55.99; H, 4.27; N, 5.94; Found: C, 55.85; H, 4.35; N, 6.02. Molar conductance, Λ_M: (MeOH) = 30 Ω^{-1} cm^2 mol^{-1}. FTIR (KBr pellet, cm^{-1}): ν = 3338(b), 1634(vs), 1607(s), 1591(vs), 1567(s), 1385(vs), 1202(s), 1157(s), 1015(s), 951(s), 891(s), 836(s), 724(s), 609(s). UV–vis (H_2O): λ_{max} (ε, l mol^{-1} cm^{-1}) = 733 (137), 270 (5672)^{sh}, 209 (35,317). μ_{eff} (tot.): 2.18 μ_B; μ_{eff}/Cu: 1.54 μ_B.

2.5. X-ray crystallography and data analysis

Crystal data as well as data collection and refinement for the complex $[Cu_2(pda)_4]_n$ are summarized in Table 1. Selected bond

Table 1
Crystal data and structure refinement parameters of the complex $[Cu_2(pda)_4]_n$.

Empirical formula	$C_{44}H_{40}N_4O_{12}Cu_2$
Formula weight	943.9
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.113(3)
b (Å)	13.431(3)
c (Å)	11.246(2)
α (°)	90.00
β (°)	98.273(4)
γ (°)	90.00
Volume	1960.0(7)
Z	4
Density	1.599 Mg/m^3
Wavelength	0.71073 Å
Temperature	100 K
$F(000)$	972
Absorption coefficient	1.154 mm^{-1}
θ range for data collection	1.57–27.00°
Reflections collected	22,613
Independent reflections	2289
R(F obsd data) [$I > 2\sigma(I)$]	0.0429
wR(F2 all data)	0.0807
Goodness-of-fit on F2	1.040
Largest diff. peak and hole	+0.565 to −0.444 e/$Å^3$

$wR2 = \{\sigma[w(F_o^2 - F_c^2)2]/\sigma[w(F_o^2)^2]\}^{1/2}$.
$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.

distances and bond angles are given in Table 2. A clear blue block shaped single crystal of the title complex with approximate dimensions of 0.203 × 0.156 × 0.115 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker SMART ccd area detector [29,30] and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 22,613 data were measured with Miller indices $h_{min} = -16$, $h_{max} = 16$, $k_{min} = -17$, $k_{max} = 17$, $l_{min} = -14$, $l_{max} = 10$, in the range $1.57 < \theta < 27°$ using ω oscillation frames. The data were corrected for absorption by the multi-scan method [31] giving minimum and maximum transmission factors. The data were merged to form a set of 2289 independent reflections with R = 0.0429. The residual electron density is in the range +0.565 to −0.444 e $Å^{-3}$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 [32,33]. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated at ideal positions (C—H, 0.96 Å), and fixed with isotropic thermal parameters.

Table 2
Selected bond lengths (Å) and angles (°) in the complex $[Cu_2(pda)_4]_n$.

Bond lengths (Å)	
Cu(1)—O(1)	2.134(3)
Cu(1)—O(2)	1.964(2)
Cu(1)—O(3)	1.967(2)
Cu(1)—O(4)	1.962(2)
Cu(1)—O(5)	1.956(2)
Bond angles (°)	
O(5)—Cu(1)—O(4)	89.05(10)
O(5)—Cu(1)—O(2)	87.46(10)
O(4)—Cu(1)—O(2)	167.78(11)
O(5)—Cu(1)—O(3)	168.45(10)
O(4)—Cu(1)—O(3)	90.07(10)
O(2)—Cu(1)—O(3)	91.01(10)
O(5)—Cu(1)—O(1)	102.89(10)
O(4)—Cu(1)—O(1)	97.67(10)
O(2)—Cu(1)—O(1)	94.52(10)
O(3)—Cu(1)—O(1)	88.63(10)

3. Results and discussion

3.1. Synthesis and characterization

The Hpda ligand has been synthesized from a precursor unsymmetrical amino dicarboxylic ligand, N-(2-carboxybenzomethyl)-β-alanine (H_2cbal) following our published procedure [27,28] (Fig. 2) and fully characterized by elemental analysis, FTIR, ^1H and ^{13}C NMR spectroscopic analyses. The reaction of the precursor ligand H_2cbal with $Zn(ClO_4)_2{\cdot}6H_2O$ in aqueous acidic medium at ambient temperature afforded the bifunctional Hpda ligand. The precursor ligand H_2cbal has undergone intra-cyclization reaction between the secondary amine and the benzoate functionality to produce Hpda consisting of an isoindol moiety. The 1-oxo-1,3-dihydro-isoindol ring is most likely achieved via similarly known mechanism that involves the activation of the secondary amine and aromatic carboxylate backbone promoted by the zinc(II) ions [34,35]. It is noteworthy to see that under the specified reaction conditions, Hpda remains uncoordinated to the zinc(II) ions in solution. Corona et al. have reported the synthesis of a series of novel isoindolone derivatives in goods yields via aza-Wittig reaction of iminophosphoranes with dialdehydes under different reaction conditions [36]. Recently, Dietrich et al. have also reported the complexation behavior of isoindolone pincer ligands towards Zn(II), Cd(II) and Pd(II) ions [37].

The reaction of $Cu(NO_3)_2{\cdot}3H_2O$ with the ligand Hpda in 1:2 molar ratio in the presence of stoichiometric amounts of NaOH in methanol–water at room temperature resulted in a blue solution that was easily crystallized into a new polymeric $[Cu_2(pda)_4]_n$ complex (Fig. 3). Molecular structure of the complex has been established using the techniques such as elemental analysis, solution electrical conductivity, FTIR, UV–vis, fluorescence spectroscopy, room temperature magnetic moment measurement and single crystal X-ray structure determination. The molar conductivity value of the complex in MeOH is 30 Ω^{-1} cm^2 mol^{-1} at room temperature, confirming the nonelectrolytic nature of the complex. The room temperature magnetic moment per Cu in the monomeric complex is 1.54 μ_B indicating the strong antiferromagnetic coupling between the two copper centers having one unpaired electron in each copper ion [38–40].

3.2. Crystal and molecular structure of the complex $[Cu_2(pda)_4]_n$

The solid state X-ray crystal structure reveals that the complex adopts a three-dimensional network of coordination polymer with

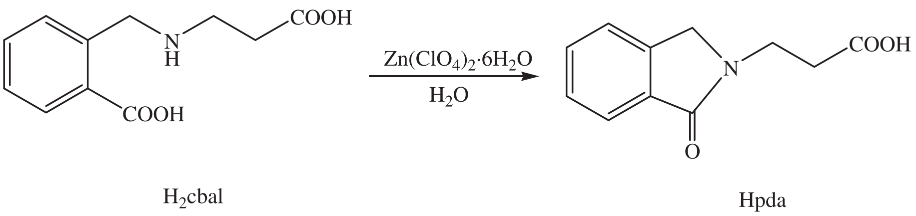
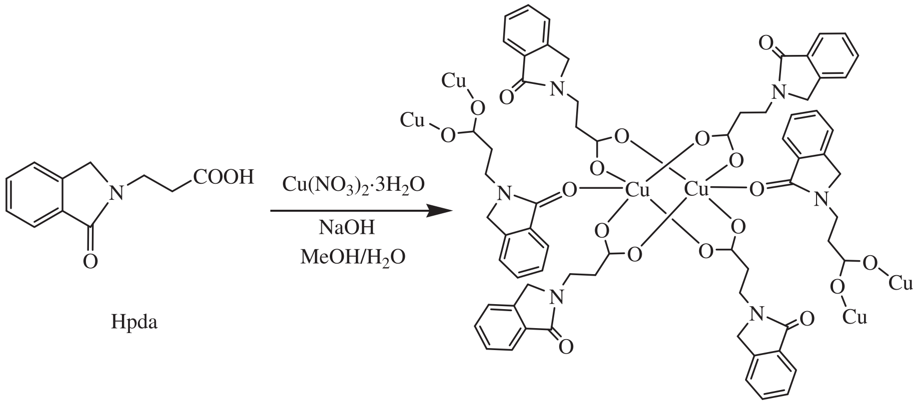


Fig. 2. Synthesis of the ligand Hpda.



Hpda

[Cu$_2$(pda)$_4$]$_n$

Fig. 3. Synthesis of the complex [Cu$_2$(pda)$_4$]$_n$.

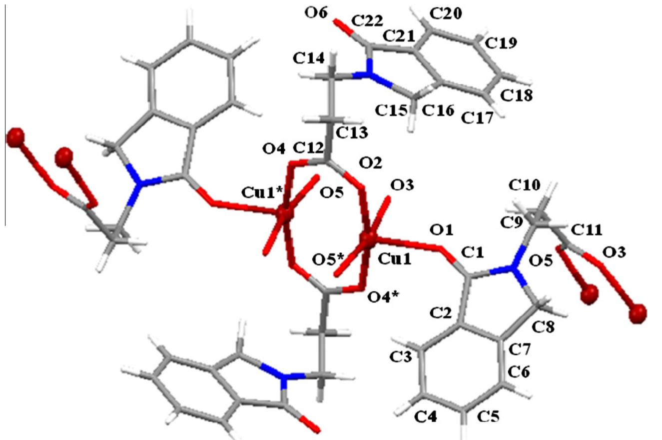


Fig. 4. Labelled stick representation of the molecular structure of the monomeric unit of [Cu$_2$(pda)$_4$]$_n$.

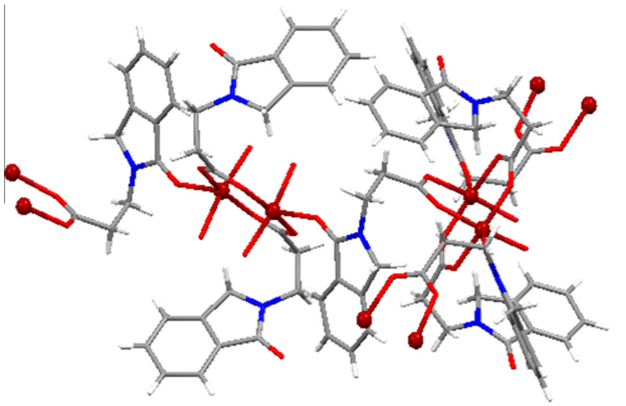


Fig. 5. Stick representation of the molecular structure of the dimeric unit of [Cu$_2$(pda)$_4$]$_n$.

two copper(II) ions and four (pda)$^-$ ligands in the monomeric unit. The structural view of the monomeric unit is depicted in Fig. 4. The crystal structure of the monomeric unit consists of a neutral [Cu$_2$(pda)$_4$] species. The coordination geometry around each copper center is best described by a distorted square pyramidal geometry. Four carboxylate groups from four separate ligands bridge the two copper(II) ions in η^1:η^1:μ_2 fashion placing the carboxylate oxygen donor atoms at the equatorial positions of the five coordinate square pyramidal copper centers. The remaining axial site on each copper center is completed by a oxygen of the isoindol unit of another (pda)$^-$ ligand coming from a neighboring monomeric unit. In this new dinuclear core, the two copper centers and all four carboxylate functionalities form a plane.

The square base of the pyramid around the Cu(1) center is defined by the O2, O3, O4* and O5* atoms. The axial position of the square pyramidal geometry around the Cu1 center is occupied by O1 atom coming from the amide oxygen of isoindol functionality. For carboxylate coordination, the Cu(l)—O(2) bond distance of 1.964(2) Å differs from the Cu(1)*—O(4) bond distance of 1.962(2) Å by 0.002 Å. Again, the Cu(l)—O(3) bond distance of

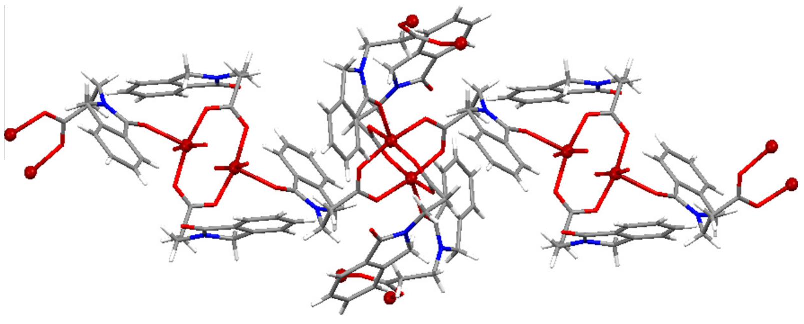


Fig. 6. Stick representation of the molecular structure of the trimeric unit of [Cu$_2$(pda)$_4$]$_n$.

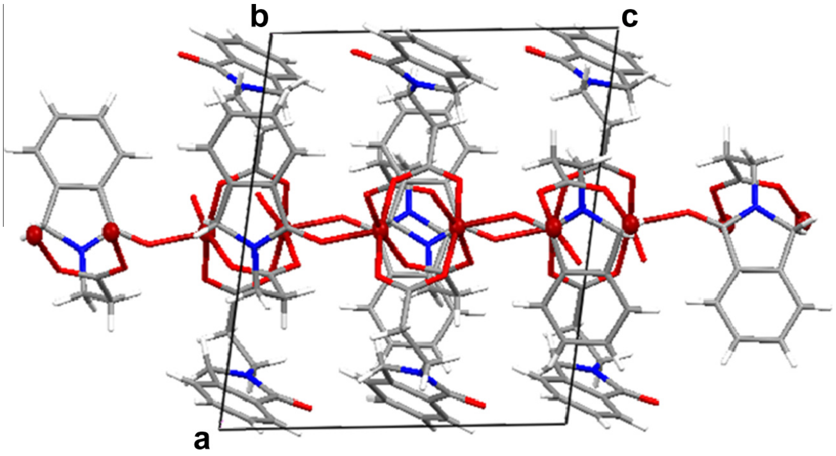


Fig. 7. A unit cell packing diagram of $[Cu_2(pda)_4]_n$.

1.967(2) Å differs from the Cu(1)*—O(5) bond distance of 1.956(2) Å by 0.011 Å. These differences in bond distances of the two metal ions to the oxygen atoms of the *syn–syn* bidentate carboxylate bridges are usually not larger than 0.11 Å as in other diiron or dimanganese complexes [41,42] showing a high degree of symmetry with respect to the carboxylate bridges. The non-bonding Cu···Cu distance is 2.635 Å, the value is within the range for other reported paddlewheel tetracarboxylato dicopper(II) complexes [20,23–25]. The Cu(1)—O(1) axial bond distance is quite longer than the other Cu—O equatorial bond distances [2.134(2) Å vs 1.962(2) Å]. The observed long $Cu—O_{amide}$ axial bond distance could be partly due to the participation of a loan pair of electrons of the amide oxygen during the coordination with copper(II) ions. This $Cu—O_{amide}$ bond distance is in agreement with the values reported in the literature for similar complexes [43].

More interestingly, the solid state X-ray crystal structure of title complex features the ligand's carboxylate and amide oxygens susceptible of being involved in a 3D coordination polymeric network (Figs. 5 and 6). In this network, the $(pda)^-$ ligand which axially coordinates to the copper(II) ions through amide oxygen acts as the linker between the two $[Cu_2(pda)_4]$ monomeric units and connect them to form the 3D coordination network. A unit cell packing diagram (Fig. 7) of the title complex indicates the presence of four monomers in the asymmetric unit cell.

3.3. Spectroscopic properties of the complex

The FTIR spectrum of the complex exhibits two strong bands at 1591 and 1385 cm^{-1} which are due to the asymmetric and symmetric stretching vibrations of the carboxylate functionality of the ligand, respectively. The difference of ~206 cm^{-1} between the asymmetric and symmetric stretching vibrations is attributed to the *syn–syn* bidentate bridging (η^1:η^1:μ_2) mode of carboxylate functionality [44,45]. The band at 1634 cm^{-1} in the spectrum of the complex is assigned to C═O group of the isoindol functionality [46–48]. Comparing this amide carbonyl stretching band with that of the free ligand (~1695 cm^{-1}), it can be suggested that the amide oxygen of the isoindol functionality is involved in strong coordination with copper(II) ion. The FTIR spectrum of the complex also shows a broad band at 3338 cm^{-1} (stretching mode) [28] and a sharp band 1607 cm^{-1} (bending mode) [49] assignable to the ν(O—H) vibrations of the water molecule coming from the moisture of air.

The electronic spectra of the complex in aqueous solution display a single absorption band at 733 nm (ε, 137 l mol^{-1} cm^{-1}) (Fig. 8a). The position of this band is consistent of a d–d transition in copper(II) ions with the observed square-based geometry around the copper centers. Two distinct charge transfer transitions appear in the spectra at 270 nm (ε, 5672 l mol^{-1} cm^{-1}) and 209 nm (ε, 35,317 l mol^{-1} cm^{-1}) (Fig. 8b).

Upon excitation in the UV domain at 270 nm, the ligand Hpda gives rise to a very low intense broad fluorescence spectrum at 401 nm in aqueous solution (Fig. 9). The fluorescence property of the coordination polymer of Hpda with copper(II) ions has been examined in aqueous solution. The copper(II) complex displays a

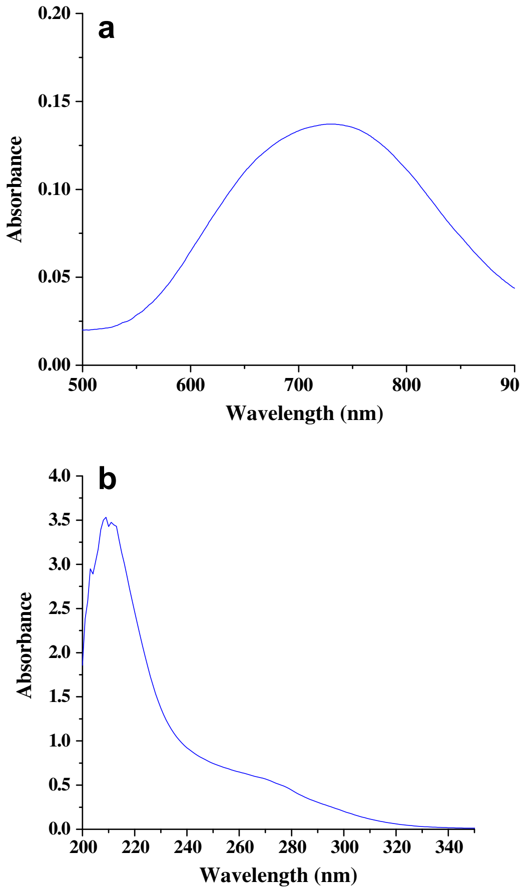


Fig. 8. Electronic spectra of the complex $[Cu_2(pda)_4]_n$ in aqueous solution: (a) 1×10^{-3} (M) and (b) 1×10^{-4} (M).

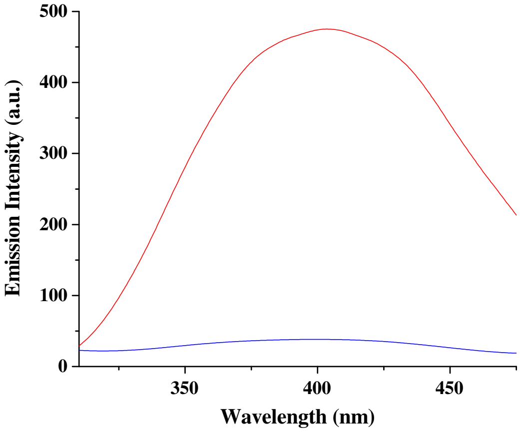


Fig. 9. Emission spectra of the ligand Hpda (– line; 1×10^{-3} M; $\lambda_{exi} = 270$ nm; $\lambda_{emi} = 401$ nm) and the complex $[Cu_2(pda)_4]_n$ (– line; 1×10^{-3} M; $\lambda_{exi} = 270$ nm; $\lambda_{emi} = 402$ nm) in aqueous solution.

highly intense broad emission band with maximum at 402 nm upon excitation at 270 nm (Fig. 9). There is a significant increase in the fluorescence intensity of the ligand Hpda upon addition of copper(II) ions. Recently, it has been reported that the fluorescence emission of various substrates containing fluorophores have significantly been enhanced due to the interaction with copper(II) ions [50,51].

4. Concluding remarks

In conclusion, we have demonstrated that a bifunctional ligand effectively promotes the formation of a novel dinuclear copper(II) coordination polymer under specific experimental conditions. The single crystal X-ray structure analysis reveals that the title complex consists of the square $Cu_2(O_2CR)_4$ paddlewheel secondary building unit, where the copper centers acquire distorted square pyramidal geometry. The 3D coordination network of the polymer is the result of the aggregation of the $[Cu_2(pda)_4]$ monomers connected by the isoindol oxygen on one side and carboxylate oxygen on the other side of the ligand. The fluorescence spectroscopic study indicates that the binding of copper(II) ions with this ligand enhances its emission intensity. The current investigation shows two different types of coordination modes of the bifunctional ligand that will positively contribute to the expansion of the field of coordination and supramolecular chemistry.

Supplementary material

CCDC 930040 contains the supplementary crystallographic data in CIF format for the $[Cu_2(pda)_4]_n$. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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