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Methyl- and methoxysalicylatocopper complexes with 2-pyridylmethanol: Synthesis, spectral properties, structure and EPR characterization in solid-state and in solution

Research Article

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Abstract: The syntheses and characterizations of salicylatocopper(II) complexes of the formula $Cu(X\text{-}sal)_2(2\text{-}pyme)_2$ (X = 3-MeO (**1**), 4-MeO (**2**), 3-Me (**3**), 4-Me (**4**) and 5-Me (**5**), where 3-MeOsal$^-$ = 3-methoxysalicylate, 4-MeOsal$^-$ = 4-methoxysalicylate, 3-Mesal$^-$ = 3-methylsalicylate, 4-Mesal$^-$ = 4-methylsalicylate, 5-Mesal$^-$ = 5-methylsalicylate anion, and 2-pyme = 2-pyridylmethanol) are reported. The composition was determined by elemental analysis, and ligand coordination modes have been determined by spectroscopic methods (IR, UV-VIS). The crystal structure determination of $[Cu(3\text{-}MeOsal)_2(2\text{-}pyme)_2]$ (**1**) and $[Cu(5\text{-}Mesal)_2(2\text{-}pyme)_2]$ (**5**) have confirmed conclusions originally based on spectral data. EPR measurements of frozen water/methanol solutions containing different copper(II) : 2-pyme molar ratios have indicated presence of complexes with only two nitrogen donor atoms bonded to each central atom.

Keywords: *Copper(II) complex • Salicylate • 2-Pyridylmethanol • Crystal structure*

1. Introduction

All of the dominant chemical properties of prepared compounds are greatly dependent on their composition, structural organization and to some extent on mutual interactions with other molecules. In the case of metal complexes the composition, and the arrangement of ligands around the central atom are the most influential factors. The variable mode of coordination of the carboxylate group to a central atom (*e.g.* monodentate, bidentate chelating and/or bidentate bridging) [1] is a very useful tool in constructing different types of complexes. Moreover, it is possible to obtain a wide variety of different carboxylatocopper complex structures by using different reaction conditions [2,3]. On the other hand, complexes with 2-pyridylmethanol (abbreviated as 2-pyme) exhibit little variation of character due to a predominant bidentate chelating coordination mode [4-28]. Only three complexes are known showing a monodentate coordination *N*-donor ligand mode of pyme: $[AuCl_3(2\text{-}pyme)]$ [29], *trans*-$[PtCl_2NH_3(2\text{-}pyme)]$ [30] and [Ag(5,5-diethylbarbiruate)(2-pyme)]•H_2O [31], and only a single example of a structure with *O*-donor ligand: [Zn(tbusalphen)(2-pyme)] {tbusaphen = (*N*,*N*'-bis(3,5-di-t-butylsalicylidene)-1,2-phenylenediamine)} [32]. There are also two complexes with bidentate *N*,*O*-bridging: $[Ag(saccharinate)(\mu\text{-}2\text{-}pyme)]_n$ [33] and $[Hg(saccharinate)_2(\mu\text{-}2\text{-}pyme)]_n$ [8]. For copper(II) complexes with 2-pyme ligand predominantly $[Cu(X)_2(2\text{-}pyme)_2]$ stoichiometry [4,11,15,22,25] has been reported. However, an exceptional complex of composition $[CuCl_2(2\text{-}pyme)]$•MeOH [20] has been prepared and studied. Moreover, pyridylmethanolate anions were found in some complexes [23,34-37]. In contrast to

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the dominant $[Cu(X)_2(2\text{-pyme})_2]$ molecular complexes [4,11,15,22,25] ion-pair formation in $[Cu(X)(2\text{-pyme})_2]X$ (where X = 3,5-dinintrobenzoate anion) can be given as an example [19] of anion driven variation of structure within a group of complexes with very similar compositition.

In this context, the preparation under different reaction conditions and the product properties of the *x*-methyl- (*x* = 3, 4 and 5) and/or *x*-methoxysalicylatecopper(II) complexes (*x* = 3 and 4) with 2-pyme, as obtained, have been studied. The properties of three new $(Cu(3\text{-MeOsal})_2(2\text{-pyme})_2$ (**1**), $Cu(4\text{-Mesal})_2(2\text{-pyme})_2$ (**4**) and $Cu(5\text{-Mesal})_2(2\text{-pyme})_2$ (**5**) complexes together with structures of (**1**) and (**5**) are presented here. All of these properties are compared with those of $[Cu(4\text{-MeOsal})_2(2\text{-pyme})_2]$ (**2**) and $[Cu(3\text{-Mesal})_2(2\text{-pyme})_2]$ (**3**) that have been published recently [22], and that have again been produced in this project under different reaction conditions. Finally, the influence of varying the neutral ligand concentration on the composition of complex species has been studied by EPR spectroscopy.

2. Experimental procedure

2.1. Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA™ 1112 Automatic Elemental Analyzer. The copper content was determined by electrolysis of an aqueous solution obtained following sample mineralization with a mixture of sulfuric acid and potassium peroxodisulfate.

The electronic spectra (190 – 1100 nm) of the complexes were measured in nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer at room temperature. The infrared spectra (4000–100 cm^{-1}) were recorded on a MAGNA 750 IR (Nicolet) and Nicolet 5700 FT-IR spectrophotometers at room temperature using KBr and ATR techniques. The EPR spectra of the solutions and powdered samples were recorded on a Bruker EMX EPR spectrometer operating at X-band.

2.2. Preparation of the complexes

The blue complexes (**1–5)** have been prepared under different reaction conditions. The general procedure used was as follows. The appropriate methyl-, or methoxy-salicylic acid (2 mmol) was added under stirring to an aqueous solution of copper(II) acetate (1 mmol) with 2-pyridylmethanol (2 mmol) and the total volume of reaction mixture was made up to 100 mL or 30 mL with different solvents (water, ethanol or acetonitrile). The reaction mixtures were stirred until the reaction finished and the colour of products remained unchanged. The precipitated products were filtered off, washed with small amounts of appropriate solvent mixture, and dried at ambient temperature. The mother liquids were left to crystallize at ambient temperature. After a time small amounts of crystals suitable for X-ray structure analysis were obtained in some cases.

Analysis $[Cu(3\text{-MeOsal})_2(2\text{-pyme})]$ *(**1**)*: Calc. for $C_{28}H_{28}CuN_2O_{10}$ C, 54.59; H, 4.58; N, 4.55%. Found: C, 54.15; H, 4.45; N, 4.90%.

Analysis $[Cu(4\text{-MeOsal})_2(2\text{-pyme})]$ *(**2**)*: Calc. for $C_{28}H_{28}CuN_2O_{10}$ C, 54.59; H, 4.58; N, 4.55%. Found: C, 54.49; H, 4.59; N, 4.99%.

Analysis $[Cu(3\text{-Mesal})_2(2\text{-pyme})_2]$ *(**3**)*: Calc. For $C_{28}H_{28}CuN_2O_9$ C, 57.58; H, 4.83; N, 4.79%. Found: C, 57.24; H, 4.99; N, 4.31.

Analysis $[Cu(4\text{-Mesal})_2(2\text{-pyme})_2]$ *(**4**)*: Calc. For $C_{28}H_{28}CuN_2O_9$ C, 57.58; H, 4.83; N, 4.79%. Found: C, 57.00; H, 4.95; N, 4.25%.

Analysis $[Cu(5\text{-Mesal})_2(2\text{-pyme})_2]$ *(**5**)*: Calc. For $C_{28}H_{28}CuN_2O_9$ C, 57.58; H, 4.83; N, 4.79%. Found: C, 57.22; H, 4.98; N, 4.28%.

2.3. Preparation of Cu(II) complex solutions for EPR measurements

The solutions for EPR measurements were prepared by mixing copper acetate ($Cu(ac)_2$) with 3-Methylsalicylic acid (3-MeSalH) and 2-pyridylmethanol in appropriate molar ratios. The resulting solutions were then stirred carefully to homogenize and poured into quartz capillaries for EPR measurements. Sets of samples with varying ligand to metal ratio were thus obtained. Copper(II) systems with varying ligand to metal ratio, $[Cu(ac)_2$ (aq) + 2 (3-MesalH(solv)) + *x* (2-pyme(l))], where *x* = 0, 2, 4, 6, 8, 16 in water/methanol solutions were prepared for EPR measurement.

2.4. Measurements and simulations of EPR spectra

The Cu(II) EPR spectra were measured on a EMX X-band (≈ 9.4 GHz) EPR spectrometer (Bruker, Germany) in frozen water/methanol solutions at 98 K, immediately after synthesis was finished in the batch reactor. During EPR measurement temperature control was achieved using a Bruker temperature control unit ER 4111 VT. Further information about the EPR experiment, instrumental parameters (which were, except for the receiver gain, the same for all samples), interpretations, processing (WinEPR) [38] and simulations (SimFonia)

Table 1. Crystallographic data for compounds **1** and **5**.

	(1)	(5)
Code	LK17/MK35	ZP296/MK53
Chemical formula	$C_{28}H_{28}CuN_2O_{10}$	$C_{28}H_{28}CuN_2O_8$
M	616.06	584.06
Temperature (K)	293(2)	293(2)
Crystal size (mm³)	0.25×0.35×0.42	0.21×0.23×0.40
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	*P-1*
***a* (Å)**	8.308(1)	10.608(1)
***b* (Å)**	10.408(1)	10.924(1)
***c* (Å)**	16.115(2)	12.835(1)
α (°)	90	90.03(1)
β (°)	101.83(1)	103.50(1)
γ (°)	90	110.01(1)
***V* (Å³)**	1363.9(3)	1353.7(2)
Z	2	2
D_c/mg m⁻³	1.500	1.433
μ(MoKα)/mm⁻¹	0.863	0.860
***F*(000)**	638	606
Θ Range (°)	4.12–26.37	*4.13*–26.37
T_{min}/T_{max}	0.712/0.813	0.725/0.840
h* / *k* / *l	-1,10/-1,13/-20,20	-1,13/-13/13/-16/15
Unique reflections (R_{int})	3678 (0.0378)	6388 (0.0996)
Data / restraints / parameters	2751/0/189	5478/0/359
S	1.003	1.015
R_1, wR_2 (observed reflections)	0.0349, 0.0848[a]	0.0517, 0.1046[b]
R_1, wR_2 (all reflections)	0.0496, 0.0927[a]	0.1042, 0.1257[b]
$-\Delta_\rho/\Delta_\rho$ (e⁻¹ Å⁻³)	-0.38/0.26	-0.57/0.55
CCDC deposition no.	860404	860405

Calculated weights: [a] $w = 1/[\sigma^2(F_o^2)+(0.0463P)^2+0.3089P]$; [b] $w = 1/[\sigma^2(F_o^2)+(0.0481P)^2]$, *where* $P = (F_o^2 + 2F_c^2)/3$

[39] of EPR spectra, calculations of the geometric parameter (G) [40] and empirical factor (f) [41] are given in detail in our previous papers [42,43].

2.5. Crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement were carried out using a Siemens P4 diffractometer [44] at 293 K with graphite monochromated Mo Kα radiation. The diffraction intensities were corrected for Lorentz and polarization factors. Semi-empirical absorption corrections were applied using the program XEMP [45]. The structures were solved by direct methods using SHELXS-97 [46]. and refined by the full-matrix least-squares procedure with SHELXL-97 [46]. Geometrical analyses were performed with SHELXL-97. The structures were drawn with XP in SHELXTL [46].

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre CCDC nos. 860404 (**1**), and 860405 (**5**). Further details of the crystal structure investigations are available free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Preparation and spectral properties

The "uniformity" of 2-pyridylmethanolatocopper(II) complexes with x-methyl- or x-methoxysalicylato anions becomes evident after all products of synthesis obtained at different conditions have been analysed – only $Cu(X\text{-}sal)_2(2\text{-}pyme)_2$ complexes were obtained. It should be stressed, that using an aqueous medium at laboratory temperature was a suitable way of preparing complexes containing 3- and 4-methoxysalicylato anions. Products containing x-methylsalicylato anions also contained some hydrolytic byproducts. Using acetonitrile/water or ethanol/water as the medium for reactions again only produced methoxysalicylatocopper complexes of suitable quality. Finally, the best results for preparation of all complexes under study were obtained when aqueous medium at slightly higher temperature (T = 343 K) and the shortest possible reaction time were used. In this way all five complexes of composition $Cu(X\text{-}sal)_2(2\text{-}pyme)_2$ (where X = 3-MeO, 4-MeO, 3-Me, 4-Me and 5-Me) were isolated and characterized. Finally, for two of them, suitable crystals were obtained from mother liquids, and the crystal structures of $Cu(3\text{-}MeOsal)_2(2\text{-}pyme)_2$ (**1**) and $Cu(5\text{-}Mesal)_2(2\text{-}pyme)_2$ (**5**) were obtained. These supplement recently published [22] structures of $Cu(4\text{-}MeOsal)_2(2\text{-}pyme)_2$ (**2**), and $Cu(3\text{-}Mesal)_2(2\text{-}pyme)_2$ (**3**) complexes.

The IR spectra of the compounds (**1**–**5**) exhibit bands confirming the presence of all characteristic functional groups. The bands corresponding to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are about 1634 cm⁻¹ and 1442 cm⁻¹ respectively (Table 2). The differences between antisymmetric and symmetric stretch ($\Delta\nu = \nu_{as} - \nu_s$) are greater than $\Delta\nu$ for the ionic form. This corresponds to the unidentate bonding mode. For all complexes there are broad asymmetric bands of medium intensity attributed to the system of intramolecular and intermolecular hydrogen bond vibrations in the region of 3100 – 2700 cm⁻¹. These broad envelopes are very similar each to other. The solid-state electronic spectra of all complexes

Table 2. Wavenumbers (cm^{-1}) of the COO^- stretches and solid-state electronic spectra (nm) for complexes (**1–5**).

	ν_{as}	ν_s	$\Delta\nu$	λ(d→d)	Reference
(1) [(Cu(3-MeOsal)$_2$(2-pyme)$_2$]	1630	1440	190	690	This work
(2) [(Cu(4-MeOsal)$_2$(2-pyme)$_2$]	1629	1440	189	634	[22]
(3) [(Cu(3-Mesal)$_2$(2-pyme)$_2$]	1627	1440	187	653	[22]
(4) [(Cu(4-Mesal)$_2$(2-pyme)$_2$]	1634	1436	198	640	This work
(5) [(Cu(5-Mesal)$_2$(2-pyme)$_2$]	1633	1431	202	686	This work

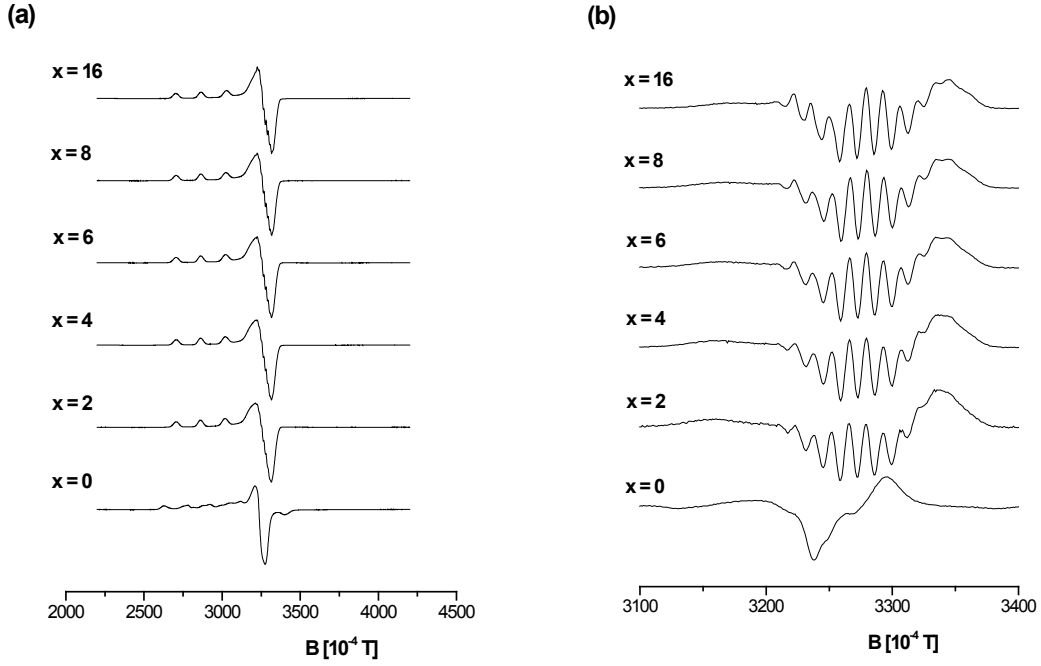

Figure 1. **a**) Experimental first-derivative Cu(II) EPR spectra of system [Cu(ac)$_2$ (aq) + 2 (3-MesalH(solv)) + *x* (2-pyme(l)))], where *x* = 0, 2, 4, 6, 8 and 16, measured in frozen water/methanol solutions at 98 K. **b**) Expansion of perpendicular region with ^{14}N superhyperfine splitting of the second-derivative Cu(II) EPR spectra.

studied exhibit broad asymmetric ligand field bands, attributed to d→d transitions, with maximum intensities in the range 634 - 690 nm. There are also intraligand charge transfer bands (250 – 300 nm), and charge transfer bands in the range 300 - 350 nm.

3.2. EPR spectra

The experimental Cu(II) EPR spectra of system [Cu(ac)$_2$ (aq) + 2 (3-MesalH(solv)) + *x* (2-pyme(l))], where *x* = 0, 2, 4, 6, 8, 16, which were measured in the frozen water/methanol solution at 98 K are illustrated in Fig. 1a. When *x* = 0 (ligand is not present) the EPR spectra exhibited multicomponent character. However, single EPR spectra with axial symmetry were observed, when ligand was added. In all cases, the EPR spectra (including subspectra of the composite spectrum) showed unresolved perpendicular and well-resolved parallel copper hyperfine splitting of ^{63,65}Cu isotopes (*I* = 3/2).

Additionally, in the presence of ligand, the EPR spectra showed well-resolved perpendicular superhyperfine splitting of ^{14}N isotope (*I* = 1). The details of ^{14}N superhyperfine splitting in the expanded perpendicular region of the second-derivative Cu(II) EPR spectra are shown in Fig. 1b. No superhyperfine splitting was monitored when *x* = 0. Likewise, the EPR spectra of samples stored three days after their synthesis were measured, and the absence of any measurable changes indicates stability of the structure. In additional experiments, the Cu(II) EPR spectra were recorded at the wide sweep width of 800 mT and no EPR resonances due to Cu(II)-Cu(II) interactions were observed.

The spin-Hamiltonian parameters obtained from the experimental spectra were refined by computer simulations, and the values of the averaged g-factor (g_{av}), geometric parameter (*G*) and empiric factor (*f*) were calculated. The values of both g-factors

Table 3. Selected bond lengths and hydrogen bond parameters (Å, °) for (**1**) and (**5**).

	(1)	(5) molecule A	(5) molecule B
Cu–O1	2.197(2)	2.382(3)	2.374(3)
Cu–N1	1.988(2)	1.993(3)	1.996(3)
Cu–O3	2.163(2)	2.000(2)	2.002(3)
N1—Cu—O3	93.53(7)	89.63(11)	90.62(11)
N1—Cu—O1	80.46(6)	77.79(11)	77.41(11)
O3—Cu—O1	91.34(6)	94.70(10)	95.67(10)

($g_\perp$ = 2.062 ± 0.002 and $g_\parallel$ = 2.291 ± 0.002) remain (within experimental error) constant for all ligand to metal ratio, *x*. All the Cu(II) EPR spectra of the copper complexes studied showed axial symmetry with the relations $g_\parallel > g_\perp > 2.0023$ indicating the d_{x2-y2} ground state [40].

The parallel copper hyperfine splitting ($A_\parallel$) values slightly increased with increasing ligand concentration (from $A_\parallel$ = (15.63 ± 0.02) mT for x = 2 up to $A_\parallel$ = (16.18 ± 0.02) mT for x = 16). The perpendicular ^{14}N superhyperfine splitting values are independent of ligand concentration ($A^N_\perp$ = (1.37 ± 0.02) mT. The above values are in good accordance with those published for similar copper complexes, see elsewhere [40,47-53].

The G-parameter values (G ≈ 4.7) are (within experimental error) independent of ligand concentration. The relation *G* > 4 indicates negligible exchange interaction between the copper centres [40,54]. The f-factor values slightly varied from minimal (f = 142 cm, for x = 16) to maximal (f = 147 cm, for x = 2) values. All the *f*-values are higher than the limit value of 135 cm, which could support the suggestion of square planar geometry around the Cu(II) ions with a small but significant tetrahedral distortion [41,50,55-57].

The second-derivative Cu(II) EPR spectra (see Fig. 1b) were used to extract the most precise number of lines in nitrogen superhyperfine multiplet patterns. It is evident that, the increase of ligand to metal ratio, *x*, did not change the spectral parameters of nitrogen superhyperfine multiplets; only an increase in signal intensity was observed.

The nitrogen superhyperfine splitting provides an opportunity to study nitrogen donors occupying equatorial sites of copper(II) complexes [56,58-61]. Applying the results of Brauer *et al.* [62], there are indications that two nitrogen atoms could be coordinated to the central copper atom, suggesting that the prevalent species in the solution has occupying equatorial positions two molecules of the ligand coordinated to the central copper atom *via* the nitrogen atom of the heterocyclic ring. It could be proposed for these 2-pyme containing copper complex systems that the number of coordinated nitrogen atoms seems to be independent of ligand concentration within the range of molar ratio from *x* = 2 up to *x* = 16.

The spectral characteristics of all the Cu(II) EPR spectra of copper complex systems [$Cu(ac)_2$ (aq) + 2 (3-MesalH(solv)) + *x* (2-pyme(l))], where *x* = 2, 4, 6, 8, 16, are very similar, indicating that at all ligand concentrations the dominant complexes have similar structures of the first order coordination sphere around the copper atom. This particular conclusion concerning the chelating 2-pyme ligand should be seen in relation to similar studies where it was shown that dominantly monodentate ligands such as *N*,*N*-diethylnicotinamide [43], or dominantly bridging ligands such as 3-pyridylmethanol [42] could, in similar conditions, form complexes containing up to four nitrogen donor atoms in the equatorial plane.

3.3. Structure of $[Cu(X\text{-}sal)_2(2\text{-}pyme)_2]$ complexes (1) and (5)

The compound (**1**) crystallizes in the monoclinic system with space group $P2_1/c$. The molecular structure of complex (**1**) is drawn in Fig. 2. The asymmetric unit of the crystallographic cell is occupied by one half of centrossymetric complex molecule of (**1**). The copper(II) atom in complex (**1**) lies in the centre of symmetry, and it is coordinated in tetragonal-bipyramidal manner. The equatorial plane is formed by two nitrogen atoms of the pyridine ring [Cu1–N1 = 1.988(2) Å] and two carboxylato oxygen atoms of monodentate coordinated 3-methoxysalicylato anions [Cu1–O3 = 2.163(2) Å] in *trans*-positions. Two axial positions are occupied by hydroxyl oxygen atoms of 2-pyridylmethanol [Cu1–O1 = 2.197(2) Å] (Fig. 2, Table 3).

There are strong intramolecular hydrogen bonds involving the uncoordinated oxygen atom of the carboxyl group of salicylato anions and the methanol hydrogen atom of 2-pyridylmethanol ligands (O1–H1O···O4), thus forming six-membered metallocyclic rings (Table 4). The hydroxyl hydrogen atoms of 3-methoxysalicylate anions are linked to the uncoordinated carboxylato oxygen atoms by intramolecular hydrogen bonds (O5–H5O···O4) and create other six-membered rings.

On the other hand, the compound (**5**) crystallizes in triclinic system with space group $P\bar{1}$. The molecular structure of complex (**5**) is very similar to complex (**1**), but the asymmetric unit of the crystallographic cell is occupied by two halves of two centrosymmetric complex molecules (Fig. 3). The copper(II) atoms are also tetragonal-bipyramidal coordinated with two 2-pyridylmethanol nitrogen atoms

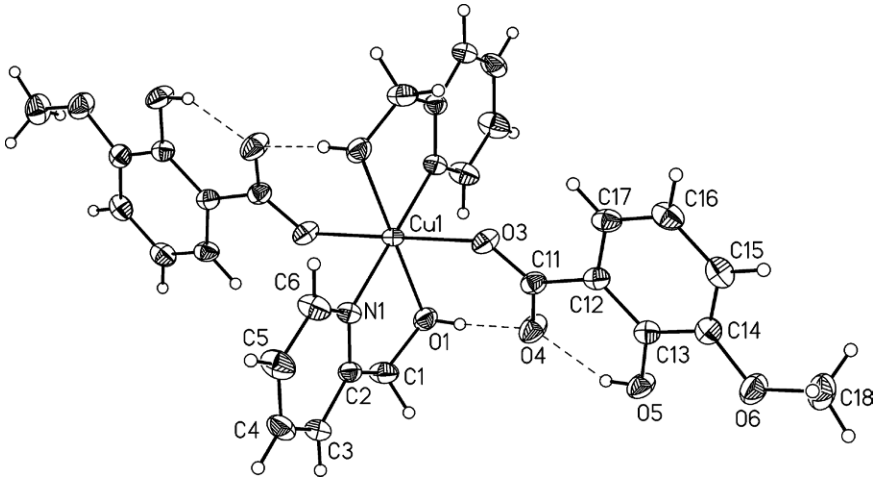

Figure 2. Perspective view of [Cu(3-MeOsal)$_2$(2-pyme)$_2$] **(1)**, with the atom numbering scheme. The all thermal ellipsoids are drawn at 30% probability level.

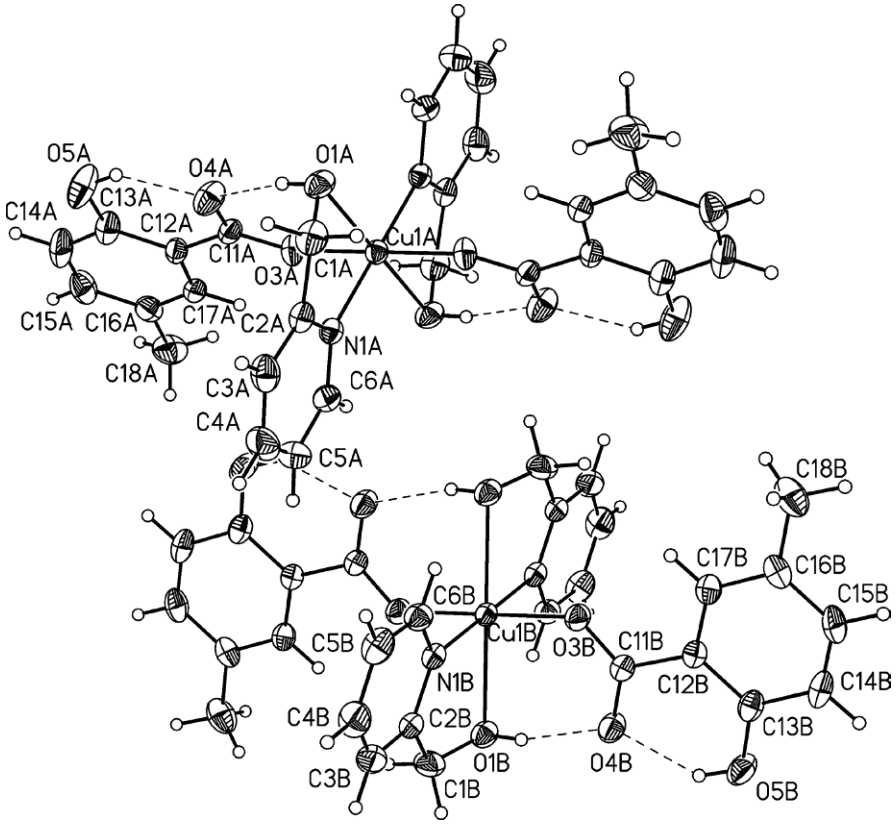

Figure 3. View of [Cu(5-Mesal)$_2$(2-pyme)$_2$] **(5)** with the atom numbering scheme. The all thermal ellipsoids are drawn at 30% probability level.

[Cu1–N1 = 1.993(2) and 1.996(2) Å] and two carboxylato oxygen atoms of 5-methysalicylate anions [Cu1–O3 = 2.000(2) and 2.002(2) Å] in equatorial plane. Both axial positions are occupied by hydroxyl oxygen atoms of 2-pyridylmethanol [Cu1–O1 = 2.382(2) and 2.374(2) Å] (Table 3).

In this case, the same system of intramolecular hydrogen bonds occurs: the uncoordinated oxygen atom of salicylato anions are linked to the methanol hydrogen atoms of 2-pyridylmethanol ligands (O1–H1O···O4) and are forming six-membered metallocyclic rings. The other six-membered rings are formed also with hydrogen bonds involving the hydroxyl hydrogen atoms and the uncoordinated carboxylato oxygen atoms of salicylato anions. In every basic cell there are two independent structural units, which in fact are *cis*

Table 4. Parameters of hydrogen bonds within the structure.

	d(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	<(DHA)/°
(1)				
O1—H1O···O4	0.82	1.77	2.583(2)	173
O5—H5O···O4	0.82	1.81	2.537(2)	146
C1—H1A···O5^{i}	0.97	2.54	3.401(4)	148
C4—H4···Cg^{v}	0.93	2.70	3.542(5)	150
(5)				
O1A—H1OA···O4A	0.82	1.83	2.638(4)	168
O5A—H5OA···O4A	0.82	1.85	2.556(4)	144
O1B—H1OB···O4B	0.82	1.85	2.647(4)	164
O5B—H5OB···O4B	0.82	1.87	2.575(4)	143
C6A—H6A···O4B^{ii}	0.93	2.57	3.339(5)	140
C1A—H1A···O5A^{iii}	0.97	2.60	3.568(5)	175
C4B—H4B···O5B^{iv}	0.93	2.64	3.315(6)	130

Symmetry codes: (i) –x–1, y–1/2, –z–1/2; (ii) –x, –y, –z; (iii) –x+2, –y, –z+1; (iv) x+1, y, z; (v) –x, y–1/2, –z–1/2

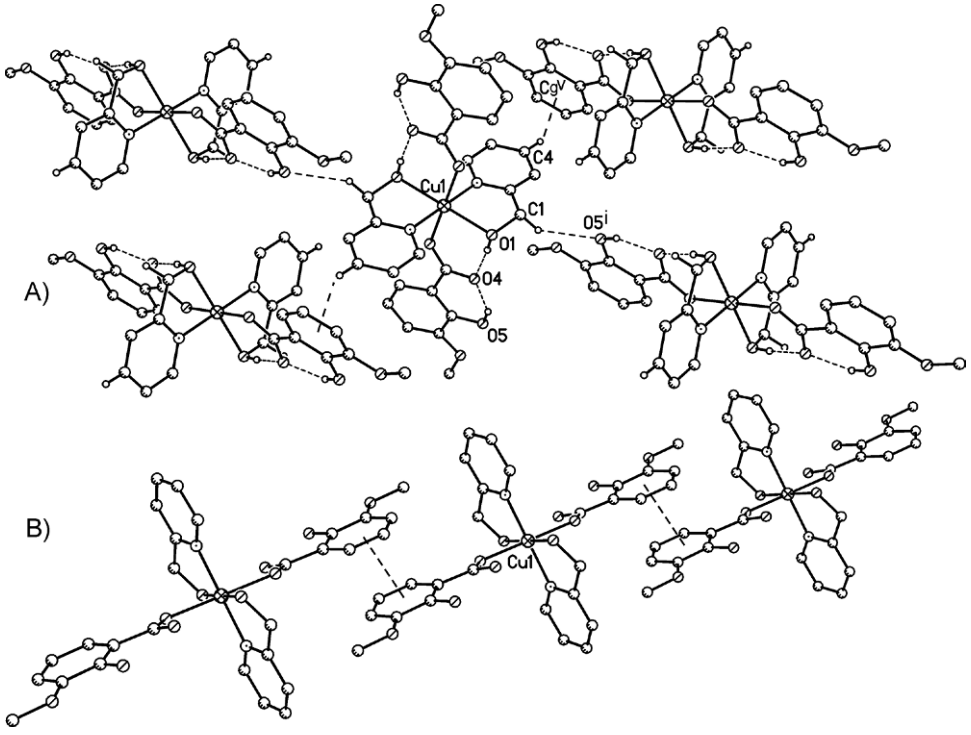

Figure 4. Crystal packing of [Cu(3-MeOsal)$_2$(2-pyme)$_2$] **(1)**. Hydrogen atoms are omitted for clarity. A) The O—H···O, C—H···O and C—H···Cg (CH\ϖ) hydrogen bonds in crystal structure of **1**. B) The ϖ–ϖ stacking interactions between benzene rings of 3-methoxysalicylate anions. [Symmetry codes: (i) –x–1, y–1/2, –z–1/2; (v) –x, y–1/2, –z–1/2].

and *trans* isomers (Fig. 3, Table 4). We have previously published the crystal structures of also complexes (**2**) and (**3**) [22]. These published complexes have similar molecular structures to complexes (**1**) and (**5**). In both cases they crystallize in the monoclinic crystallographic system, in space groups C2/c and P2$_1$/c, respectively [22].

Figs. 4 and 5 show crystal packing of (**1**) and (**5**), respectively. The complex molecules of (**1**) are connected through C1—H1···O5^{i} (Symmetry code: (i) –x–1, y–1/2, –z–1/2) hydrogen bonds between methylene group and hydroxyl oxygen atoms [distance of C1···O5 is 3.401(4) Å] (Table 4) into 2-D supramolecular networks (Fig. 4A). The CH\π [hydrogen bonds [C4—H4···Cg^{v} (Symmetry code: (v) –x, y–1/2, –z–1/2) with C4···Cg distance of 3.542(5) Å] [63] is also observed in crystal packing of **1** (Fig. 4A). And finally, 3-methoxysalicylate anions are stacked to 3-methoxysalicylate anions of neighbouring complex molecule [Symmetry: –x–1, –y+1, –z] in π–π stacking interactions [64]. The distance

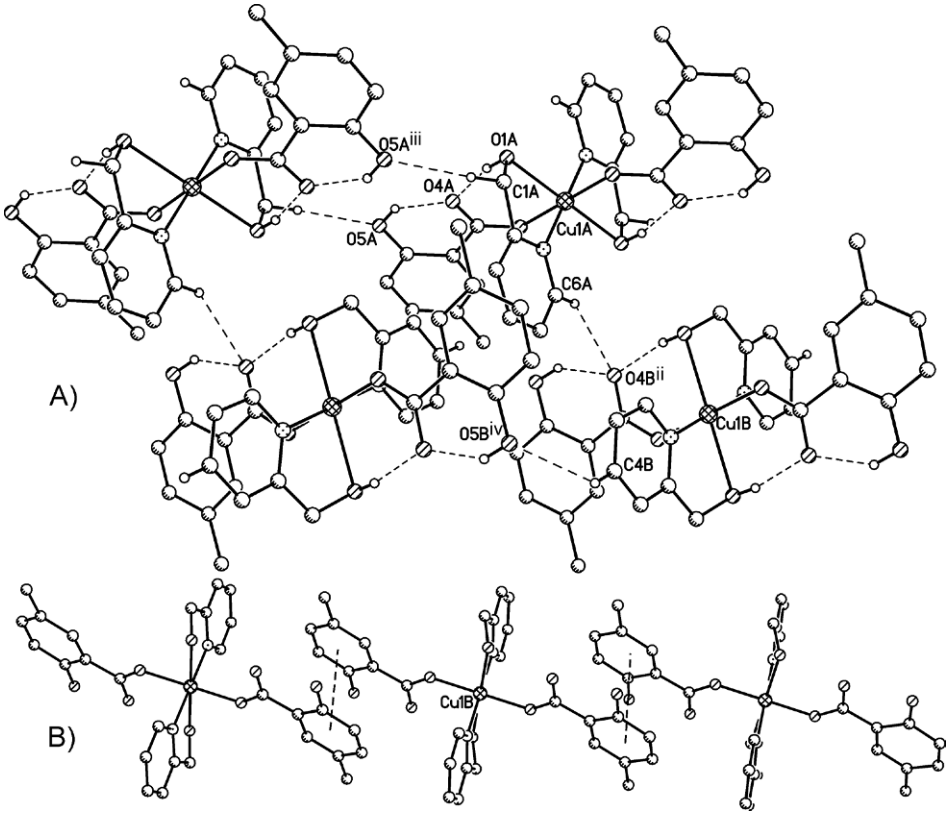

Figure 5. Crystal packing of $[Cu(5\text{-Mesal})_2(2\text{-pyme})_2]$ **(5)**. Hydrogen atoms are omitted for clarity. A) The O—H···O and C—H···O hydrogen bonds in crystal structure of **5**. B) The ϖ–ϖ stacking interactions between benzene rings of 5-methylsalicylate anions. [Symmetry codes: (ii) –x, –y, –z; (iii) –x+2, –y, -z+1; (iv) x+1, y, z].

between planes of benzene rings [C12–C17] is 3.42 Å and distance between centroids of benzene rings of 3-methoxysalicylate anions is 3.58 Å.

The structural nonequivalent complex (**5**) molecules A and B show different C—H···O hydrogen bonds in 2-D supramolecular networks (Fig. 5A). The two A molecules are connected through C1A—H1A···O5A^{iii} (Symmetry code: (iii) –x+2, –y, –z) hydrogen bonds between methylene group of 2-pyridylmethanol ligands and hydroxyl oxygen atoms of 2-pyridylmethanol ligands [distance of C1A···O5A is 3.568(5) Å] (Table 4). The two B molecules are joined through C4B—H4B···O5B^{iv} (Symmetry code: (iv) x+1, y, z) hydrogen bonds between aromatic H4B of pyridine ring of 2-pyridylmethanol ligands and hydroxyl oxygen atoms of 2-pyridylmethanol ligands [distance of C4B···O5B is 3.315(6) Å] (Table 4). The C6A—H6A···O4B^{ii} (Symmetry code: (ii) –x, –y, –z) hydrogen bonds between aromatic H6A of pyridine ring of 2-pyridylmethanol ligands from molecule A and uncoordinated oxygen atom of carboxyl group of 5-methylsalicylate anions from molecule B [distance of C6A···O4B is 3.339(5) Å] (Table 4) are the connectors between the structurally nonequivalent complex molecules. The π–π stacking interactions [64] are observed between benzene rings [C12B–C17B] of 5-methysalicylate anions only from molecules B [Symmetry: –x, –y+1, –z] (Fig. 5B). The plane–plane and centroid–centroids distances are of values 3.49 and 3.74 Å, respectively.

4. Conclusions

In conclusion it should be stressed that three novel monomeric complexes of composition $CuX_2(L)_2$ have been characterized. They consist of 3-methoxysalicylate and 4-, 5-methylsalicylate anions as anionic ligand X and 2-pyridylmethanol as bidentate ligand L. The EPR measurements of frozen solutions containing different Cu(II) : L molar ratios from 1 : 2 up to 1 : 16 gave us evidence about the probable existence of species containing only two nitrogen donor ligands in equatorial positions of the coordination sphere.

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