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REGULAR ARTICLE

Dimeric complexes of copper (II) arylcarboxylate with 4-cyanopyridine: synthesis, structural characterization and linear absorption properties

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Abstract. Two new dimeric copper (II) complexes containing 2-chlorobenzoato/4-formylbenzoato and 4-cyanopyridine ligands, $[Cu_2(\mu_2\text{-}O_2CC_6H_4\text{-}Cl)_4(C_5H_4N\text{-}CN)_2]$ (**1**) and $[Cu_2(\mu_2\text{-}O_2CC_6H_4\text{-}CHO)_4(C_5H_4N\text{-}CN)_4]$ (**2**), were synthesized and characterized by elemental analysis, FT-IR and ESR spectroscopy and single-crystal X-ray diffraction methods. In the structure of **1**, each copper^{II} cation was surrounded by four oxygen atoms from four different carboxylate of four 2-chlorobenzoate molecules and one nitrogen atom of one 4-cyanopyridine ligand. In the crystal structure of **2**, each copper^{II} cation was coordinated by four oxygen atoms from one chelating and two bridging 4-formylbenzoate anions and two nitrogen atoms of two 4-cyanopyridine ligands. C–H···O and C–H···Cl hydrogen bonds (for **1**) and C–H···O hydrogen bonds and weak C–H···π interactions (for **2**) further stabilize the crystal structures. The linear optical absorption characterizations of the complexes were performed by using UV-Vis spectrophotometer. The results obtained from the linear absorption spectra of the complexes observed that these complexes can be used for optical filtration among nearly 600 and 950 nm wavelengths for concentrations which are higher than 4 g/L.

Keywords. Dimeric complex; paddle-wheel; copper (II); linear absorption.

1. Introduction

Metal-Organic Frameworks (MOFs) are composed of organic ligands and metals and have porous structures. They are widely used in gas storage thanks to their excellent gas adsorption capabilities in their pores. Thanks to these pores, the ability of MOFs to adsorb the various liquids and gases is increased and thus it is thought that they can provide the solution of energy and environmental problems.[1,2] MOFs are also used in different areas including absorption,[1] storage,[2] separation,[3] catalysis,[4] magnetic,[5] luminescence,[6] sensor[7] and biomedical applications.[8] Secondary building units (SBU) with the interesting supramolecular structures such as 1D chains, 2D networks and 3D porous structures are milestones for inorganic chemistry. These building units are also from MOFs. A lot of new crystalline materials have been synthesized to develop new strategies for crystal engineering.[7,11–13] One of the most interesting architectural examples of secondary building units is the paddle-wheel structures.[9] Paddle-wheel complexes, with the general formula $[M_2L_4]$, attract attention with their good adsorption properties. The dimeric paddle-wheel complexes with various carboxylate and dicarboxylate groups form pseudo metal-metal bond bridges with four μ_2 carboxylate parts. In addition, the crystal structure is becoming much more stable with *N*-donor ligands in the axial positions. The pyridine and its derivatives, which are among these *N*-donors, help to build hydrogen bonds, and they provide increased rigidity of the crystal structures. Carboxylate groups exhibit different coordination behaviors such as 'monodentate', 'chelating', 'monoatomic bridging', 'syn, syn-', 'syn-anti-', 'anti, anti-', 'syn, anti, anti-' and 'syn, syn, anti-'. One of the most common examples of "syn, syn- conformation" is paddle-wheel structures.[10–16] One of the first examples of these

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complexes is $[Cu_2(acetate)_4]$,[17] which is known with good sorption, and another one is $[Cu_2(pyrazine)_2(acetate)_4]_n$, which is known for its strong antiferromagnetic properties.[18] There are also a few examples of complexes having 'anti, anti-conformation' in the literature. The carboxylate complexes having this conformation are the copper (II) acetate and chloroacetate with isonicotinamide complexes having general formulas $[Cu_2(chloroacetato_2)_4(isonicotinamide)_4]$ and $[Cu_2(acetato)_4(isonicotinamide)_4]$, respectively.[19,20] Moreover, there are also only four arylcarboxylates complexes. Three of these structures have copper atom as the central atom[21–23] and cobalt atom in one.[24]

π-Conjugated systems are used as optical materials due to their electron transport properties. The *N*-heterocyclic aromatic compounds which include these systems have gained importance in modern research due to their photothermal stabilities and photophysical properties. Especially, ligands with electron donor or acceptor groups connected to π-conjugated systems are used for designing of new fluorescence materials. The fluorescence properties of the materials used in molecular sensors and optoelectronic devices are based on the electron push-pull. Pyridine does not have fluorescence properties. However, electron-donating groups such as the -OH, $-OCH_3$ and $-NH_2$ connected to the ring, and the electron-withdrawing groups such as -CN cause the presence and increase of fluorescence, phosphorescence and luminescence properties. Cyanopyridines that contain nitrile group in 2-, 3- and 4- positions have very good fluorescence properties. The spectral characteristics of cyanopyridines are influenced by the inductively electron-withdrawing pyridine ring's nitrogen, ring's π-conjugated system and the intramolecular n-π* and π-π* electronic transitions of the electron-withdrawing –CN group. Charge transport capacity, high thermal, photochemical and photophysical stability increase the potential for cyanopyridines and their compounds to be used as fluorescence material.[25–29] In addition to these properties, there are many metal complexes with cyanopyridine. In some monomeric and dimeric copper complexes, cyanopyridine act as a co-ligand coordinated *via* the nitrogen atom in the pyridine ring.[30–32]

In this context, two new dimeric complexes, $[Cu_2(\mu_2\text{-}O_2CC_6H_4\text{-}Cl)_4(C_5H_4N\text{-}CN)_2]$ (**1**) and $[Cu_2(\mu_2\text{-}O_2CC_6H_4\text{-}CHO)_4(C_5H_4N\text{-}CN)_4]$ (**2**), were prepared and their spectral, structural and linear absorption properties were investigated.

2. Experimental

2.1 *Materials and physical measurements*

4-Formylbenzoic acid (Fluka, Germany); 2-chlorobenzoic acid and copper (II) sulfate pentahydrate (Aldrich, Germany); 4-cyanopyridine (4-pyridinecarbonitril) (Sigma-Aldrich, Germany) and sodium bicarbonate (Merck, Germany) were purchased commercially and used without any purification process.

2.2 *Preparation of tetra-μ-2-chlorobenzoato-κ^{8}O:O'-bis[(4-cyanopyridine-κN)copper(II)]*

Sodium bicarbonate (0.84 g, 10 mmol) and 2-chlorobenzoic acid (1.56 g, 10 mmol) were dissolved in 100 mL distilled water in an erlenmeyer to obtain sodium 2-chlorobenzoate. The reaction was continued until CO_2 gas was completely removed from the medium. In separate beakers, 4-cyanopyridine (1.04 g, 10 mmol) and $CuSO_4.5H_2O$ (1.24 g, 5 mmol) were dissolved in 30 mL distilled water. 4-Cyanopyridine and sodium 2-chlorobenzoate solutions were added to the prepared $CuSO_4$ solution, respectively. After a week, the dark green crystals formed were filtered off and washed with distilled water and dried at room temperature. Yield 1.96 g (82.01%). Anal. Calcd. (%) for the Complex 1, $C_{40}H_{24}Cl_4Cu_2N_4O_8$ (MW = 957.51 g/mol) C, 50.17; H, 2.53; N, 5.85. Found: C, 50.05; H, 2.52; N, 5.80.

2.3 *Preparation of bis(μ-4-formylbenzoato-κ^{2}O:O')bis[(4-formylbenzoato-κ^{2}O:O'-bis(4-cyanopyridine-κN)copper(II)]*

Sodium bicarbonate (0.84 g, 10 mmol) and 4-formylbenzoic acid (1.50 g, 10 mmol) were dissolved in 100 mL distilled water in erlenmeyer to obtain sodium 4-formylbenzoate. The reaction was continued until CO_2 gas was completely removed from the medium. In separate beakers, 4-cyanopyridine (1.04 g, 10 mmol) and $CuSO_4.5H_2O$ (1.24 g, 5 mmol) were dissolved in 30 mL distilled water. 4-Cyanopyridine and sodium 4-formylbenzoate solutions were added to the prepared $CuSO_4$ solution, respectively. After one day, blue and green colored crystals were formed. The crystals were filtered off and washed with distilled water. The green colored crystals were separated under a microscope. The blue colored crystal was not suitable for the single X-ray diffraction method. The green colored crystals were selected for the single X-ray diffraction method. Green colored crystals were used in all analyzes. Yield 1.08 g (37.16%). Anal. Calcd. (%) for the Complex 2, $C_{56}H_{36}Cu_2N_8O_{12}$ (MW = 1140.01 g/mol) C, 59.00; H, 3.18; N, 9.83. Found: C, 58.95; H, 3.18; N, 9.85.

2.4 *X-ray crystal structure analysis*

Single-crystal X-ray diffraction analysis of the obtained complex was performed on a Bruker APEX-II CCD diffractometer. Structures were solved by direct methods and refined by full-matrix least squares against F^2 using SHELXS-97.[33] All non-H atoms were refined anisotropically. APEX2,[34] SAINT,[34] SAINT, SHELXS97,[33] SHELXL97, ORTEP-3 for Windows,[35] WinGX publication routines[35] and PLATON[36] computer programs were used. The experimental details related to the determination of crystal structures were given in Table 1.

2.5 *Spectroscopic measurements*

The elemental contents (C, H and N) of the complexes were determined by a LECO, CHNS-932 elemental analyzer. FT-IR spectra were recorded on Alpha-P Bruker FT-IR spectrometer with solid samples in the range of 4000–400 cm^{-1}. The resolution was set up to 4 cm^{-1}, signal/noise ratio was established by 4 scans. The linear absorption spectra of the ligands and complexes with different concentrations (1 g/L and 4 g/L) were recorded among 262 and 1100 nm wavelengths at room temperature by using UV-Vis spectrophotometer. The optical emission (fluorescence) spectra of the complex 1 and 2 were measured with the help a fluorescence spectrophotometer (*Perkin Elmer LS55*) under different excitation wavelengths among 200 nm and 780 nm. ESR spectra of complexes were measured using a JEOL-JESFA300 X-band ESR spectrometer at liquid nitrogen temperature.

3. Results and Discussion

3.1 *Crystal structure of 1*

Complex 1 has a centrosymmetric paddle-wheel unit (Figure S1, Supplementary Information). Cu1 is penta-coordinated by one nitrogen atom from one 4-cyanopyridine (CP) ligand and four O_{COO} atoms from four 2-chlorobenzoate (CHLB) anions and has square pyramidal geometry. The copper^{II} cations are bridged by two carboxylate oxygen atoms of four CHLB anions, as indicated in Figure 1. The four

Table 1. Experimental details.

	1	**2**
Crystal data		
Chemical formula	$C_{40}H_{24}Cl_4Cu_2N_4O_8$	$C_{56}H_{36}Cu_2N_8O_{12}$
M_r	957.51	1140.01
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	296	296
a, b, c (Å)	12.8086 (3), 10.2819 (3), 15.5258 (4)	9.0893 (2), 23.0052 (5), 13.0503 (3)
β (°)	97.666 (3)	109.861 (2)
V (Å^3)	2026.42 (9)	2566.52 (10)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.37	0.90
Crystal size (mm)	0.11 × 0.10 × 0.07	0.09 × 0.07 × 0.06
Data collection		
Diffractometer	Bruker *APEX*-II CCD [[38]]	Bruker *APEX*-II CCD [[38]]
Absorption correction	Multi-scan *SADABS*; [[38]]	Multi-scan *SADABS*; [[38]]
T_{min}, T_{max}	0.859, 0.905	0.916, 0.935
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	61186, 4828, 4226	54388, 5237, 4269
R_{int}	0.045	0.086
(sin θ/λ)$_{max}$ (Å^{-1})	0.659	0.626
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.110, 1.28	0.089, 0.165, 1.29
No. of reflections	4828	5237
No. of parameters	262	360
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
		$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 11.5316P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.42	0.44, −0.46

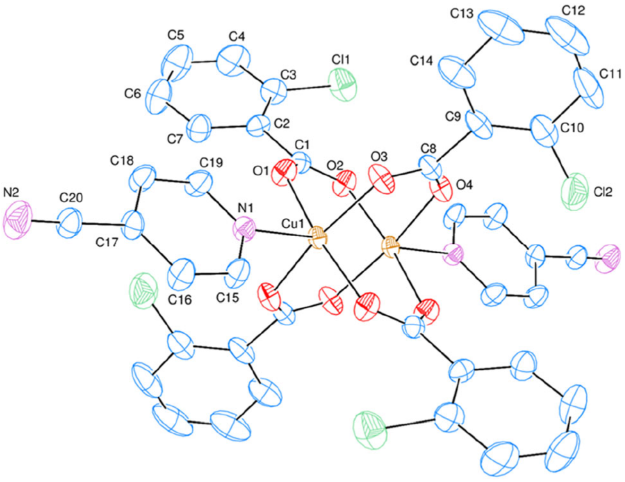

Figure 1. The molecular structure of the dinuclear compound (1) with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

oxygen atoms form a distorted square-planar environment around the Cu1 atom with an average Cu1-O bond length of 1.976(2) Å. The CP ligand is coordinated to the Cu^{II} cation *via* nitrogen atom of pyridine ring only. The distorted square-pyramidal coordination is completed by the pyridine ring's nitrogen atom, N1, of the CP ligand at a distance of 2.173 (3) Å (Table 2). The N1-Cu1$\cdots$Cu1^{i} angle is 174.44(5)°. In the previous researches, the Cu$\cdots$Cu distances in the paddlewheel complexes having similar ligands were reported to be between 2.61–2.69 Å. Cu1$\cdots$Cu1^{i} distance, which corresponds to 2.6533(8) Å in our synthesized paddlewheel unit, is consistent with the literature (Table 2).[16,37,38] The dihedral angles between the planar carboxylate groups and the neighboring benzene rings are 30.3 (2)° and 36.3 (2)°. Inter-benzene dihedral angle of CHLB is 86.7 (2)°. The dihedral angles between the pyridine ring of CP C (N1/C15-C19) and benzene rings are 23.5 (1)° and B/C = 84.8 (1)°. The molecules were assembled by the bifurcated C–H$\cdots$O and C–H$\cdots$Cl hydrogen bonds into a network (Figure 2), and these bonds contributed to the stabilization of the crystal structure.

3.2 *Crystal structure of 2*

The asymmetric unit of the dinuclear complex 2 comprised of one half of the complex molecule (Figure S2, Supplementary Information). The Cu^{II} cations are surrounded by two nitrogen atoms of two 4-cyanopyridine (CP) ligands, two carboxylate oxygen atoms of two bridged 4-formylbenzoate (FBA) anions and two oxygen atoms of one chelating FBA anion (Figure 3). The CP ligands are coordinated to the Cu^{II} cation *via* heteronitrogen atoms only. Two FBA anions act as both bridging and chelating coordinated to the Cu^{II} cation. The four carboxylate oxygen atoms around the Cu1 atom exhibit a distorted square-planar geometry with the Cu-O bond lengths are 1.945 (3), 1.974 (3), 2.306 (4) and 2.306 (4) Å (Table 2). The distorted octahedral

Table 2. Selected geometric parameters (Å, °).

1			
Cu1—O3	1.969 (2)	Cu1—O2^{i}	1.981 (2)
Cu1—O1	1.974 (2)	Cu1—N1	2.173 (3)
Cu1—O4^{i}	1.981 (2)	Cu1—Cu1^{i}	2.6533 (8)
O3—Cu1—O1	91.25 (11)	O4^{i}—Cu1—N1	93.47 (11)
O3—Cu1—O4^{i}	167.80 (11)	O2^{i}—Cu1—N1	96.37 (10)
O1—Cu1—O4^{i}	88.42 (11)	O3—Cu1—Cu1^{i}	85.55 (8)
O3—Cu1—O2^{i}	86.56 (11)	O1—Cu1—Cu1^{i}	80.45 (7)
O1—Cu1—O2^{i}	167.83 (10)	O4^{i}—Cu1—Cu1^{i}	82.38 (7)
O4^{i}—Cu1—O2^{i}	91.21 (11)	O2^{i}—Cu1—Cu1^{i}	87.44 (7)
O3—Cu1—N1	98.69 (11)	N1—Cu1—Cu1^{i}	174.44 (8)
O1—Cu1—N1	95.79 (10)	O2—C1—O1	125.8 (3)
Symmetry code: (i) −x+1, −y+1, −z+1.			
2			
Cu1—O5	1.945 (3)	Cu1—N3	2.050 (5)
Cu1—O2	1.974 (3)	Cu1—O4^{i}	2.306 (4)
Cu1—N1	2.041 (5)	O4—Cu1^{i}	2.306 (4)
O5—Cu1—O2	155.37 (16)	O5—Cu1—O4^{i}	117.75 (15)
O5—Cu1—N1	93.37 (17)	O2—Cu1—O4^{i}	86.74 (15)
O2—Cu1—N1	90.88 (17)	N1—Cu1—O4^{i}	85.84 (17)
O5—Cu1—N3	90.68 (17)	N3—Cu1—O4^{i}	86.29 (17)
O2—Cu1—N3	88.23 (17)	O1—C1—O2	123.8 (5)
Cu1—Cu1^{i}	4.355(3)		
Symmetry code: (i) −x, −y, −z.			

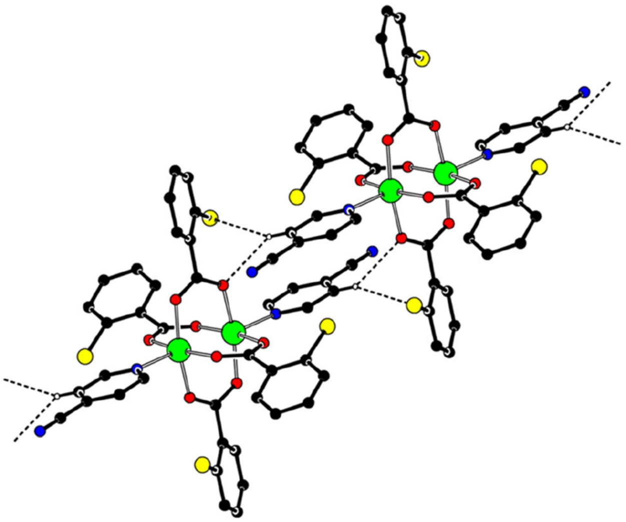

Figure 2. A partial packing diagram for 1.

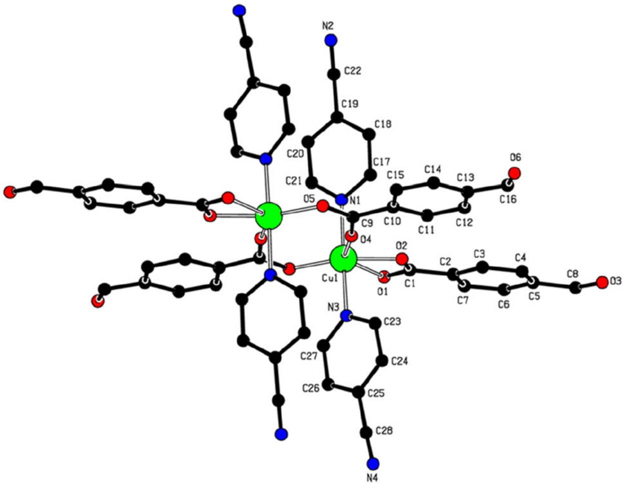

Figure 3. The molecular structure of the dinuclear compound (2). Thermal ellipsoids are drawn at the 50% probability level.

environment is completed by the hetero-nitrogen atoms. Cu1-N1 and Cu1-N3 distances are 2.041(5) and 2.050(5) Å, respectively. The N-Cu···Cu angles (a = x, - y, - z) are 81.98 (12) and 92.44 (12)°. The dihedral angles between the planar carboxylate groups (O1/O2/C1), (O4/O5/C9) and the neighboring benzene rings A (C2-C7), B (C10-C15) are 0.8 (4)° and 8.2 (3)°, respectively, while that between planar benzene rings A and B is A/B = 7.7 (2)°. The dihedral angle of inter-pyridine rings of CP ligands (C (N1/C17-C21) and D (N2/C23-C27)) is 12.5 (2)°. The O1-Cu1-O2 angle containing the chelating FBA anion is 55.09 (14)°. The corresponding O-Cu-O angles are 53.50 (14)° in [Cu$_2$ (4-formylbenzoato)$_4$(isonicotinamide)$_4$],[22] 57.75 (2)° in [Cu(4-fluorobenzoato)$_2$(4-fluorobenzoic acid)(nicotinamide)$_2$],[39] 58.3 (3)° in [Cu(benzoato)$_2$ (N,N'-diethylnicotinamide)$_2$][40] and 55.2 (1)° in [Cu(acetylsalicylate)$_2$(pyridine)$_2$].[41] In complexes of similar structure, Cu···Cu distance has been reported in the range of 3.94–4.45 Å.[21–23] The Cu1···Cu1a distance of the synthesized dimeric complex 2 is 4.355 (3) Å. In the crystal structure, the bifurcated C–H···O and C–H···Cl hydrogen bonds assembled the molecules into a network (Table 3 and Figure 4), and contributed the stabilization of the crystal structure. In addition, the crystal structure is also stabilized by the weak C–H···π interaction. The *D*-H···*A* angles and the *D*—H, H···*A* and *D*···*A* distances are due to the presence of hydrogen bonds and these bonds are responsible for crystal stabilization of both complexes.

3.3 *FT-IR spectra*

The FT-IR Spectra of the synthesized complexes are given in Figures S3 and S4 (Supplementary Information). In the FT-IR spectra of Complex 2, the C-H stretching vibrations which are doublet caused by the formation of fermi resonance show at 2818 and 2725 cm^{-1} similar to literature.[42] The C=O absorption bands of the aldehyde group were observed at 1698 (for 2) cm^{-1}. Aldehyde group peaks are generally observed strong band at 1730 cm^{-1}.[42] This shift is due to the intermolecular interactions the O3 oxygen atom of the ligand with an aldehyde in the crystal structure of Complex 2. The absorption bands which were observed at about 2250 cm^{-1} can be attributed to the CN group of the 4-cyanopyridine ligand. In the synthesized complexes, the absorption peak of this group was observed in the same area.[43] In the literature, the vibrations of aryl chloride, which is reported to be 870 cm^{-1}, are recorded in the near area (881 cm^{-1}).[43] Asymmetric and symmetric ν(COO$^-$) vibrations of the carboxyl group of the complexes were showed at 1557–1386 (1) and 1558–1402 (2) cm^{-1}, respectively. 'Δν' is the difference between the asymmetric carboxylate (ν_{asym}(COO$^-$)) and symmetric carboxylate (ν_{sym}(COO$^-$)) absorption peaks and it give information about related to the coordination mode of the carboxylate. Δν values for complexes 1 and 2 are 171 cm^{-1}, 156 cm^{-1}, respectively. When comparing the metal carboxylates with the sodium salt of the acid, the following order of coordination is proposed: $\Delta\nu_{monodentate} >> \Delta\nu_{ionic} \geq \Delta\nu_{bridging} >> \Delta\nu_{chelate}$. Our results indicate that carboxylate ligands have bridging (Complex 1) and bridging-chelating (Complex 2) coordination mode.[21,23,44–46]

Table 3. Hydrogen-bond geometry (Å, °).

1				
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···Cl2^{ii}	0.93	2.82	3.670 (4)	153
C16—H16···O4^{ii}	0.93	2.54	3.315 (5)	140
Symmetry code: (ii) *x*, *y*+1, *z*.				
2				
C20—H20···O3^{ii}	0.93	2.41	3.202 (8)	143
C26—H26···O1^{iii}	0.93	2.49	3.073 (7)	121
C27—H27···O1^{iii}	0.93	2.44	3.066 (7)	124
C15—H15···*Cg*4^{iv}	0.93	2.77	3.658 (6)	159

Symmetry codes: (ii) x−1, y, z−1; (iii) −x+1, −y, −z; (iv) x−1, y, z. Cg4 is the centroid of the ring D (N2/C23—C27).

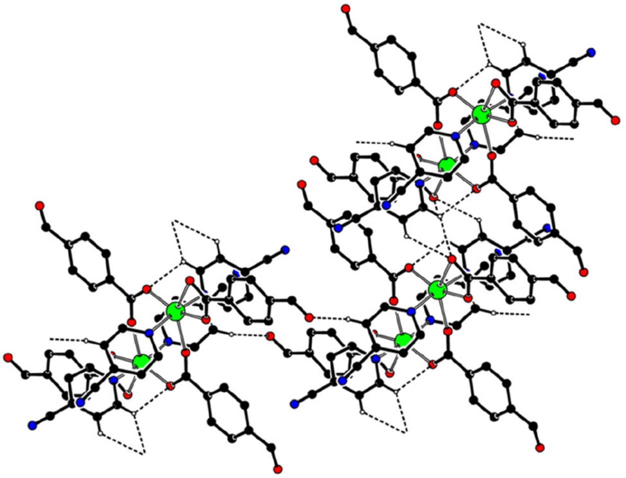

Figure 4. A partial packing diagram for 2.

3.4 *Linear absorption and emission spectra results*

The recorded linear absorption spectra of the complexes were given in Figure 5. The UV-Vis spectra of the ligands were given as Figure 6. As seen from Figure 5, the complexes are showing strong linear absorption behaviors in the ultraviolet region and among 600 and 950 nm wavelengths. The comparison of linear absorption spectra of the complexes with that of the ligands has been clearly shown that the formation of the complexes lead to occurring of the Q-bands which are represented with linear absorption peaks among 600 and 950 nm. When the linear absorption behavior in the ultraviolet region causes from the σ → σ* and π → π* transitions, the n → π* transitions mainly contribute to linear absorption behavior among 600 and 950 nm wavelengths. The linear absorption peaks from 600 nm to 950 nm are the result of the linear combination of the atomic orbital coefficients of the highest occupied molecular orbital (HOMO). Under the light of the obtained linear absorption results, it can be said that these complexes are good candidates for optical filtration applications in the ultraviolet region within 600 and 950 nm wavelengths.

Complex **1** and **2** did not exhibit emission spectra and are therefore considered to have no fluorescence, unlike 4-cyanopyridine, which is one of the starting components.

3.5 *ESR spectra*

Electron paramagnetic resonance (ESR) spectroscopy is a useful technique and gives information about the distribution of the unpaired electrons and bonding between the metal cation and ligands. The ESR spectra recorded in DMF at 0.01 g/mL concentration at liquid nitrogen temperature (Figures 7 and 8). The obtained spectra of complexes observed signals related to the dissociation of the dimers into monomers caused by the presence of 4-cyanopyridine. ESR spectra of complexes are similar to those of dimeric complexes obtained in previous studies. The solid-state ESR spectra of the Cu(II) complexes is consistent with the coordination observed in the single-crystal X-ray crystallography of the structures. The magnetic sensitivity of the dinuclear Cu (II) complex χ_M.T (B_0=0.1T)) and the effect of two Cu (II) cores in dimeric geometry on each other resulting from the increased magnetism resulting from the low temperature (123 K) ESR spectrum of a typical strong antiferromagnetic structure feature. ESR peaks seen in +48/−80 (for 1), +48/−84 (for 2) and +460/−475 (for 1), +462/−477 (for 2) B(mT) regions support the strong antiferromagnetic structure of the interconnected dimeric structure with carboxylate blinds having dinuclear Cu (II) nuclei in both complexes. The strong antiferromagnetic property also shows that the distance between the two Cu (II) nuclei is the distance that can form a bond close enough to affect each other. The ESR spectra are expected to show six signals for spin state S=1. However,

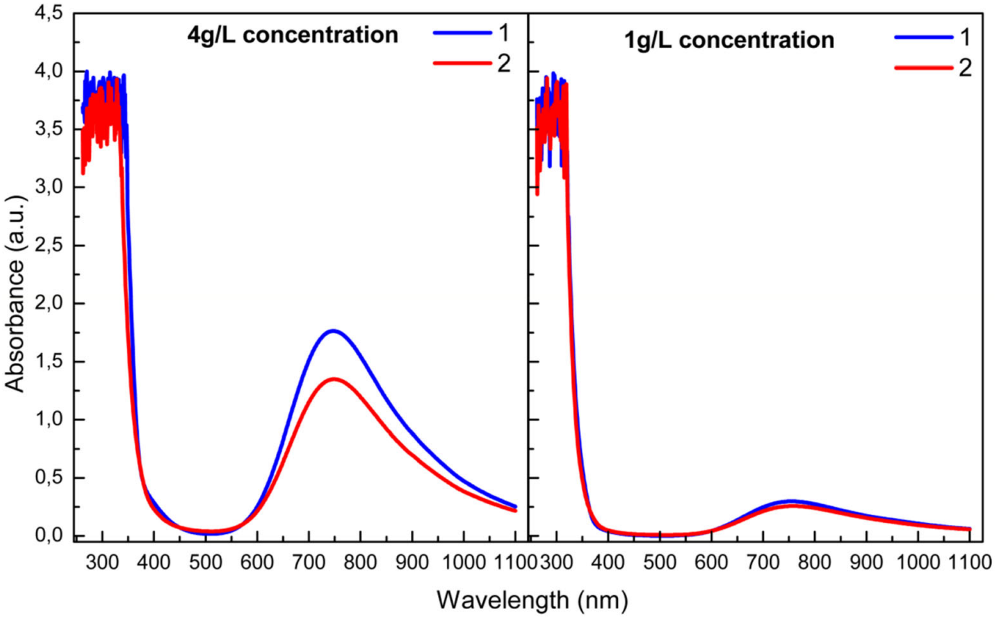

Figure 5. The linear absorption spectra of the complexes.

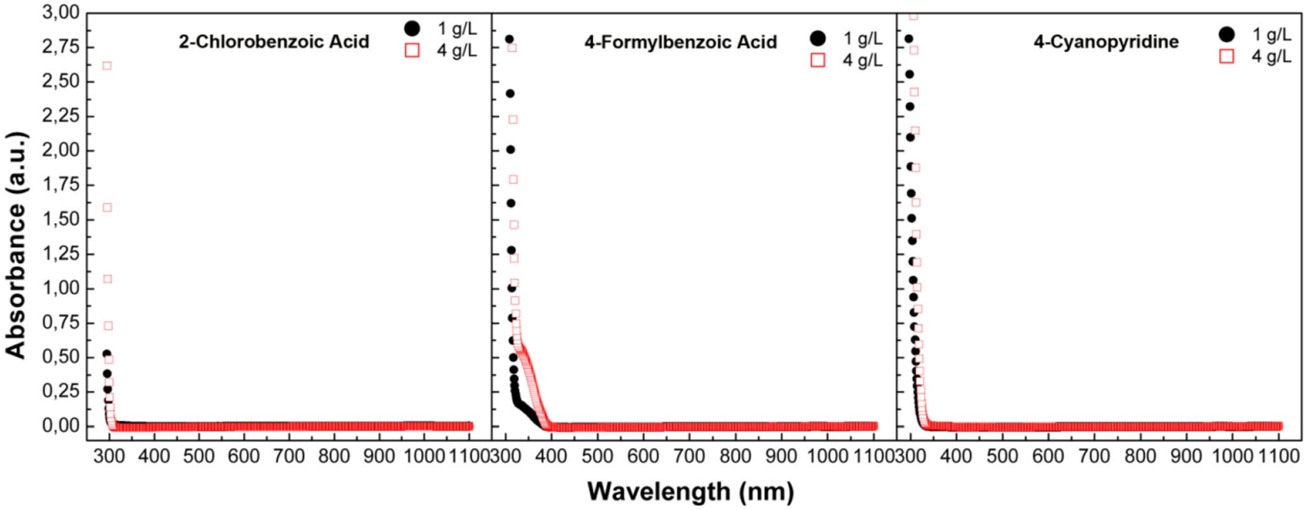

Figure 6. The linear absorption spectra of the ligands.

usually, only four of them are very prominent. The expected peaks in the +340/−350 B(mT) region were found to be very weak.[47–52]

4. Conclusions

Two new dimeric copper(II) complex were synthesized and characterized structurally. In the complex 1, $[Cu_2(\mu_2\text{-}O_2CC_6H_4\text{-}Cl)_4(C_5H_4N\text{-}CN)_2]$, Cu^{II} cations are completed a distorted square-pyramidal geometry via four oxygen atoms from the four bridging 2-chlorobenzoate anions in the basal plane and the two nitrogen atoms of the 4-cyanopyridine ligand in the apical position. In the complex 2, The Cu^{II} ions are coordinated as octahedral form by four oxygen atoms from one chelating and two bridging 4-formylbenzoate anions and two nitrogen atoms of two 4-cyanopyridine ligands leading to an overall MO4N2 coordination environment. In crystal structures, the complexes are formed three-dimensional supramolecular networks by C–H···O and C–H···Cl hydrogen bonds and C–H···π interactions. The Cu-Cu distances in both the complexes are 2.6533 (8) and 4.355(3). It can be recommended that these complexes are as optical filtration material according to the linear absorption results. The emission spectra of the complexes do not exhibit any

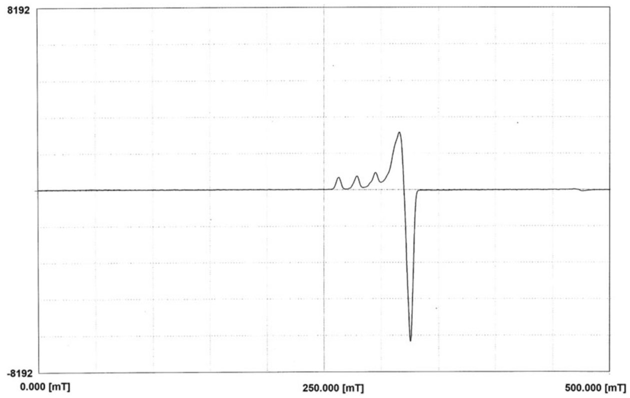

Figure 7. Electron paramagnetic resonance (ESR) spectra of Complex 1.

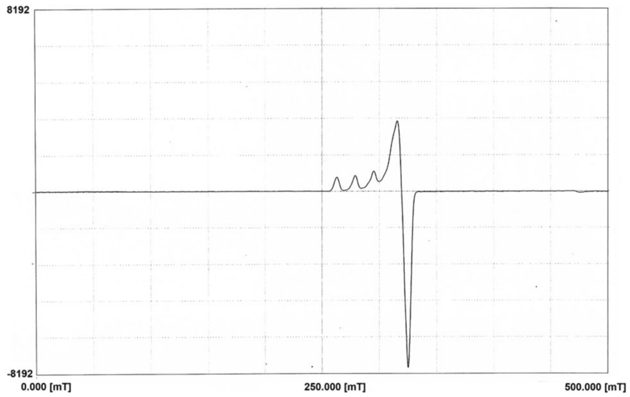

Figure 8. Electron paramagnetic resonance (ESR) spectra of Complex 2.

significant excitation (emission band (200–700 nm)). Therefore, two synthesized dimeric copper complexes are not recommended as fluorescence materials. ESR spectra prove that complexes are dimeric. In addition, dissociation in the presence of 4-cyanopyridine that is a pyridine derivative is similar to previous research.

Supplementary Information (SI)

CheckCIF files and Supplementary Figures S1–S4 are available at www.ias.ac.in/chemsci. Crystallographic data for the structures **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 1937871 (**1**) and 1937872 (**2**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; FAX: (+44) 1223 336033, or online via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

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