

Solid State Coordination Chemistry and Supramolecular Assemblies of M(II)/Benzilato/2,2'-Dipyridylamine Systems

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Abstract

Two new mixed-ligand complexes of benzilato (bz) and 2,2'-dipyridylamine (dipyam), **1** [Ni(bz)(dipyam)₂](bz)·2MeOH and **2** [Cu(bz)₂(dipyam)]·EtOH, have been synthesized by refluxing benzoic acid and 2,2'-dipyridylamine with nickel(II) acetate for **1** and copper(II)carbonate hydroxide for **2**. The new compounds have been characterized by elemental analysis, IR and electronic absorption spectroscopy, magnetic measurements, thermogravimetric analysis and single-crystal X-ray diffraction. The role of non-covalent interactions, such as hydrogen bonds, $\pi\cdots\pi$ and/or C-H $\cdots\pi$, in the creation of supramolecular assemblies is analyzed.

Keywords: Nickel; Copper; Benzilato; Mixed-ligands complexes; Metallo-supramolecular chemistry; Non-covalent interactions

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Introduction

In recent decades, research in metallosupramolecular chemistry has gone together with an important attention to studies of non-covalent intermolecular interactions and to analyses of self-assembled structures. These extended frameworks of coordination compounds present great interest because of their fascinating topologies and their potential applications [1-3]. Benzilato ligand is a α -hydroxycarboxylate which may exhibit various coordination modes and provide potential intermolecular interactions such as hydrogen bonds involving the hydroxyl and carboxylate functionalities, and $\pi\cdots\pi$ and C-H $\cdots\pi$ interactions through the phenyl substituents [4]. The probability of formation of supramolecular arrays can be increased by the use of the auxiliary ligand 2,2'-dipyridylamine with N-H group potentially donor in hydrogen bonds and with aromatic rings suitable to establish $\pi\cdots\pi$ and/or C-H $\cdots\pi$ interactions. The work described here contains the preparation, properties and a detailed supramolecular structural analysis of two new mixed-ligand complexes of nickel(II) and copper(II) with benzilato and 2,2'-dipyridylamine.

Results and Discussion

Reaction of benzoic acid (Hbz) and 2,2'-dipyridylamine

(dipyam) in EtOH/PrOH or EtOH with Ni(AcO)₂·4H₂O and CuCO₃·Cu(OH)₂·0.5H₂O led to the isolation of crystalline products after recrystallization in MeOH/PrOH for **1** [Ni(bz)(dipyam)₂](bz)·2MeOH and after slow evaporation of the mother liquor for **2** [Cu(bz)₂(dipyam)]·EtOH. Both compounds are stable in air, very poorly soluble in water, but soluble in methanol and ethanol.

The infrared spectra of both compounds contain bands in the 3000–3250 cm⁻¹ region assigned to the N-H (dipyam) stretching frequency and in the 3300–3450 cm⁻¹ region corresponding to ν (OH) of benzilate and solvation molecules. The intense bands that appear around 1650 cm⁻¹, which in most cases overlap with bands associated with the 2,2'-dipyridylamine ligand, are assigned to the asymmetric COO⁻ vibration. The bands observed between 1340 and 1370 cm⁻¹ correspond to the symmetric COO⁻ vibration in the benzilate ions [5]. These bands are consistent

with the monodentate carboxylate coordination of monoanionic benzilate ions.

The electronic spectra of the complexes were recorded at the solid state by diffuse reflectance. The electronic spectrum of nickel(II) compound **1** shows two bands at 935 and 570 nm which are typical for octahedral symmetry. Therefore, assignments of the observed absorption bands can be made to ${}^3T_{1g}(P) \leftarrow {}^3A_g(F)$ (ν_1) and ${}^3T_{2g}(F) \leftarrow {}^3A_g(F)$ (ν_2) transitions, respectively. The band corresponding to ${}^3T_{2g}(F) \leftarrow {}^3A_g(F)$ (ν_3) transition is overlapped with the charge-transfer band [6]. The magnetic moment value at room temperature for **1** is 3.11 B.M. being consistent with an octahedral stereochemistry for the nickel(II) complexes [7]. The spectrum of copper(II) complex **2** exhibit a broad band at around 810 nm, which is characteristic of a copper(II)d-d transition in a tetragonal field with the copper(II)ion in a distorted square-based pyramidal coordination environment [6]. The magnetic moment value at room temperature of 1.65 B.M. in **2** lies in the range expected for pentacoordinated complexes of copper(II) [7].

Thermogravimetric analysis (TGA) was performed to investigate the thermal stability of compounds **1** and **2**. The degradation of species was investigated by monitoring the evolved gases by infrared spectroscopy. The thermal behavior is very similar in both compounds showing three mass loss steps. The first step corresponds to the loss of the solvation molecules, the second mass loss corresponds to pyrolysis of the benzilate anions followed, in a last step, by the loss of 2,2'-dipyridylamine. Finally, the complexes give residues of NiO at 410°C (**1**) and CuO at 475°C (**2**).

Structural analysis

Selected interatomic distances are listed in **Table 1** and the main hydrogen parameters in **Table 2**. **Figures 1 and 2** show representations of complex structures of **1** and **2**, respectively, together with the atom-numbering schemes used.

The asymmetric unit in **1** is composed of one cationic complex $[Ni(bz)(dipyam)_2]^+$ (**Figure 1**), one benzilate anion and two methanol molecules. The nickel(II)ion is hexacoordinated by four nitrogen atoms from two N,N'-bidentate-chelating 2,2'-dipyridylamine ligands and by one carboxylate and one hydroxyl oxygen atoms of the monoanionic O,O''-bidentate-chelating benzilate ligand. The coordination polyhedron is a distorted octahedron due to the presence of three chelate rings, with N-Ni-N angles of 85.2(3) and 86.5(3)° and O-Ni-O angle of 76.8(2)°. The Ni-O_{hydroxyl} and Ni-O_{carboxy} distances [2.122(5) and 2.037(6) Å, respectively] are similar to those found in other nickel mixed-ligand complexes with benzilate [8-10] and the Ni-N distances, in the range 2.070-2.106 Å, fall within the interval usually observed in nickel mixed-ligand complexes with 2,2'-dipyridylamine [11].

The structure of **2** is based on neutral units $[Cu(bz)_2(dipyam)]$ (**Figure 2**) and ethanol molecules. The copper(II)center is pentacoordinated by two nitrogen atoms from one N,N'-bidentate-chelating 2,2'-dipyridylamine ligand and by three oxygen atoms from two monoanionic benzilate ligands with different coordination behaviors, O,O''-bidentate-chelating,

using one carboxylate oxygen and the hydroxyl oxygen, and O-monodentate, involving only one carboxylate oxygen. This is the first example of the O,O''-bidentate-chelating coordination mode of monoanionic benzilate ligand with copper(II) since this behavior was only found in copper(II) complexes with dianionic benzilate ligand [12,13]. The usual coordination behaviors of monoanionic benzilate ligand in copper(II) complexes are O-monodentate, O,O'-bidentate-chelating (through two carboxylate oxygens) or O,O''-bidentate-bridging [14-21]. The coordination geometry can be described as a very distorted square pyramid ($\tau=0.41$) [22], with the hydroxyl oxygen atom in the apical position [Cu-O_{hydroxyl} distance 2.178(5) Å], and two carboxylate oxygen atoms [Cu-O_{carboxy} distances 1.913(4) and 2.009(5) Å] and two nitrogen atoms in the basal positions. The Cu-N distances [1.952(5) and 2.017(6) Å] and N-C-N chelating angle (92.4°) are similar to those found in other mixed-ligand copper(II) complexes with 2,2'-dipyridylamine [23-25].

In both compounds, the nature of benzilate, 2,2'-dipyridylamine and the solvation molecules (methanol and ethanol) allows the formation of supramolecular assemblies based on hydrogen bonding (**Table 2**) and $\pi\cdots\pi$ and/or C-H $\cdots\pi$ interactions.

In **1**, the cationic complex, the benzilate counterion and the methanol molecules of asymmetric unit are linked by hydrogen bonds generating a discrete supramolecule with a 14-membered ring (**Table 2**; **Figure 3a**). These supramolecules are joined by additional hydrogen bonds involving a N-H group of one 2,2'-dipyridylamine as donor and non-coordinated carboxylate oxygen atom as acceptor, resulting a dimeric assembly (**Table 2**; **Figure 3b**). In addition, the dimers establish a weak non-classical hydrogen bonds (C19-H19 \cdots O23ⁱⁱ, ii: -x+2,-y+1,-z) forming

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

1		2	
Ni-O11	2.037(6)	Cu-O11	1.913(4)
Ni-O13	2.122(5)	Cu-O13	2.178(5)
Ni-N1	2.106(7)	Cu-O21	2.009(5)
Ni-N3	2.070(7)	Cu-N1	2.017(6)
Ni-N4	2.076(7)	Cu-N3	1.952(5)
Ni-N6	2.103(7)		
O11-Ni-N3	91.1(2)	O11-Cu-N3	170.2(2)
O11-Ni-N4	171.5(2)	O11-Cu-O21	88.7(2)
N3-Ni-N4	96.7(3)	N3-Cu-O21	91.0(2)
O11-Ni-N6	89.6(3)	O11-Cu-N1	93.4(2)
N3-Ni-N6	94.2(3)	N3-Cu-N1	92.4(2)
N4-Ni-N6	86.5(3)	O21-Cu-N1	145.5(2)
O11-Ni-N1	91.2(3)	O11-Cu-O13	77.41(18)
N3-Ni-N1	85.2(3)	N3-Cu-O13	93.0(2)
N4-Ni-N1	92.8(3)	O21-Cu-O13	98.6(2)
N6-Ni-N1	179.0(3)	N1-Cu-O13	115.4(2)
O11-Ni-O13	76.8(2)		
N3-Ni-O13	167.0(2)		
N4-Ni-O13	95.6(2)		
N6-Ni-O13	90.4(2)		
N1-Ni-O13	90.3(3)		

chains (**Figure 3c**), which are joined creating sheets (**Figure 3d**) through edge-to-face C-H $\cdots\pi$ interactions between a C-H group of 2,2'-dipyridylamine and a phenyl ring of benzilate counterion [C28-H28 \cdots Cg(1)ⁱ, *i*: -x+1,-y+1,-z, Cg(1): C208-C209-C210-C211-C212-C213, d(H \cdots Cg) 2.75 Å, d(C \cdots Cg) 3.605(13) Å].

In **2**, the intramolecular hydrogen bonds involving the hydroxyl group and the non-coordinated carboxylate oxygen atoms of the monodentate benzilate ligand are the strongest interaction. In this case, the supramolecular organization is a consequence of the existence of intermolecular hydrogen bonds and $\pi\cdots\pi$

interactions. Two different types of hydrogen bonds between the bidentate-chelating benzilate ligands and the ethanol molecules form a polymeric chain along the crystallographic *b* axis. One of them involve the hydroxyl group of bidentate benzilate ligand as donor and the oxygen of ethanol molecule as acceptor and, in the second, the hydroxyl group of ethanol acts as donor and towards the non-coordinated carboxylate oxygen of bidentate benzilate ligand is the acceptor (**Table 2; Figure 4a**). The chains are linked by other hydrogen bonds, involving a N-H group of the 2,2'-dipyridylamine as donor and non-coordinated carboxylate

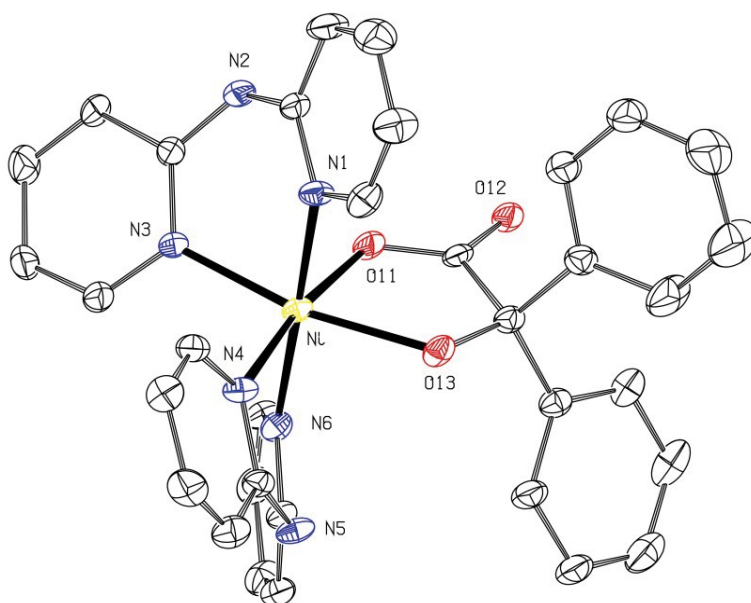


Figure 1 Structure of $[\text{Ni}(\text{bz})(\text{dipyam})_2]^+$ in **1** showing 30% probability displacement ellipsoids. Hydrogen atoms have omitted for clarity.

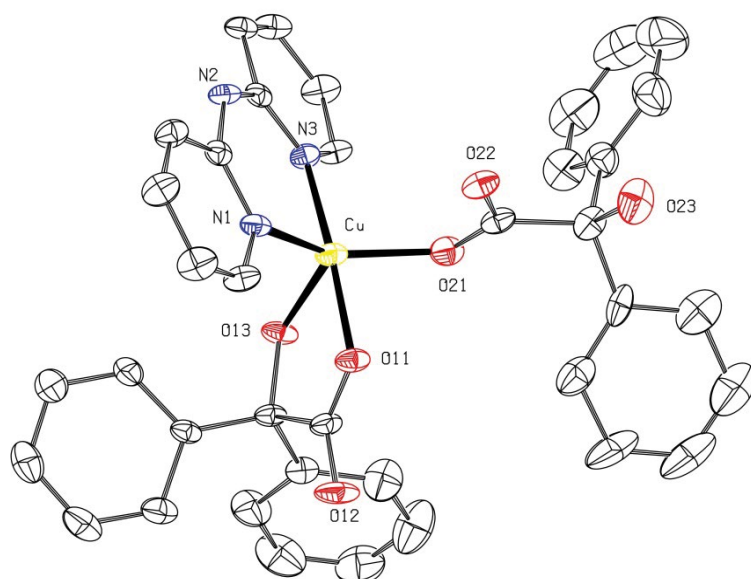


Figure 2 Structure of $[\text{Cu}(\text{bz})(\text{dipyam})]$ **2** showing 30% probability displacement ellipsoids. Hydrogen atoms have omitted for clarity.

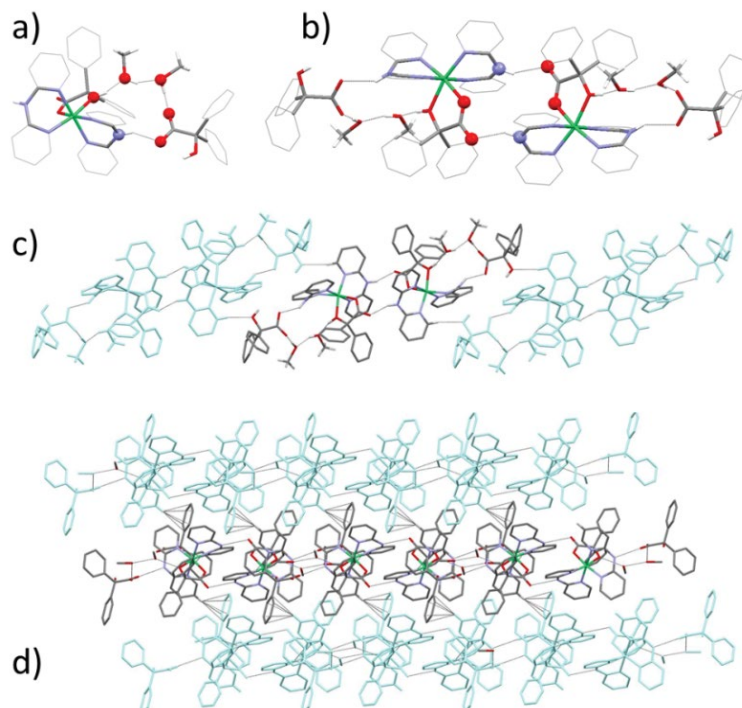


Figure 3 Views of the supramolecular organizations in **1** a) Supramolecule b) Dimer c) Chain (1D) d) Sheet (2D).

oxygen from the monodentate benzilato ligand as acceptor, and by $\pi \cdots \pi$ interactions [Cg(1) \cdots Cg(2)ⁱ and Cg(2) \cdots Cg(1)ⁱ, Cg(1):N1-C10-C11-C12-C13-C14 Cg(2):N2-C15-C16-C17-C18-C19, d(Cg \cdots Cg)=3.784(5) Å], forming a double-chain organization (Table 2; Figure 4b).

Experimental section

General information: All reagents and solvents were obtained commercially and were used as supplied. Elemental analyses (C, H, N) were carried out on a Fisons EA-1108 microanalyser. Melting points (m.p.) were measured with a Gallenkamp MBF-595 apparatus. IR spectra were recorded from KBr discs (4000-400 cm^{-1}) or polyethylene-sandwiched Nujol mulls (500-100 cm^{-1}) on a Bruker Vector 22 and IFS66v spectrophotometers, respectively. A Shimadzu UV-3101PC spectrophotometer was used to obtain electronic spectra in the solid state. Magnetic susceptibility measurements were performed at room temperature using a Johnson Matthey Alfa MSB-MK1 Gouy balance. TG/DTG analysis profiles were recorded under a 100 $\text{mL}\cdot\text{min}^{-1}$ air flow using a TA Instruments Hi-Res TGA2950 Thermobalance coupled to a Bruker Tensor 27 550 FT-IR spectrophotometer for identification of evolved gases.

Synthesis of complexes: $[\text{Ni}(\text{bz})(\text{dipyam})_2](\text{bz})\cdot 2\text{MeOH}$ (**1**) A solution of benzoic acid (2.0 mmol) in 10 mL of EtOH and a solution of 2,2'-dipyridylamine (2.0 mmol) in 10 mL of ⁱPrOH were added to a solution of $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ acetate (1.0 mmol) in 10 mL of EtOH. The mixture was refluxed for 2 h, left to cool to room temperature and stirred for a week yielding a purple precipitate that was filtered out and dried in vacuum. Purple single crystals of **1** were obtained by recrystallization of the

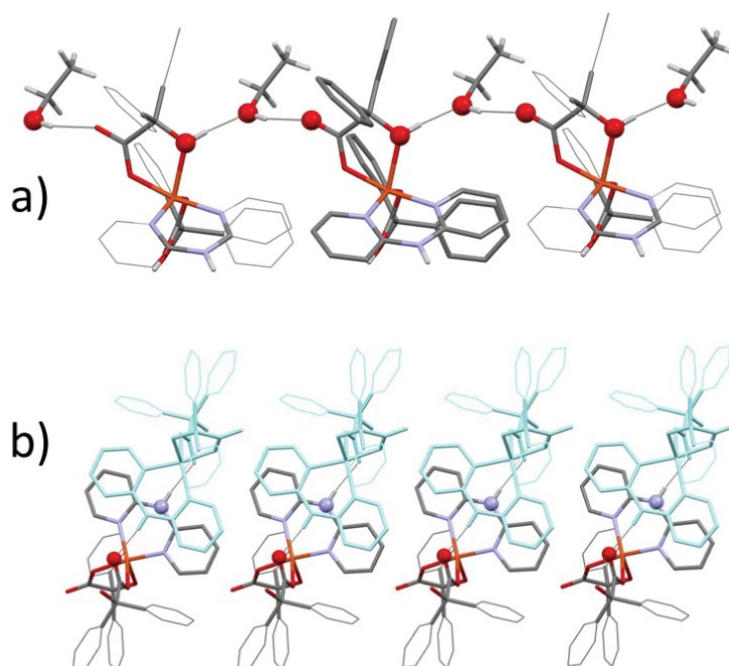
solid in a 1:1 MeOH/ⁱPrOH mixture. Yield: 83%. M.p.: 185°C. Anal. Calcd. For $[\text{Ni}(\text{bz})(\text{dipyam})_2](\text{bz})\cdot 2\text{MeOH}$ ($\text{C}_{50}\text{H}_{48}\text{NiN}_6\text{O}_8$) (MW=918.28 g/mol): C 65.3, H 9.1 and N 5.3; found C 65.6, H 9.1 and N 5.0. IR (KBr, cm^{-1}): 3302m, 3197m, 3136m, 3065m, 3025m $\nu(\text{OH}) + \nu(\text{NH})$; 1652m, 1629m, 1599s, 1582m, 1534m, 1478vs, 1428m, 1365m $\nu_{\text{asym}}(\text{COO}) + \nu_{\text{sym}}(\text{COO}) + \nu(\text{CC}, \text{CN})$, 1160m $\nu(\text{CO})$, 771s $\nu(\text{CH})$, 431w $\nu(\text{NiO})$, 252m $\nu(\text{NiN})$. UV-vis (cm^{-1}): 10700 (ν_1) and 17550 (ν_2). μ_{eff} at 25°C=3.11 MB. TG analysis: n^o mass loss steps=3, $\Delta T(^{\circ}\text{C})=\text{r.t.}-410$; 1st step methanol, 2nd bz, 3rd dipyam; final residue: NiO. $[\text{Cu}(\text{bz})_2(\text{dipyam})]\cdot \text{EtOH}$ (**2**).

A solution of benzoic acid (2.00 mmol) in 10 mL of EtOH and a solution of 2,2'-dipyridylamine (1.00 mmol) in 10 mL EtOH were added to a suspension of $\text{CuCO}_3\cdot \text{Cu}(\text{OH})_2\cdot 0.5\text{H}_2\text{O}$ (0.50 mmol) in 10 mL of the same solvent. The mixture was refluxed for 2 h, left to cool to room temperature and stirred for a week. Slow concentration of the resulting green solution afforded green single crystals of **2**. Yield: 60%. M.p.: 167°C. Anal. Calcd. for $[\text{Cu}(\text{bz})_2(\text{dipyam})]\cdot \text{EtOH}$ ($\text{C}_{40}\text{H}_{37}\text{CuN}_3\text{O}_7$) (MW=735.28 g/mol): C 63.5, H 5.1 and N 5.7; found C 63.4, H 5.4 and N 5.3. IR (KBr, cm^{-1}): 3436m, 3205m, 3142w, 3086w, 3030w $\nu(\text{OH}) + \nu(\text{NH})$; 1648s, 1589s, 1535m, 1481vs, 1425m, 1344m $\nu_{\text{asym}}(\text{COO}) + \nu_{\text{sym}}(\text{COO}) + \nu(\text{CC}, \text{CN})$, 1162m $\nu(\text{CO})$, 767m $\nu(\text{CH})$, 425w $\nu(\text{CuO})$, 277w $\nu(\text{CuN})$. UV-vis (cm^{-1}): 12375 (ν_1). μ_{eff} at 25°C=1.65 MB. TG analysis: n^o mass loss steps=3, $\Delta T(^{\circ}\text{C})=\text{r.t.}-475$; 1st step ethanol, 2nd bz, 3rd dipyam; final residue: CuO.

X-Ray structure determination: Crystallographic data were collected at 293 K on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The software SMART [26] was used for collecting frames

Table 2 Hydrogen bonds parameters, distances (Å) and angles (°) for **1** and **2**.

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
1	O13-H13...O1	0.93	1.68	2.590(13)	165.5
	N2-H2n...O12 ⁱ	0.86	2.04	2.805(8)	147.7
	C16-H16...O12 ⁱ	0.93	2.58	3.302(12)	134.6
	C19-H19...O23 ⁱⁱ	0.93	2.44	3.280(11)	150.7
	N5-H5n...O21	0.86	2.01	2.772(9)	147.2
	C20-H20...N1	0.93	2.65	3.102(11)	110.7
	O23-H23a...O21	0.82	1.99	2.500(9)	119.9
	O1-H1...O2	0.81	1.59	2.34(2)	153.2
	O2-H2...O22	0.89	1.54	2.43(2)	176.7
			i: -x+1,-y,-z+1	ii: -x+2,-y+1,-z	
2	O13-H13...O1	0.85	1.82	2.657(8)	169.0
	O23-H23...O22	0.82	2.06	2.570(8)	120.4
	N2-H2n...O22 ⁱ	0.86	2.01	2.866(8)	170.5
	C10-H10...O11	0.93	2.32	2.910(10)	121.0
	C16-H16...O22 ⁱ	0.93	2.56	3.297(10)	137.0
	O1-H1...O12 ⁱⁱ	0.83	1.91	2.706(8)	160.7
		i: -x+1,-y+1,-z+1	ii: x,y+1,z		


Figure 4 Views of the supramolecular organizations in **1** a) Supramolecule b) Dimer c) Chain (1D) d) Sheet (2D).

of data, indexing reflections, and the determination of lattice parameters, SAINT [27] for integration of intensity of reflections, and SADABS [28] for scaling and empirical absorption correction. The structure was solved by dual-space algorithm using the program SHELXT [29]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL [30] with OLEX2 [31]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Drawings were produced with PLATON [32] and Mercury [33]. Crystal data and

structure refinement parameters are reported in **Table 3**. CCDC 1811239 and 1811240 contain the supplementary data for **1** and **2**, these data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

Conclusion

In summary, two novel mixed-ligand of nickel(II) and copper(II) formed with benzilato and 2,2'-dipyridylamine have been isolated and characterized. The supramolecular organizations due to non-covalent intermolecular interactions have been analyzed.

Table 3 Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	C ₅₀ H ₄₈ N ₆ NiO ₈	C ₄₀ H ₃₇ CuN ₃ O ₇
Formula weight	919.65	735.26
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /n
Unit cell dimensions		
<i>a</i> (Å)	9.789(5)	19.777(7)
<i>b</i> (Å)	15.854(8)	8.503(3)
<i>c</i> (Å)	16.220(8)	22.713(9)
α (°)	66.956(5)	
β (°)	82.099(6)	107.078(5)
γ (°)	87.774(5)	
Volume (Å ³)	2294.3(19)	3651(2)
Z	2	4
$\rho_{\text{calculated}}$ (Mg/m ³)	1.331	1.338
Absorption coefficient (mm ⁻¹)	0.484	0.652
F(000)	964	1532
Crystal size (mm ³)	0.35 × 0.25 × 0.22	0.22 × 0.15 × 0.12
θ range for data collection (°)	1.376 to 25.100	1.203 to 24.865
Max. and min. transmission	0.7451 and 0.6190	0.7451 and 0.5775
Reflections collected	11227	17960
Independent reflections (R_{int})	7937 (0.0636)	6257 (0.1469)
Final R indices	$R_1=0.1016$ $wR_2=0.2303$	$R_1=0.0830$ $wR_2=0.1707$

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