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Self-assembled hydrogen-bonded coordination networks in two copper(II) carboxylates with 4-pyridylmethanol

Research Article

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Abstract: The crystal and molecular structure of $[Cu(nif)_2(4\text{-}PM)_2]\cdot CH_3OH$ (1) and $[Cu(2\text{-}Clbz)_2(4\text{-}PM)_2(H_2O)]$ (2), (where nif = niflumate anion, 2-Clbz = 2-chlorobenzoate anion and 4-PM is the 4-pyridylmethanol), have been determinated by X-ray crystallography. The Cu^{2+} cation in (1), is coordinated by two pairs of oxygen atoms from asymmetric bidentate niflumate anions and by a pair of pyridine nitrogen atoms from monodentate 4-pyridylmethanol ligands in trans position forming an extremely elongated bipyramid. The Cu^{2+} cation in (2), is coordinated by a pair of oxygen atoms from monodentate 2-chlorobenzoate anions, further by a pair of pyridine nitrogen atoms from monodentate 4-pyridylmethanol ligands and finally by a water oxygen atom forming a tetragonal-pyramidal coordination polyhedron. The molecules of both complexes in crystal structures are linked by O–H···O hydrogen bonds, which created a three-dimensional hydrogen-bonding networks. The π-π stacking interactions are also observed in crystal structures of complex 2. The spectral properties (IR and electronic spectra) of both complexes were also investigated.

Keywords: *Copper complexes • Carboxylates • Supramolecular chemistry • Hydrogen bonds • Crystal structure*

1. Introduction

Crystal engineering and rational design of metal-containing supramolecular systems, including hydrogen bonds, π-π stacking, or by other intermolecular interactions, keep record of rapid developing in recent time [1-4]. Interesting metal-containing supramolecular systems consist of coordination or organometallic complexes connected by strong hydrogen bond motifs, including type of interactions: O–H···O, N–H···O, N–H···N and O–H···N [5-9]. The construction of hydrogen-bonded coordination networks is achieved by employing organic ligands with H-bonding functionalities of *e.g.* $–NH_2$, –OH, $–CO_2H$, –CONHR and $–CONH_2$ combined with coordination sites of transition metals [2-6]. One of the most potential ligands for construction hydrogen-bonded networks is 4-pyridylmethanol (4-PM). Only few complexes with 4-pyridylmethanol have been studied by X-ray so far. 4-pyridylmethanol in these complexes exists as a terminal ligand, thus complex molecules contain terminal O–H functionality, which are connected by O–H…O hydrogen bonds [10-16] into supramolecular structure. Only one complex is known, where 4-pyridylmethanol is N,O-bridging ligand [17] so far. In comparison 4-pyridylmethanol as a ligand with related 3-pyridylmethanol, 3-pyridylmethanol is usually N,O-bridging ligand and it is complexes are coordination polymers resulting 1-D chains [18-23] or 2-D sheets [18,19,24-28]. In only few complexes, 3-pyridylmethanol appears as a terminal N-donor ligand which is additionally connected by some O–H…O hydrogen bonds [18,29-33].

In this paper, we present our results of structural and spectral investigation of two copper(II) carboxylate complexes with 4-pyridylmethanol $[Cu(nif)_2(4\text{-}PM)_2]\cdot CH_3OH$, (nif = niflumate (2-{[3-(trifluoromethyl)

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phenyl]amino}-3-pyridinecarboxylate) anion) (**1**); [Cu(2-Clbz)$_2$(4-PM)$_2$(H$_2$O)], (2-Clbz = 2-chlorobenzoate anion) (**2**).

2. Experimental Procedure

2.1. Preparation of the complex [Cu(nif)$_2$(4-PM)$_2$]•CH$_3$OH (1)

A green copper(II) niflumate monohydrate has been prepared by method Viossat *et al.* [34]. The crystals of (**1**) were prepared by adding 20 mL of a methanol solution of the 4-pyridylmethanol (0.02 mol) to 100 mL of a methanol solution of the copper(II) niflumate monohydrate (0.01 mol). The mixture was stirred, filtered, left to cool and stand at room temperature. The green product precipitated was collected and used for re-crystallization from methanol solution to give air stable crystals. Yield: 70%. *Anal.* Calc. for [Cu(nif)$_2$(4-PM)$_2$]•CH$_3$OH (**1**): C, 53.46; H, 3.91; N, 9.59%. Found: C, 53.39; H, 3.95; N, 10.03%. IR data (KBr, cm^{-1}): 3388s,sh ν(O–H)$_{4PM}$, 3277s ν(O–H)$_{4PM}$, 1625s,br ν$_{as}$(COO$^-$), 1617s,br ν(C=N)$_{4PM}$, 1597vs ν(C=N)$_{nif}$, 1446vs ν$_s$(COO$^-$), 1065m ν(C–O)$_{4PM}$.

2.2. Preparation of the complex [Cu(2-Clbz)$_2$(4-PM)$_2$(H$_2$O)] (2)

A green copper(II) 2-chlorobenzoate monohydrate was prepared by adding aqueous solution of cupric sulfate to sodium 2-chlorobenzoate obtained by the reaction of an aqueous solution of NaOH (0.05 mol) by addition of 2-chlorobenzoic acid (0.05 mol) in water. The crystals of (**2**) were prepared by adding 20 mL of a methanol solution of the 4-pyridylmethanol (0.02 mol) to 100 mL of a methanol solution of the copper(II) 2-chlorobenzoate monohydrate (0.01 mol). After heating to boil, the solution was left to cool and stand at room temperature. A blue product precipitated, was filtered, washed with cold water and dried in air. Crystals of (**2**), suitable for X-ray analysis, were obtained from the mother liquor after slow room-temperature crystallization. Yield: 80%. Calc. for [Cu(2-Clbz)$_2$(4-PM)$_2$(H$_2$O)] (**2**): C, 51.12; H, 3.96; N, 4.59%. Found: C, 51.23; H, 3.98; N, 5.03%. IR data (KBr, cm^{-1}): 3404s ν(O–H)$_{H2O}$, 3389s,sh ν(O–H)$_{H2O}$, 3215s ν(O–H)$_{4PM}$, 1617s,br ν$_{as}$(COO$^-$), 1609vs ν(C=N)$_{4PM}$, 1396vs ν$_s$(COO$^-$), 1062m ν(C–O)$_{4PM}$.

2.3. Analysis and spectral measurements

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA 1112 elemental analyser. Electronic spectra (190–1100 nm) of the complexes were measured in Nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrometer, and infrared spectrum in the region of 4000–100 cm^{-1} were measured with a Nicolet MAGNA 750 IR or NICOLET 5700 FT-IR spectrometer using KBr pellet and Nujol suspension techniques for 4000–400 cm^{-1} region and Polyethylene pellet for 400–100 cm^{-1} region.

2.4. Crystallography

Crystal data and details of data collections for all structures are given in Table 1. Data for (**1**) were collected using a diffractometer Nonius KappaCCD [35,36] with graphite monochromated Mo Kα radiation at 173 K. Data for (**2**) were collected using a diffractometer Kuma KM-4 CCD [37] with graphite monochromated Mo Kα radiation at 100 K. The diffraction intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using methods multi-scans [38] for (**1**) or analytical [39] (**2**). The structures were solved by direct methods using the program SIR-97 [40] (**1**,**2**) and refined by the full-matrix least-squares method on all *F*^{2} data using the program SHELXL-97 [41]. Geometrical analysis were performed using SHELXL-97 and PLATON [42] programs. The structures were drawn by ORTEP-3 [43], XP in SHELXTL [41] and PLATON programs.

The methanol solvate molecule of (**1**) has orientation disorder with refined site-occupancy factors of the two

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{39}H_{34}CuF_6N_6O_7$	$C_{26}H_{24}Cl_2CuN_2O_7$
***M*$_r$ / mol^{-1}**	896.26	610.91
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pca*2$_1$	*Pna*2$_1$
***T* /K**	173(2)	100(2)
***a* /Å**	30.120(5)	24.744(2)
***b* /Å**	5.391(1)	8.301(4)
***c* /Å**	23.641(3)	13.542(6)
***α* /°**	90	90
***β* /°**	90	90
***γ* /°**	90	90
***V* /Å^3**	3838.8(11)	2781.5(18)
Z	4	4
ρ_{calc} /g cm^{-3}	1.516	1.459
***μ* /mm^{-1}**	0.657	1.023
crystal size /mm	0.40 x 0.35 x 0.20	0.63 x 0.52 x 0.36
***F*(000)**	1796	1252
θ_{max} /°	24.7	26.4
reflections collect.	20371	28092
***R*1 (2σ)**	0.0491	0.0278
w*R*2 (all data)	0.1025	0.0680
Data / restrains / parameters	6290/4/541	5009/1/362
S	1.012	1.064
$\Delta_{\rho max}$ /e Å^{-3}	0.497	0.258
$\Delta_{\rho min}$ /e Å^{-3}	–0.363	–0.275

disordered parts (full methanol molecule) of 0.68 and 0.32, respectively. The C–O distances have been restrained by SADI instructions [SADI O1A C1S O1B C2S].

2-chlorobenzoate anions of (**2**) have orientation disorders, and the refined site-occupancy factors of the disordered parts (chlorophenyl groups: Cl2/C14–C19; Cl2'/C14'–C19'; Cl1/C21–C26; Cl1'/C21'–C26' and associated H atoms) are 0.925(2); 0.075(2); 0.844(2); 0.156(2), respectively. The benzene rings (C21'–C26') and (C14'–C19') (in the Fig. 5 dashed open lines) of the disordered anions were refined only as rigid ideal hexagons with C—C = 1.39 Å and constrained with the same isotropic displacement parameters.

The remaining H atoms were positioned with C-H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxyl H atoms were positioned with O-H = 0.84 Å and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(O)$. The hydroxyl H atoms were positioned with N-H = 0.88 Å and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(N)$.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC nos.690403 (**1**) and 690404 (**2**). Further details of the crystal structures investigations are available free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.htmL (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Structure of $[Cu(nif)_2(4\text{-}PM)_2]\bullet CH_3OH$ (1)

Molecular structure of **1** is shown in Fig. 1. The coordination polyhedron around the copper atom in **1** is asymmetric elongated tetragonal bipyramidal (4 + 1 + 1). The tetragonal plane is built up by a pair of asymmetric bidentate niflumate anions using carboxyl oxygen atoms [Cu1–O1 = 1.926(3) Å and Cu1–O3 = 1.924(3) Å] and by a pair of neutral 4- pyridylmethanol molecules using pyridine ring nitrogen atoms [Cu1–N5 = 2.062(4) Å and Cu1–N6 = 2.058(4) Å] (Table 2) in *trans* positions. The axial positions are occupied by the other pairs of oxygen atoms from niflumate anions [Cu1–O2 = 2.779(4) Å and Cu1–O4 = 2.797(4) Å]. The value of the *T* parameter [$T = R_S/R_L$] [44], of 0.71 is in agreement with the small bond angle O1–Cu–O2 as a consequence of Jahn-Teller effect [44].

Molecular structure of complex **1** can be compared with complex *trans*-bis(niflumato-*O*,*O'*)-bis(N,N-diethylnicotinamide-*N*)copper(II) [45], where the Cu^{2+} ion is coordinated as elongated tetragonal bipyramidal (4 + 2), but it lies in inversion centre. An axial bonds Cu—O_{carb} are shorter (2.643(3) Å). The orientation of torsion angles C2—C3—C8—C9 and C16—C17—C22—C23 in complex **1** of 172 and 168°, respectively, are comparable with another copper(II) niflumate complexes [34,45,46]. The amine hydrogen atoms are linked to the carboxyl oxygen atoms of the niflumate anions by N3—H3N···O2 and N4—H4N···O4 by intramolecular hydrogen bonds, (Table 3). Donor-acceptor atoms distances (N···O) are 2.677(5) and 2.672(6) Å, respectively, creating six-membered rings *S*(6) [47] thus stabilizing the molecular structure.

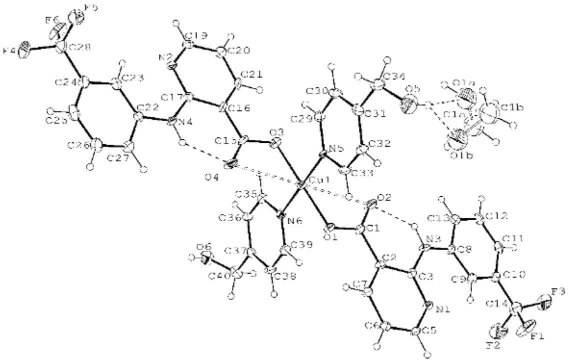

Figure 1. Perspective view of complex (**1**), with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The disordered methanol molecule is drawn by open lines.

Table 2. Selected bond lengths (Å) for **1** and **2**.

1	
Cu1–O1	1.926(3)
Cu1–O3	1.924(3)
Cu1–N5	2.062(4)
Cu1–O2	2.779(4)
Cu1–O4	2.797(4)
Cu1–N6	2.058(4)
2	
Cu–O3	1.973(2)
Cu–O1W	2.216(2)
Cu–N2	2.030(2)
Cu–O5	1.978(2)
Cu–N1	2.029(2)

The complex and methanol molecules, which lie in the cavities (See Supplementary Fig. 1) of **1** are linked to adjacent methanol ligands of complex molecules by O—H···O bonds in 2-D hydrogen bonding sheets. The cavities represent 2.8% per unit cell. The uncoordinated methanol molecules are linked to hydroxyl groups of complex molecules by O5—H5O···O1A or O5–H5O···O1B, O6—H6O···O5 (-*x*+2, -*y*, *z*-1/2) and O1A—H1A···O6 (-*x*+2, -*y*+1, *z*+1/2) hydrogen bonds in infinite supramolecular chains $C_3^3(6)$ [47] (Fig. 2), with donor-acceptor atoms distances = 2.640(10) 2.86(2), 2.694(7) and 2.767(12) Å, respectively.

Table 3. Hydrogen bonds geometries (Å, °) for complexes **1** and **2**.

D—H···A		H···A	D···A	D–H···A
1				
N3–H3N···O2		1.95	2.677(5)	139
N4–H4N···O4		1.95	2.672(6)	138
O5–H5O···O1A		1.81	2.640(10)	171
O5–H5O···O1B		2.13	2.86(2)	146
O6–H6O···O5	(-x+2, –y, z–1/2)	1.87	2.694(7)	165
O1A–H1A···O6	(-x+2, –y+1, z+1/2)	1.87	2.767(12)	168
2				
O1–H1O···O4	(-x+1, -y+1, z+1/2)	1.82	2.650(2)	172
O2–H2O···O6	(-x+3/2, y-1/2, z-1/2)	1.84	2.643(2)	159
O1W–H2W···O2	(-x+3/2, y-1/2, z+1/2)	1.89	2.717(2)	168
O1W–H1W···O1	(-x+1, -y, z-1/2)	1.93	2.765(2)	178
C6–H6A···O3	(-x+1, -y, z+1/2)	2.46	3.343(3)	148
C12–H12B···O5	(-x+3/2, y+1/2, z-1/2)	2.54	3.401(3)	145

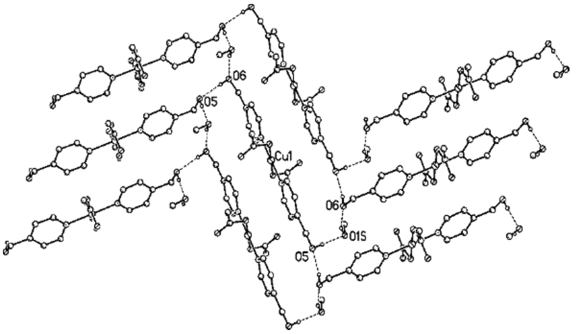

Figure 2. The layers in crystal structure of complex (1) with hydrogen bonding chains $C_3^3(6)$. Only methanol molecules from majority part of disorder are drawn. The aromatic rings and trifluoromethyl groups of niflumate anions are omitted for clarity.

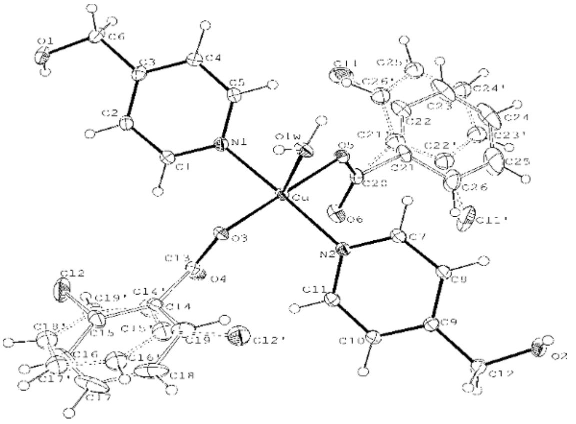

Figure 3. Perspective view of (**2**), with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Open and dashed open lines indicate the main and side populations, respectively, of disordered 2-chlorophenyl groups.

The additional π-π stacking interactions [48] (See Supplementary Fig. 2) are found between the pyridine ring [N1/C2-C7 (Φ1)] and benzene [C8-C13 (Φ2) (*x*, *y*-1, *z*)] and between pyridine ring [N2/C16-C21 (Φ3)] and benzene ring [C22-C27 (Φ4) (*x*, *y*+1, *z*)] of niflumate anions. The centroids…centroids (C_g…C_g) distances are 3.68 [π(Φ1)-π(Φ2)] and 3.78 Å [π(Φ3)-π(Φ4)] and distances between two planes are in the ranges 3.12-3.59 and 3.00-3.66 Å, respectively.

3.2. Structure of [Cu(2-Clbz)$_2$(4-PM)$_2$(H$_2$O)] (2)

The coordination polyhedron around the copper atom in **2** (Fig. 3, Table 2) is tetragonal pyramid (4 + 1). The tetragonal basal plane is built up by a pair of unidentate 2-chlorobenzoate anions using carboxyl oxygen atoms [Cu–O3 = 1.973(2) Å and Cu–O5 = 1.978(2) Å] and by a pair of neutral 2-pyridylmethanol molecules using pyridine ring nitrogen atoms [Cu–N1 = 2.029(2) Å and Cu–N2 = 2.030(2) Å] (Table 2) in *trans* positions, forming the basal plane. The axial position is occupied by water molecule [Cu–O1W = 2.216(2) Å]. The O3–Cu–O5 and N1–Cu–N2 bond angles are 178.05(8)° and 173.42(8)°, respectively. The Cu atom lies in the equatorial plane O3–N1–O5–N2. In this case τ = 0.07, which agree with tetragonal-pyramidal geometry [48]. The complex **2** can be compared with [Cu(clof)$_2$(4PM)$_2$(H$_2$O)]•2H$_2$O (clof$^-$ = clofibriate anion) [16], which has the same penta-coordination, but copper atoms lie on twofold rotation axis.

Molecules of complex **2** are linked to adjacent molecules by O–H···O and C–H···O hydrogen bonds, which created 3-D hydrogen bonding network (Table 3). The 3-D hydrogen bonding network consists of 2-D sheets approximately along *b* axis (Fig. 4). The packing diagram of **2** in the 2-D sheet is shown in Fig. 5. The coordinated water hydrogen atoms are linked to hydroxyl oxygen atoms of the 4-pyridylmethanol ligands of the adjacent complex molecules by hydrogen bonds [O1W– H1W···O2 (3/2 − *x*, *y* − 1/2, *z* − 1/2) and O1W–H2W···O1 (1 − *x*, −*y*, 1/2 + *z*)] with interatomic distance O···O of 2.717(2) and 2.765(2) Å, respectively. The hydroxyl hydrogen atoms of 4-pyridylmethanol are linked to the uncoordinated carboxyl oxygen atoms of 2-chlorobenzoate anions of adjacent complex molecules by other hydrogen bonds [O1–H1O···O4 (1 − *x*, 1 − *y*, *z* − 1/2) and O2–H2O···O6 (3/2 − *x*, *y* − 1/2, 1/2 + *z*)] with interatomic distance O···O of 2.650(2) and 2.643(2) Å, respectively, which creating $R_4^4(14)$ [47] supramolecular synthons. The O–H···O hydrogen bonds in crystal structure of **2** are supported by very weak C–H···O hydrogen bonds between methylene hydrogen atoms of 4-pyridylmethanol ligands and coordinated carboxyl oxygen atoms of 2-chlorobenzoate anions of adjacent complex molecules [C6–H6B···O3 (1 − *x*, −*y*, *z* − 1/2) and C12–H12A···O5 (3/2 − *x*, 1/2 + *y*, 1/2 + *z*)] with

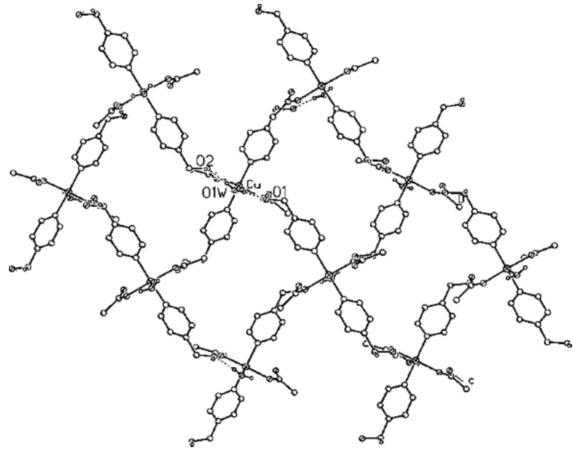

Figure 4. View of the two-dimensional sheet of (**2**). Dashed lines indicate O–H···O and C–H···O hydrogen bonds. The 2-chlorophenyl groups are omitted for clarity.

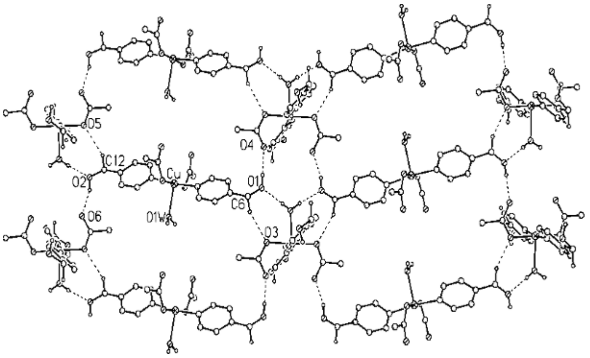

Figure 5. View of the two-dimensional sheet of (**2**). Dashed lines indicate O–H···O and C–H···O hydrogen bonds. The 2-chlorophenyl groups are omitted for clarity.

interatomic distance C···O of 3.343(3) and 3.401(3) Å, respectively, and creating $R_2^2(7)$ [47] metallocyclus. This system of hydrogen bonds is different from those one in the complex $[Cu(clof)_2(4PM)_2(H_2O)]\cdot 2H_2O$ [16].

3.3. IR and electronic data

All the typical features of IR spectra are clearly compatible with the characteristics of the complexes under study. The IR spectra of both complexes (**1, 2**) shows a strong absorption bands in the region 3404–3215 cm^{-1}. These frequencies correspond to the O–H stretches of hydroxyl group of 4-pyridylmethanol as well as in complex **2** to the antisymmetric and symmetric O–H stretches of coordinated water molecule. Some characteristic IR bands in the IR spectra corresponding to carboxyl group stretching vibrations are found in the expect regions. The values of Δν in the IR spectra of the complexes **1** and **2** are larger than 271 and 221 cm^{-1}, respectively. They correspond to the bidentate for **1** and unidentate for **2** modes of coordination. The $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in the complex **1** are present at 1625 and 1345 cm^{-1}, respectively. The same bands in the complex **2** are present at 1617 and 1396 cm^{-1}, respectively. The vibrations of the C=N within the pyridine rings of coordinated 4-pyridylmethanol of all complexes are at 1605, 1617 and 1609 cm^{-1}, respectively. The IR spectrum of complex **1** has also other band at 1597 cm^{-1}, and it could be attributed to the vibrations of the C=N within the uncoordinated pyridine ring of niflumate anions. The band positions of all complexes in the range 1062–1065 cm^{-1} could be attributed to C–O vibrations of 4-pyridylmethanol ligands.

The solid-state electronic spectrum of complex **1** exhibits a broad ligand field band with a maximum at 17600 cm^{-1} as well as a weak shoulder at 14500 cm^{-1}. These electronic d-d transitions are typical for bipyramidal arrangements around copper(II) atom [44]. Maxima of these bands are consistent with other copper(II) carboxylates with a *trans*-$Cu^{II}N_2O_2O'_2$ chromophore [50]. The other shoulder at 23200 cm^{-1} has been assigned to a charge-transfer LMCT absorption and it is very similar in many monomeric [45] and polymeric [22] copper(II) niflumates with a *trans*-$Cu^{II}N_2O_2O_2$ chromophore [51,52]. The solid-state electronic spectrum of complex **2** is very similar to observed for **1** complex and exhibit a broad band with a maximum at 15500 cm^{-1}. Maximum of the band is consistent with other copper(II) carboxylates with a tetragonal pyramidal arrangement around copper(II) atom and $Cu^{II}N_2O_2O$ chromophore [53].

4. Conclusions

Two novel hydrogen-bonded coordination polymers formed by copper(II) carboxylate with 4-pyridylmethanol have been prepared and characterized. The crystal structure of **1** consists of 2-D hydrogen-bonded framework, which is formed by O—H···O hydrogen atoms of hydroxyl donor oxygen atoms. The weak C—H···O hydrogen bonds support supplemented system hydrogen bonds in the frameworks of complex **2**. We propose that the 4-pyridylmethanol can conveniently be used as terminal ligand for the construction of hydrogen bonding-coordination networks.

Acknowledgements

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