

[Cu(X-salicylato)₂(*N,N*-diethylnicotinamide)₂(H₂O)₂] complexes: conformational polymorphism and its consequence in supramolecular hydrogen-bonding networks formation

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Abstract Novel copper(II) X-salicylate complexes with *N,N*-diethylnicotinamide (dena) of the formula [Cu(R-COO)₂(dena)₂(H₂O)₂] (RCOO = 3-methylsalicylate anion (3-Mesal, **1**), 4-methylsalicylate anion (4-Mesal, **2**), 5-methylsalicylate anion (5-Mesal, **3**), 5-methoxysalicylate anion (5-MeOsal, **4**) or 4-methoxysalicylate anion (4-MeOsal, **5**)), and complex [Cu(3-MeOsal)₂(dena)₂(H₂O)₂]•2H₂O (3-MeOsal = 3-methoxysalicylate anion (**6**)) have been prepared in the crystalline forms and characterized by spectroscopic methods (IR, Vis–UV, EPR). All the compounds according to their composition (**1**–**5**) seem to possess octahedral copper(II) stereochemistry. The complex **1** has been prepared in two different forms. X-ray analyses of the complexes **1**, **4**, and **5** were carried out and they featured a tetragonal-bipyramidal geometry around the copper atoms. The tetragonal

planes are created by X-salicylate anions bonded to the copper(II) atoms via unidentate carboxylate oxygen atoms and the pyridine ring nitrogen atoms of the neutral ligand *N,N*-diethylnicotinamide, while in axial positions are water molecules. The two forms of complex **1** present conformational polymorphs and supramolecular isomers.

Keywords Copper complexes · Crystal structure · Hydrogen bonds · Spectra polymorphism · Supramolecular isomerism

Introduction

Polymorphism has been one of integral part of solid state supramolecular chemistry and polymorphism phenomenon is the last and most challenging hurdle for the success of designed synthesis of materials [1]. Various forms of polymorphism, including concomitant [2], packing [3], and conformational [4] have been studied as interesting phenomena in the solid-state sciences. The development of novel polymorphs of potential and existing drugs has for some time been a method for modifying and improving their physical properties [5]. The control of the process of nucleation and/or crystal growth at the beginning of crystallization from solvents is potential way for modifications of novel polymorphs across a range of industries involving dye [6], food stuff [7], drugs [8], and explosives [9]. The control of morphology and polymorphism is essential to achieve optimized molecular configurations and physical properties and to understand the structure–property relationships and design of new materials [10].

N,N-Diethylnicotinamide (dena) is a toxic agent, but coordinated in the form of complexes it shows different biological activity [11–16]. The coordination of the dena

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ligand occurs via the pyridine ring nitrogen atom and the other possible donor atoms for coordination bonds are less preferred. There are 60 structures of metal complexes containing the dena moiety bonded to a metal atom via the pyridine nitrogen donor atom and only nine of those structures contain dena as a bridging ligand bonded to the metal atom by carbonyl oxygen donor atoms too [17–25]. The monodentate bonding mode of the dena ligand is even more dominant for carboxylatocopper(II) complexes and there are two main stoichiometries within this group of complexes with the dena ligand. The 1:1 stoichiometry is found in paddle-wheel dinuclear complexes type $[\text{Cu}_2(\text{RCOO})_4(\text{dena})_2]$ [12, 26–28]. The most frequent 1:2 stoichiometry can be found in monomeric complexes of $\text{Cu}(\text{RCOO})_2(\text{dena})_2(\text{H}_2\text{O})_x$, where $x = 0$, [29, 30], $x = 2$ [18, 31–35], or $x = 4$ [36], and in all those complexes the dena molecules are monodentate N donor ligands. Recently, the first two polymeric complexes with bridging dena molecules, of the composition $[\text{Cu}_2(\text{RCOO})_4(\text{dena})_1]_n$, have been structurally characterized [17, 18].

In this article, we report on the preparation and spectral properties, of six copper(II) complexes containing $\{\text{Cu}(X\text{-sal})_2(\text{dena})_2(\text{H}_2\text{O})_2\}$ core moiety (where $X = 4\text{-}, 5\text{-MeO}$ and $3\text{-}, 4\text{-}, 5\text{-Me}$), together with spectral data of $[\text{Cu}(3\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ that structure has been already published [36], but according to its structure it belongs to this group. For four of presented new complexes their X-ray structures are reported too.

Experimental

Materials and methods

Analytical grade (Aldrich, or Sigma) chemicals were used without further purification. Carbon, hydrogen, and nitrogen analyses were carried out on a CHNSO FlashEA™ 1112 Automatic Elemental Analyzer. The copper content was determined by electrolysis of water solution obtained by the sample mineralization with a mixture of sulfuric acid and potassium peroxodisulfate.

The infrared spectra ($4,000\text{--}400\text{ cm}^{-1}$) were measured with a NICOLET 5700 FT-IR (Nicolet) spectrophotometer at room temperature using ATR technique. The electronic spectra (190–1,100 nm) of the complexes were measured in Nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer at room temperature. EPR spectra of the powdered samples were recorded at room temperature with a spectrometer Bruker ESP 300 operating at X-band equipped with an ER 035 Bruker NMR gaussmeter and HP 5350B Helwett Packard microwave frequency counter.

Syntheses of **1a**

3-Methyl-salicylic acid (336 mg, 2.0 mmol) was by rinsing added to an aqueous solution of copper(II) acetate (10 mL, 1.0 mmol) with diethylnicotinamide (0.17 cm^3 , 2.0 mmol) under stirring and total volume of reaction mixture about 30 mL was reached. The reaction mixture was stirred at ambient temperature until the reaction finished. The product which precipitated was filtered off and mother liquid was left to crystallize at ambient temperature. The crystals suitable for X-ray structure determination were separated and dried at ambient temperature.

$\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**1a**): Yield: 0.41 g; 55%. Anal Calc.: C, 56.57; H, 6.11; N, 7.39. Found: C, 56.42; H, 5.86; N, 7.36.

Syntheses of **1b**, **2–4**

Appropriate methyl- or methoxy-salicylic acid (336 mg, 2.0 mmol for methoxysalicylic acid or 304 mg, 2.0 mmol for methylsalicylic acid) was under stirring added to the mixture of copper(II) acetate solution (1.0 mmol copper(II) acetate in 10 cm^3 of water) with diethylnicotinamide (0.34 cm^3 , 2.0 mmol) and solvent added to obtain total volume of reaction mixture 200 cm^3 for aqueous solutions or 30 cm^3 for acetonitrile–water (1:1) ones. The reaction mixture was stirred at ambient temperature until the reaction finished. The products which precipitated (with exception of 3- and 5-methoxysalicylate, where no precipitation were observed) were filtered off and mother liquids were left to crystallize at ambient temperature. The crystals suitable for X-ray structure determination were separated and dried at ambient temperature.

$\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**1b**): Yield: 0.49 g; 65%. Anal Calc.: C, 56.57; H, 6.11; N, 7.39. Found: C, 56.34; H, 5.93; N, 7.12.

$\text{Cu}(4\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**2**): Yield: 0.54 g; 71%. Anal Calc.: C, 56.57; H, 6.11; N, 7.39. Found: C, 56.24; H, 6.48; N, 7.44.

$\text{Cu}(5\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**3**): Yield: 0.59 g; 77%. Anal Calc.: C, 56.57; H, 6.11; N, 7.39. Found: C, 57.07; H, 6.04; N, 7.36.

$\text{Cu}(5\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**4**): Anal Calc.: C, 54.71; H, 5.74; N, 7.26. Found: C, 54.72; H, 5.61; N, 7.06.

$\text{Cu}(4\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2$ (**5**): Yield: 0.45 g; 59%. Anal Calc.: C, 54.71; H, 5.74; N, 7.26. Found: C, 54.85; H, 6.06; N, 7.14.

X-ray crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement

Table 1 Crystallographic data for compounds **1a**, **1b**, **4**, and **5**

	1a	1b	4	5	5
Code	ZP223	WAL16	WAL6	WAL8	ZP82C
Chemical formula	C ₃₆ H ₄₆ CuN ₄ O ₁₀	C ₃₆ H ₄₆ CuN ₄ O ₁₀	C ₃₆ H ₄₆ CuN ₄ O ₁₂	C ₃₆ H ₄₆ CuN ₄ O ₁₂	C ₃₆ H ₄₆ CuN ₄ O ₁₂
<i>M_r</i>	758.32	758.32	790.30	790.30	790.30
Cell setting, space group	Triclinic, Pī	Triclinic, Pī	Triclinic, Pī	Triclinic, Pī	Triclinic, Pī
<i>T</i> (K)	150(2)	100(2)	100(2)	100(2)	293(2)
<i>a</i> (Å)	8.673(2)	7.080(3)	8.347(3)	7.585(2)	7.694(1)
<i>b</i> (Å)	10.608(2)	8.400(3)	10.496(3)	8.267(3)	8.395(3)
<i>c</i> (Å)	11.210(3)	15.709(7)	10.718(3)	15.303(3)	15.467(3)
α (°)	67.78(3)	86.98(4)	88.48(3)	89.74(3)	87.83(2)
β (°)	85.75(3)	88.63(4)	79.18(3)	76.46(3)	76.53(1)
γ (°)	76.57(3)	76.24(4)	88.20(3)	77.33(3)	76.24(2)
<i>V</i> (Å ³)	928.6(4)	906.1(6)	921.7(5)	909.1(5)	943.5(4)
<i>Z</i>	1	1	1	1	1
Radiation type	Mo <i>K</i> α	Cu <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.65	1.38	0.66	0.67	0.65
Crystal size (mm)	0.25 × 0.25 × 0.20	0.35 × 0.11 × 0.02	0.30 × 0.22 × 0.15	0.60 × 0.15 × 0.03	0.52 × 0.32 × 0.20
Diffractometer	Bruker-Nonius KappaCCD	Xcalibur PX CCD	Kuma KM-4 CCD	Kuma KM-4 CCD	Siemens P4
Abs. correction	Multi-scan	Analytical	Analytical	Analytical	psi-scan
<i>T_{min}</i> , <i>T_{max}</i>	0.855, 0.881	0.744, 0.744	0.850, 0.912	0.842, 0.967	0.730, 0.882
<i>S</i>	1.02	1.03	1.03	1.02	1.02
<i>R</i> ₁ [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> ₂ (<i>F</i> ²)	0.046, 0.093	0.054, 0.144	0.029, 0.071	0.053, 0.122	0.045, 0.119
Data/restraints/parameters	2,433/0/236	2,822/0/236	3,755/0/245	3,695/0/245	3,837/0/245
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.16, -0.21	0.57, -0.82	0.28, -0.23	0.32, -0.72	0.48, -0.43
CCDC	773722	773723	773724	773725	773726

were carried out using Bruker-Nonius KappaCCD diffractometer [37, 38] at 150 K for (**1a**), Kuma KM-4 CCD diffractometer [39] at 100 K for (**4**, **5**) or Siemens P4 diffractometer [40] at 293 K for (**6**) with graphite monochromated Mo *K* α radiation. Data collection and cell refinement were carried out using Xcalibur PX CCD diffractometer [39] at 100 K for (**1b**) with graphite monochromated Cu *K* α radiation. The diffraction intensities were corrected for Lorentz and polarization factors. The analytical absorption corrections [41] for (**1b**, **4** and **5** at 100 K) were made by using CrysAlis-RED [39]. The semi-empirical absorption corrections for **1a** and **5** at 293 K were applied using the program SADABS [42] (multi-scan method) or the program XEMP [43] (psi-scan method). The structures were solved by direct methods using SHELXS-97 [44] or SIR-97 [45] and refined by the full-matrix least-squares procedure with SHELXL-97 [44]. Geometrical analyses were performed with SHELXL-97. The structures were drawn with XP in SHELXTL [44]. The remaining hydrogen atoms were positioned with O–H = 0.84 Å for hydroxyl and water atoms and C–H = 0.95, 0.98, and 0.99 Å for aromatic, methyl, and methylene hydrogen atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$, where $x = 1.5$ for methyl, hydroxyl and water

hydrogen atoms, and $x = 1.2$ for other hydrogen atoms. The positions of water hydrogen atoms were restrained by DFIX commands of SHELXL-97 and the refined positions have been constrained using AFIX 3 commands of SHELXL-97.

The powder samples **2** and **3** were measured with Bragg–Brentano diffractometer Philips PW 1730/1050, using β -filtered Co *K* α radiation, 40 kV/35 mA in the range of 3°–51° 2 Θ , step 0.02°.

Results and discussion

The preferential ability of dena ligand to act as pyridine nitrogen donor has its consequence in domination of Cu(RCOO)₂(dena)₂(H₂O)_{*x*} (where $x = 0$, [29, 30], $x = 2$ [18, 31–35] or $x = 4$ [36]) stoichiometry. The observation of the green [Cu₂(2-NO₂bz)₄(dena)₁]_{*n*} (2-NO₂bz = 2-nitrobenzoate) polymeric complex formation at the beginning of the reactant reaction followed by its slow transformation into the blue [Cu(2-NO₂bz)₂(dena)₂(H₂O)₂] in reaction mixture [18] was the reason why the preparation of the presented complexes were done also at different conditions (different dilution of reaction mixture, different

solvents and temperature too). The most interesting feature of the realized experiments was observation of some new types of obtained products. As the first it should be mentioned the observation that despite the condition of synthesis changing the complex $[\text{Cu}(3\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**6**) [32] is the only product obtainable independently on the reaction conditions. The second note concerning the syntheses to be mentioned is that despite the great effort the X-ray suitable crystals of complexes $[\text{Cu}(4\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**2**), and $[\text{Cu}(5\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**3**) were not obtained thus only analytical and spectral characterization is presented below. The third and the last note to be given is that the complex $[\text{Cu}$

$(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ gives two different polymorphic forms **1a** or **1b** as the consequence of changing the course of synthesis (see “Experimental” section for details).

The principal structural features of complexes **1a**, **1b**, **4**, and **5** are illustrated in Fig. 1. Selected bond distances, angles, and torsion angles of complexes **1a**, **1b**, **4**, and **5** are given in Table 2. The structures of complexes **1a**, **1b**, **4**, and **5** consist of centrosymmetric molecules with an elongated tetragonal–bipyramidal coordination polyhedron around the copper(II) atom. The coordination spheres of the all copper(II) atom are in the *trans*-equatorial planes formed by two carboxylate anions [3-methylsalicylate (**1**), 5-methoxysalicylate (**4**) or 4-methoxysalicylate (**5**)]

Fig. 1 Perspective view of $[\text{Cu}(\text{X-sal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$, with the atom numbering scheme. The all thermal ellipsoids are drawn at the 30% probability level: **a** polymorph-I of complex $[\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**1a**); **b** polymorph-II of complex $[\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**1b**); **c** complex $[\text{Cu}(5\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**4**); **d** complex $[\text{Cu}(4\text{-MeOsal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**5**)

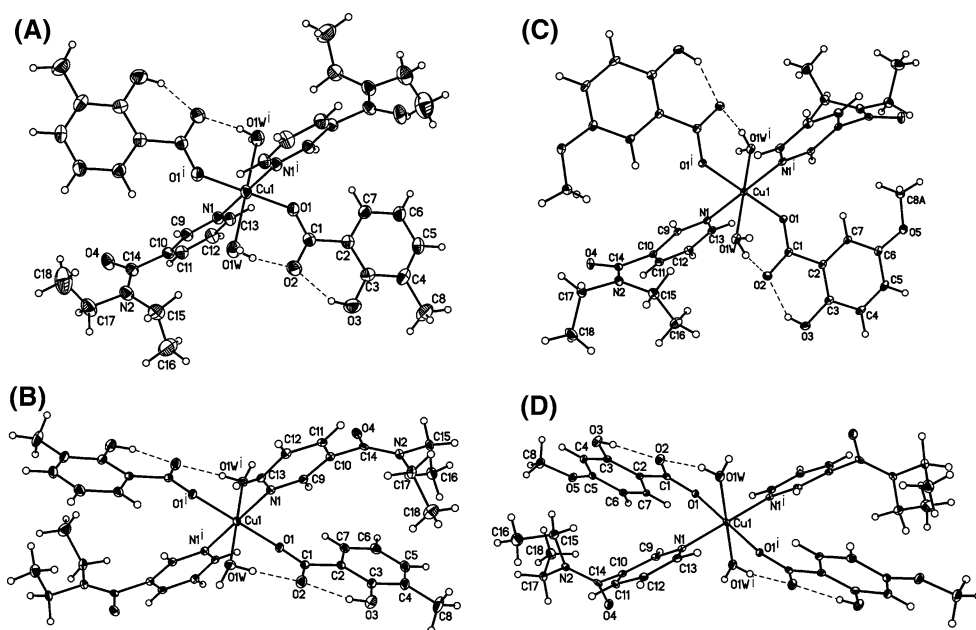


Table 2 Selected bond distances (Å) and bond angles (°) for **1a**, **1b**, **4**, **5**, and **6**

	1a	1b	4	5 at 100 K	5 at 283 K	6
Cu–O1	1.982(3)	1.985(2)	1.985(1)	1.988(2)	1.977(2)	1.982(1)
Cu–N1	2.020(2)	2.006(3)	2.004(2)	2.004(3)	2.008(2)	2.091(1)
Cu–O1W	2.458(2)	2.440(2)	2.415(1)	2.406(2)	2.457(2)	2.417(1)
T	0.814	0.818	0.826	0.830	0.810	0.843
O1–Cu–N1	88.44(10)	89.93(10)	92.99(6)	89.72(9)	89.93(8)	89.74(4)
O1–Cu–O1W	96.02(9)	92.96(9)	91.15(5)	90.97(8)	91.41(8)	95.24(3)
N1–Cu–O1W	85.56(8)	86.63(9)	83.85(5)	88.44(8)	89.33(9)	92.84(3)
C1–O1–Cu	128.4(2)	128.1(2)	128.3(1)	128.5(2)	129.3(2)	129.60(7)
C9–N1–Cu	118.9(2)	119.3(2)	117.8(1)	119.5(2)	119.2(2)	120.13(7)
C13–N1–Cu	122.4(2)	121.8(2)	123.0(1)	121.7(2)	122.5(2)	121.49(7)
C9–C10–C14–N2	–52.9(4)	–124.7(3)	–46.9(2)	–117.1(3)	–111.8(3)	–123.3(1)
C9–C10–C14–O4	126.4(3)	52.0(4)	131.5(2)	63.3(4)	66.3(4)	55.4(1)
C14–N2–C15–C16	–87.8(4)	–79.0(3)	–56.6(2)	–125.9(3)	–120.4(3)	126.3(1)
C14–N2–C17–C18	–79.7(4)	116.5(3)	95.4(2)	–89.6(3)	–88.5(3)	–77.7(1)
Ref.	[this study]	[this study]	[this study]	[this study]	[this study]	[36]

bonded via O1 atoms [the Cu–O1 lengths are in the range 1.977(2)–1.988(2) Å] and two nitrogen donor atoms of pyridine rings of *N,N*-diethylnicotinamide [the Cu–N1 lengths are in the range 2.004(2)–2.020(2) Å]. The two axial positions of tetragonal–bipyramidal coordination environments are occupied by the two water molecules [the Cu–O1W distances are in the range 2.406(2)–2.458(2) Å], thus *T* parameter values [46] exhibit also very narrow values range [$T = 0.81–0.83$] suggesting very small and similar pattern of coordination polyhedron deformation. The water molecules of all complexes under study are due to the intramolecular hydrogen bonds [O1W–H1W...O2 with O1W...O2 distances in the region 2.702(4)–2.764(3) Å] (Table 3) slightly shifted from precise apical positions and the O1–Cu–O1W angles are in the region 90.97(8)–96.02(9)° and six-membered metalocycles are formed by those bonds. The hydroxyl and carboxylate groups of salicylate anions create additional six-membered intramolecular rings *S*(6) [47] through intramolecular hydrogen bonds O3–H3O...O2 with O3...O2 distances in the range 2.518(4)–2.562(3) Å. Similar coordination environment about copper atom has been observed in crystal structure of complex [Cu(3-MeOsal)₂(dena)₂(H₂O)₂]•2H₂O (**6**) [36] (Table 2) and other [Cu(RCOO)₂(dena)₂(H₂O)₂] complexes [18, 31–35].

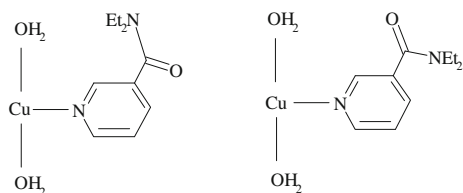
All presented structures **1a**, **1b**, **4**, and **5** exhibit similar orientation of pyridine ring in relation to equatorial plane of their coordination polyhedra and dihedral angle between pyridine ring plane and coordination polyhedron N1–O1–

Cu–O1'–N1' equatorial plane is within very narrow interval of 38.9–42.5° [39.06 for **1a**, 37.01 for **1b**, 42.52 for **4**, 38.86 for **5** at 100 K, or 38.07 for **5** at 293 K]. The carboxamide groups N2–C14–O4 are also turned away from the pyridine ring plane by 45.4–70.5° [50.07 for **1a**, 55.81 for **1b**, 45.35 for **4**, 66.48 for **5** at 100 K, 70.51 for **5** at 293 K, or 58.28 for **6**] and the carboxamide groups are nearly perpendicular (68.8–89.3°) to coordination polyhedron equatorial plane [71.50 for **1a**, 73.57 for **1b**, 68.79 for **4**, 88.10 for **5** at 100 K, or 89.30 for **5** at 293 K]. The most interesting feature of such carboxamide plane orientation is that there are two possible orientations of the O4–C14 or N2–C14 bonds. One of them is roughly perpendicular to coordination polyhedron *z*-axis (Scheme 1), it could be called as equatorial orientation, and the other one is nearly parallel with *z*-axis, so called axial orientation, similarly as it is used for the cyclohexane hydrogen atom positions. The **1a** and **4** (Fig. 1a, c) exhibit C14=O4 bond oriented perpendicularly to Cu–OH₂ bonds in equatorial C14=O4 bond orientation, while in complexes **1b** and **5** (Fig. 1b, d) the C14=O4 bonds are oriented about alongside the *z*-axis (axial C14=O4 bond). This is interesting especially for the pair of complexes **1a** and **1b**, which are two isomers of the same composition [Cu(3-Mesal)₂(dena)₂(H₂O)₂] so it can be concluded that **1a** and **1b** exist as two conformation polymorphs [48], which are simultaneously supramolecular isomers [49–51] too.

Exactly the *N,N*-diethylcarboxamide groups of *N,N*-diethylnicotinamide ligand two orientations, could be expressed by torsion angles C9–C10–C14–N4 and

Table 3 Selected parameters of hydrogen bonds (Å, °) for **1a**, **1b**, **4**, and **5**

	D–H [Å]	H...A [Å]	D...A [Å]	D–H–A [°]	Symmetry code
1a					
O1W–H1W...O2	0.84	1.87	2.702(4)	171	
O1W–H2W...O4 ⁱⁱ	0.84	1.99	2.811(3)	167	(ii) $x + 1, y, z$
O3–H3O...O2	0.84	1.78	2.518(4)	146	
1b					
O1W–H1W...O2	0.84	1.89	2.725(3)	176	
O1W–H2W...O4 ⁱⁱⁱ	0.84	1.99	2.808(3)	166	(iii) $x + 1, y - 1, z$
O3–H3O...O2	0.84	1.81	2.551(3)	147	
4					
O1W–H1W...O2	0.84	1.96	2.765(2)	160	
O1W–H2W...O4 ⁱⁱ	0.84	1.91	2.751(2)	175	(ii) $x + 1, y, z$
O3–H3O...O2	0.84	1.82	2.559(2)	146	
5 at 100 K					
O1W–H1W...O2	0.84	1.93	2.758(3)	167	
O1W–H2W...O4 ⁱⁱⁱ	0.84	2.00	2.835(3)	177	(iii) $x + 1, y - 1, z$
O3–H3O...O2	0.84	1.83	2.562(3)	146	
5 at 293 K					
O1W–H1W...O2	0.82	1.97	2.764(3)	162	
O1W–H2W...O4 ⁱⁱⁱ	0.82	2.02	2.827(3)	171	(iii) $x + 1, y - 1, z$
O3–H3O...O2	0.82	1.84	2.556(3)	145	



Scheme 1 Schematic drawing of two possible orientation of the carboxamide group in relation to part of coordination polyhedron

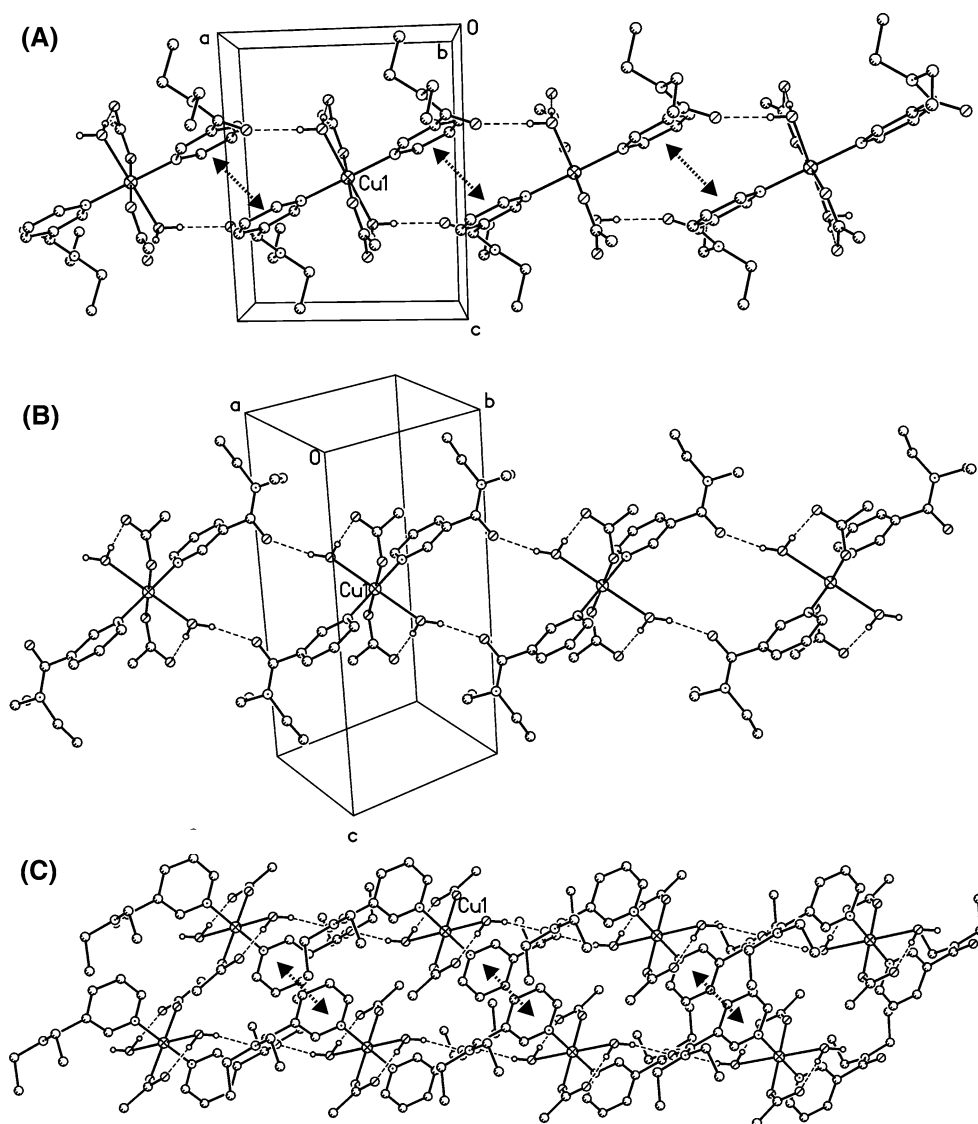
C9–C10–C14–O4 (Table 2). The polymorph **1a** of complex $[\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (Fig. 1a) and complex $[\text{Cu}(5\text{-MeOsAl})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**4**) (Fig. 1b) have equatorial C=O bond of the *N,N*-diethylcarboxamide group orientations thus C9–C10–C14–N4 torsion angle are $-52.9(4)$ and $-46.9(3)^\circ$, respectively, and C9–C10–C14–O4 torsion angles are $126.4(3)$ and $131.5(2)^\circ$, respectively. On the other hand the other polymorph **1b** of the complex $[\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (Fig. 1b) and complex $[\text{Cu}(4\text{-MeOsAl})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ (**5**) (Fig. 1d) have the C=O bond in axial orientation and the C9–C10–C14–N4 torsion angle are $-124.7(3)^\circ$ and $-117.1(3)^\circ$, respectively, and C9–C10–C14–O4 torsion angles are $52.0(4)^\circ$ and $63.3(4)^\circ$, respectively (the torsion angles of **5** at room temperature are given only in Table 2). The other differences among orientations of ethyl groups of *N,N*-diethylnicotinamide ligands are too observed in torsion angles C14–N2–C15–C16 and C14–N2–C17–C18 (Table 2). On the other hand more understandable exact parameter to evaluate position of C14=O4 bond in relation to coordination polyhedron is *quasi*-torsion angle defined by O1W–Cu···C14–O4 atoms that is 20.20 for **1a**, 4.45 for **1b**, 13.39 for **4**, and 5.77° for **5**.

Supramolecular isomerism of the polymorphs is determined by this orientations of C14=O4 relative to polyhedron *z*-axis. The molecules of polymorph **1a** (Fig. 2a) and complex **4** are linked by intermolecular hydrogen bonds between hydrogen atoms of water ligands and carboxamide oxygen atoms of *N,N*-diethylnicotinamide ligands of adjacent molecules O1W–H2W···O4ⁱⁱ [Symmetry code: (ii) $x + 1, y, z$] with O1W···O4ⁱⁱ interatomic distance of 2.811(3) and 2.751(2) Å, respectively (Table 3) through $R_2^2(16)$ rings [47], and π – π stacking interactions [52] between two symmetrically adjacent pyridine rings N1/C9–C13 [Symmetry code: (iv) $-x, -y + 1, -z + 1$] of *N,N*-diethylnicotinamide molecules (Fig. 2a), [centroid···centroid distances are 3.87 and 3.65 Å, respectively] into chain in direction [100] (Fig. 2a). The distances between two π – π stacked planes are exactly 3.55 and 3.58 Å, respectively, and the Cu···Cu distances within the chains are 8.637 and 8.347 Å for complex **1a** and **4**, respectively.

The molecules of the other polymorph **1b** (Fig. 2b) as well as complex **5** are too joined by intermolecular hydrogen bonds between hydrogen atoms of water ligands and amide oxygen atoms of *N,N*-diethylnicotinamide ligands of adjacent molecules through $R_2^2(16)$ rings [47], but the orientation of pyridine rings do not allow π – π stacking interactions within the supramolecular the chains. The supramolecular chains are due to the different orientation of the C14=O4 oriented in direction [1 $\bar{1}$ 0] (Fig. 2b) and the hydrogen bond O1W–H2W···O4ⁱⁱⁱ [Symmetry code: (ii) $x + 1, y, z$] are O1W···O4ⁱⁱⁱ interatomic distance of 2.808(3) and 2.835(3) Å, respectively (Table 3). The different chain orientation and their different packing of the **1a** or **4** molecules result in different Cu···Cu distances within the bands are 9.612 and 9.918 Å for complex **1b** and **5**, respectively. The π – π stacking interactions [52] between two pyridine aromatic rings of *N,N*-diethylnicotinamide ligands of two neighboring [Symmetry code: (v) $-x + 1, -y + 2, -z + 1$] complex molecules are localized between two supramolecular chains (Fig. 2c). The centroid···centroid distances are 3.52 and 3.65 Å, respectively, and the distances between two planes of pyridine rings are exactly 3.55 and 3.58 Å, respectively. It could be concluded that this pair of complexes (**1b** and **5**) and the previous pair (**1a** and **4**) represents two supramolecular isomers that differ by the Cu···Cu distance within the chain, by orientation of the chains in crystal structure and finally in some differences in π – π stacking interactions.

The supramolecular chains with additional the π – π stacking interactions similar to the last couple of the supramolecular isomers have been observed in crystal structures of complexes $[\text{Cu}(\text{RCOO})_2(\text{dena})_2(\text{H}_2\text{O})_2]$, where RCOO[−] is 2-chloronicotinate [34] or 4-nitrobenzoate [35], but if RCOO[−] anion is more bulky fenamate, the additional π – π stacking interactions have been not observed [31–33]. The crystal structure of complex $[\text{Cu}(\text{RCOO})_2(\text{dena})_2(\text{H}_2\text{O})_2]$, where RCOO[−] is 2-nitrobenzoate present alternative supramolecular organization of complex molecules in two-dimensional hydrogen bonds network, the molecules are linked through hydrogen bonds between water ligands and carboxamide oxygen atom of *N,N*-diethylnicotinamide molecules [18]. Finally, the crystal structure of complex $[\text{Cu}(3\text{-MeOsAl})_2(\text{dena})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**6**) presents enriched hydrogen bonds network, where hydroxyl and methoxy groups of 3-methoxysalicylate anions are specifically acceptor of hydrogen bonds and uncoordinated additional water molecules are donors of hydrogen bonds [36], which are presented by creating ring $R_2^2(5)$ [47]. These changes are partially seen in similar orientation of pyridine ring in relation to equatorial plane of the coordination polyhedra, but the dihedral angle between pyridine ring plane and coordination polyhedron equatorial plane is

Fig. 2 Crystal packing of two supramolecular isomers of $[\text{Cu}(\text{3-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$, the salicylate anions are omitted for clarity: **a** 1-D Supramolecular band chain of **1a** through O–H...O hydrogen bonds in $[100]$ axis, the π – π interactions between pyridine rings are inside supramolecular band chain; **b** 1-D Supramolecular band chain of **1b** through O–H...O hydrogen bonds in $[1\bar{1}0]$ axis. **c** The the π – π interactions between pyridine rings of **1b** are between two supramolecular band chains



significantly smaller, about 29° . The dihedral angle of carboxamide plane to pyridine ring one is about 73° for **6**. It should be pointed out that C=O bond is axially oriented in relation to coordination polyhedron z axis.

The infrared spectra were recorded for all complex series. The carboxylate stretching frequencies $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ for each of the complexes under study are in the regions at about $1,620$ and $1,420\text{ cm}^{-1}$, respectively, and are given in Table 4. Differences between antisymmetric and symmetric stretches ($\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$) are for all prepared complexes greater than $\Delta\nu$ for the ionic form, that is consistent with bonding mode of carboxylate group [53, 54] proved by X-ray analysis. The differences in position of the $\nu(\text{COO}^-)$ stretching frequencies of the individual complexes are very small and that is in good agreement with very small differences in bonding of the salicylate in copper(II) coordination sphere. Similarly, the characteristic frequencies of dena ligand (e.g. $\nu(\text{CN})$ of

pyridine ring) are due to very small differences in Cu–N1 distances found at the same positions for all studied complexes. More information could be found in the shape and intensity of bands in the region of $3,500\text{--}3,250\text{ cm}^{-1}$, which could

be attributed to O–H vibrations of coordinated ligands typical for complexes of the stoichiometry $[\text{Cu}(\text{RCOO})_2(\text{dena})_2(\text{H}_2\text{O})_2]$. Different shape of the spectra of complexes **1a** and **1b** (Fig. 3) led us to conclusion to study the X-ray structure of both complexes. It could be concluded that this spectra region could taken as the proof of existence of polymorphic form. Moreover, this region of O–H vibrations exhibits different pattern for complex $[\text{Cu}(\text{3-MeOsAl})_2(\text{dena})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ —there is also an additional sharp and stronger absorption band at $3,547\text{ cm}^{-1}$.

The electronic spectra of the discussed complexes in solid showed a typical feature of tetragonal bipyramidal arrangement around Cu(II) [55]. The broad asymmetric

Table 4 Wavenumbers (cm^{-1}) of the COO^- stretches, solid-state electronic spectra (nm) and g values for the copper(II) complexes

	ν_{as}	ν_{s}	$\Delta\nu$	λ $d \rightarrow d$	g_{\perp}	g_{\parallel}	G
[Cu(3-Mesal) ₂ (dena) ₂ (H ₂ O) ₂] 1a	1,622	1,425	197	650	2.08	2.33	4.12
[Cu(3-Mesal) ₂ (dena) ₂ (H ₂ O) ₂] 1b	1,620	1,428	192	^a	^a	^a	^a
[Cu(4-Mesal) ₂ (dena) ₂ (H ₂ O) ₂] 2	1,618	1,426	192	636	2.07	2.31	4.42
[Cu(5-Mesal) ₂ (dena) ₂ (H ₂ O) ₂] 3	1,622	1,424	198	626	2.08	2.32	4.00
[Cu(3-MeOsAl) ₂ (dena) ₂ (H ₂ O) ₂].2H ₂ O 6	1,626	1,423	203	661	2.08	2.32	4.00
[Cu(4-MeOsAl) ₂ (dena) ₂ (H ₂ O) ₂] 5	1,628	1,430	198	660	2.08	2.32	4.00
[Cu(4-MeOsAl) ₂ (dena) ₂ (H ₂ O) ₂] 5	1,627	1,427	200	652	2.08	2.31	3.88
[Cu(5-MeOsAl) ₂ (dena) ₂ (H ₂ O) ₂] 4	1,623	1,428	195	564	2.08	2.33	4.12

^a Not measured

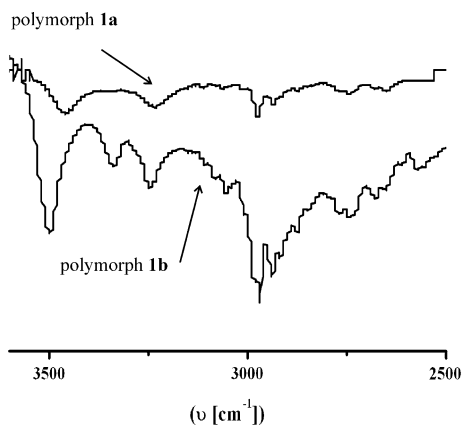


Fig. 3 Comparison of infrared spectra of both polymorphs [Cu(3-Mesal)₂(dena)₂(H₂O)₂]

ligand field band with a maximum in the range of 660–640 nm (Table 4) is attributed to $d \leftarrow d$ transition and very small differences in shape and in the maximum position are in good agreement with above mentioned differences of $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophores. There are also intraligand charge transfer bands (250–300 nm) and LMCT band in the range of 300–350 nm.

The EPR spectra signals (Fig. 4) of powdered samples measured at room temperature reflect of the axial symmetry of the complexes. The simulation of spectra gave us the g -parameter values (Table 4) in the range of 2.07–2.08 for g_{\perp} and 2.31–2.33 for g_{\parallel} , respectively. The axial

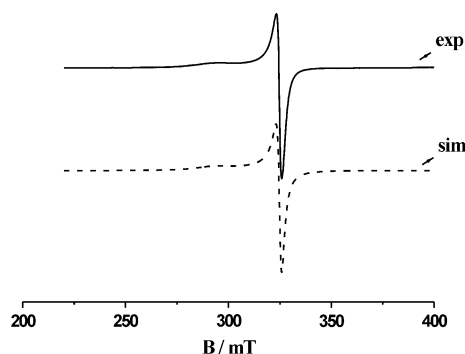


Fig. 4 EPR spectra of powdered sample of **2** (dark line measured at room temperature, and dashed line simulated)

symmetry and obtained g values are consistent with tetragonal bipyramidal symmetry of copper(II) environment [56], as well as with above mentioned differences of $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophores. The obtained G parameter [57] values (Table 4) are in all mentioned complexes within the narrow range and they are close to $G = 4$ and that could be taken as consistent with small axial distortion of coordination polyhedra and with their small differences when comparing all studied complexes. So the EPR spectra of measured samples are very similar and do not allow differentiate conformational isomers one from the other.

The above mentioned problems with using spectral methods for identification of the orientation of the $\text{C}=\text{O}$ carboxamide bond relative to coordination polyhedron axis led us to analysis of crystallographic data and they clearly confirmed that both groups showing similar $\text{C}=\text{O}$ bond orientation exhibit significantly different basic unit cell parameters. So the X-ray diffraction pattern of powdered samples **2** and **3** were compared with calculated X-ray diffraction pattern of complexes with known structure and that gave us the evidence that the samples of prepared complexes exhibit structures similar to complexes **1b**, or **5**. Finally indexing [58] of powder diffraction patterns and calculation of basic unit cell parameters (Table 5) clearly confirm this conclusion.

Table 5 Crystallographic data for compounds **2** and **3** from powder samples

	2	3
Chemical formula	$\text{C}_{36}\text{H}_{46}\text{CuN}_4\text{O}_{10}$	$\text{C}_{36}\text{H}_{46}\text{CuN}_4\text{O}_{10}$
M_r	758.32	758.32
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	7.486	7.590
b (Å)	8.497	8.840
c (Å)	15.263	15.095
α (°)	95.5	110.7
β (°)	100.2	97.3
γ (°)	77.2	77.2
V (Å ³)	930.2	922.7

The melting point determination has shown that all studied complexes undergo some changes between 95 and 105 °C associated with small color intensification to darker blue color that could be attributed to the dehydration reactions [59, 60]. The further heating of samples up to 220 °C were not associated with any observable changes thus it could be concluded that dehydrated samples decompose over this temperature.

Conclusions

In this study, we present the results on structural and spectroscopic properties of a series of five new monomeric 3-, 4-, 5- methylsalicylatocopper(II), or 4- and 5-methoxysalicylatocopper(II) complexes with *N,N*-diethylnicotinamide as monodentate terminal ligand. This study has shown that *N,N*-diethylnicotinamide in these complexes prefer monomeric structure of formula $[\text{Cu}(\text{Me}(\text{O})\text{sal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$. The complex molecules are linked to supramolecular chains through hydrogen bonds, which can exist in two alternative configurations. The $[\text{Cu}(3\text{-Mesal})_2(\text{dena})_2(\text{H}_2\text{O})_2]$ complex exist in both configuration forms and it present the example of conformation polymorphs and it could be taken as the supramolecular isomers existence.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-773722–773726. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336033; e-mail:deposit@ccdc.cam.ac.uk].

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