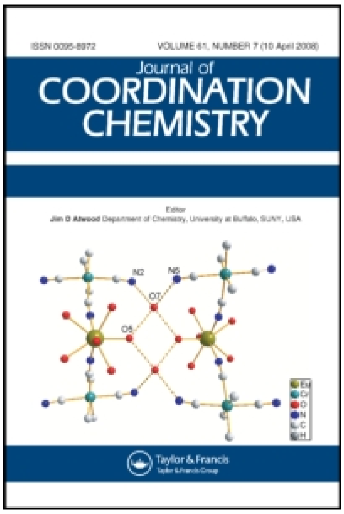

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Púčeková-Repická, Z. , Moncol, J. , Valigura, D. , Lis, T. , Korabik, M. , Melník, M. , Mroziński, J. and Mazúr, M.(2007) 'Synthesis, structure, spectral and magnetic properties of 4-methoxy- and 3-methylsalicylatocopper(II) complexes with 2-pyridylmethanol', Journal of Coordination Chemistry, 60: 22, 2449 — 2460

To link to this Article: DOI: 10.1080/00958970701272565

URL: http://dx.doi.org/10.1080/00958970701272565

Journal of Coordination Chemistry
Vol. 60, No. 22, 15 November 2007, 2449–2460

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Synthesis, structure, spectral and magnetic properties of 4-methoxy- and 3-methylsalicylatocopper(II) complexes with 2-pyridylmethanol

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(*Received 2 March 2006; revised 7 August 2006; in final form 16 August 2006*)

The synthesis and characterization of [Cu(4-MeOsal)$_2$(2-pyme)$_2$] (**1**) and [Cu(3-Mesal)$_2$(2-pyme)$_2$] (**2**) (where 4-MeOsal = 4-methoxysalicylate, 3-Mesal = 3-methylsalicylate and 2-pyme = 2-pyridylmethanol) are reported. The composition and stereochemistry as well as the mode of coordination have been determined by elemental analysis, IR, electronic and EPR spectra as well as magnetization measurements over the temperature range 1.8–300 K. The crystal structures of Cu(4-MeOsal)$_2$(2-pyme)$_2$ and Cu(3-Mesal)$_2$(2-pyme)$_2$ have been determined.

Keywords: Copper(II); Salicylate; 2-Pyridylmethanol; Crystal structure; Spectra; Magnetism

1. Introduction

The biomedical activities, chemical and industrial versatility of copper complexes have been the subject of intensive study. Copper complexes with some ligands exhibit better biological activity compared to non-coordinated ligands [1] e.g. copper(II) aspirinate complex is a more effective anti-inflammatory agent than aspirine itself [2], or the copper complex of 3,5-dimethylpyrazol has higher antimicrobial activity (testing on *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*) than 3,5-dimethylpyrazol [3]. Copper(II) complexes of carboxylato ligands have been the subject of a large number of studies [4, 5], due to the various coordination modes of carboxylato ligands. The ability of salicylic acid to act as an oxygen donor and to form complexes with different metal atoms is well known [6]. Salicylic acid and its derivatives play an important role in biological processes and a number of copper(II) salicylates have been investigated [7]. Methyl- and methoxy-derivatives of salicylic acid as a donor in solid state to our knowledge have not been studied.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701272565

In the present paper, we report as a part of our investigation of metal ion–drug interaction the complexation of 4-methoxysalicylate (4-MeOsal) or 3-methylsalicylate (3-Mesal) in the presence of 2-pyridylmethanol (2-pyme). The crystal structures of $[Cu(4\text{-}MeOsal)_2(2\text{-}pyme)_2]$ (**1**) and $[Cu(3\text{-}Mesal)_2(2\text{-}pyme)_2]$ (**2**) have been solved. Based on the molecular structure, the electronic, infrared, EPR and magnetic data are discussed.

2. Experimental

2.1. *Preparation*

2.1.1. *Bis*(4-methoxysalicylato)di(2-pyridylmethanol)copper(II) (1). 2-Pyridylmethanol (2 mmol) under stirring was added to aqueous of copper(II) acetate (1 mmol) in $V = 20\,cm^3$. After several minutes, 4-methoxysalicylic acid (2 mmol) was added to the dark blue solution. The reaction mixture was stirred for 5 days at ambient temperature. The light blue product which precipitated, was filtered off, and the mother liquid was left to crystallize at ambient temperature. Crystals which formed, were separated and dried at ambient temperature. Composition of powder product by elemental analyses is the same as the crystals (proved by X-ray structure analysis). Anal. Calcd for $CuC_{28}H_{28}N_2O_{10}$: Cu, 10.31; C, 54.59; H, 4.58; N, 4.54%. Found: Cu, 10.13; C, 54.40; H, 4.59; N, 5.12%.

2.1.2. *Bis*(3-methylsalicylato)di(2-pyridylmethanol)copper(II) (2). 2-Pyridylmethanol (2 mmol) under stirring was added to aqueous of copper(II) acetate (1 mmol) in $V = 20\,cm^3$. After several minutes, 3-methylsalicylic acid (2 mmol) was added to the solution. The reaction mixture was stirred and heated under reflux for 2 days. The subsequent procedures were similar to those of complex **1**. Anal. Calcd for $CuC_{28}H_{28}N_2O_8$: Cu, 10.88; C, 57.58; H, 4.83; N, 4.79%. Found: Cu, 10.79; C, 57.24; H, 4.99; N, 4.31%.

2.2. *Analysis and physical measurements*

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA 1112 (ThermoFinnigan) elemental analyzer. Copper was determined by electrolysis of water solution obtained by sample mineralization with a mixture of sulfuric acid and potassium peroxodisulfate.

Electronic spectra (190–1100 nm) of the complexes were measured in Nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer. Infrared spectra in the region of 4000–100 cm^{-1} were measured with a Nicolet MAGNA 750 IR spectrometer using both KBr pellet and Nujol suspension techniques for 4000–400 cm^{-1} region and polyethylene pellet for 400–100 cm^{-1}.

EPR spectra of powdered sample were recorded at room temperature on the Bruker ESP 300 spectrometer, operating at X-band equipped with an ER 035M Bruker NMR gaussmeter and a HP 5350B Hewlett Packard microwave frequency counter.

Data collection and cell refinement of the complexes were carried out using a Kuma KM4-CCD diffractometer with graphite monochromated Mo-Kα radiation, using CrysAlis software package [8] at 100 K. Intensity data were corrected for Lorenz and polarization factors; for **2** an absorption correction was applied. The structures were solved by direct methods SIR-97 [9] **1** or SHELXS-97 [10] **2** and refined by full-matrix least-squares procedure SHELXL-97. Geometrical analyses were performed using SHELXL97 [11]. The structures were drawn using XP in SHELXTL [12]. In the crystal of [Cu(4-MeOsal)$_2$(2-pyme)$_2$] a partial disorder is observed. The hydroxymethyl group of 2-pyridylmethanol ligand is found in two ortho positions (A or B) of pyridine ring (with s.o.f. of 0.590(4) (part A) and 0.410(4)) (part B) marked in figure 1(a) with dashed open lines. The disorder observed in the crystal may be the result of two different effects, both assuming/causing the existence of the molecules in two different orientations in the crystal. One of them is the two-fold rotation of the 2-pyridylmethanol ligands around the Cu–N axis, and the other – the similar rotation of the whole molecule around the same axis. The programme enCIFer has been used as software for preparing material for publication [13]. Final crystal data and structure refinement parameters are given in table 1.

Magnetization measurements in the temperature range of 1.8–300 K were carried out on powdered samples of complexes, at magnetic field 0.5 T, using a Quantum Design SQUID Magnetometer (type MPMS-XL5). Corrections for diamagnetism of the constituting atoms were calculated using Pascal constants [14], the value of $60\,10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ was used as the temperature-independent paramagnetism of Cu^{2+} ion. The effective magnetic moments were calculated from the expression

$$\mu_{\mathrm{eff}} = 2.83\sqrt{\chi_{\mathrm{M}}^{\mathrm{corr}} \cdot T}\,(\mathrm{B.M.})$$

3. Results and discusion

An ORTEP diagram of [Cu(4-MeOSal)$_2$(2-pyme)$_2$] (**1**) is shown in figure 1(a) and selected bond distances and angles are given in table 2. In the structure of **1**, the Cu atom is six-coordinated in a distorted tetragonal bipyramid (4 + 2). Two equatorial positions are occupied by nitrogen atoms of 2-pyridylmethanol (Cu–N1 = 1.986(2) Å), while the other two equatorial positions are occupied by oxygen atoms (Cu–O3 = 2.004(2) Å) of carboxyl groups of two 4-MeOSal anions, which are unidentate to the central atom, forming a *trans*-square-planar arrangement. Two axial positions are occupied by oxygen atoms of disordered hydroxymethyl groups of two 2-pyridylmethanol ligands at somewhat greater bond distances (Cu–O1 = 2.312(2) Å) in position A or (Cu–O2 = 2.329(3) Å) in position B, and complete the tetragonal-bipyramidal coordination. The N1–Cu–O1 and N1–Cu–O2 bond angles of the five-membered metallocycles (CuOC$_2$N) are 78.56(8) and 77.52(10)°, respectively. The value of the T parameter ($T = R_S/R_L$), indicating the degree of tetragonal elongation of the octahedron in **1** is 0.860. The uncoordinated oxygen atoms of the carboxyl group of the 4-MeOsal anions (O4) are "fixed" to the methanol hydrogen atoms of disordered 2-pyme molecules by hydrogen bonds O1–H1O $\cdots$ O4 ($-x+1/2$, $-y+3/2$, $-z+1$) and O2–H2O $\cdots$ O4 with interatomic distances O1 $\cdots$ O4 of 2.629(3) and O2 $\cdots$ O4 of 2.702(4) Å, thus creating six-membered metallocyclic rings (CuO$_3$CH). The other intramolecular hydrogen bonds from hydroxyl hydrogen

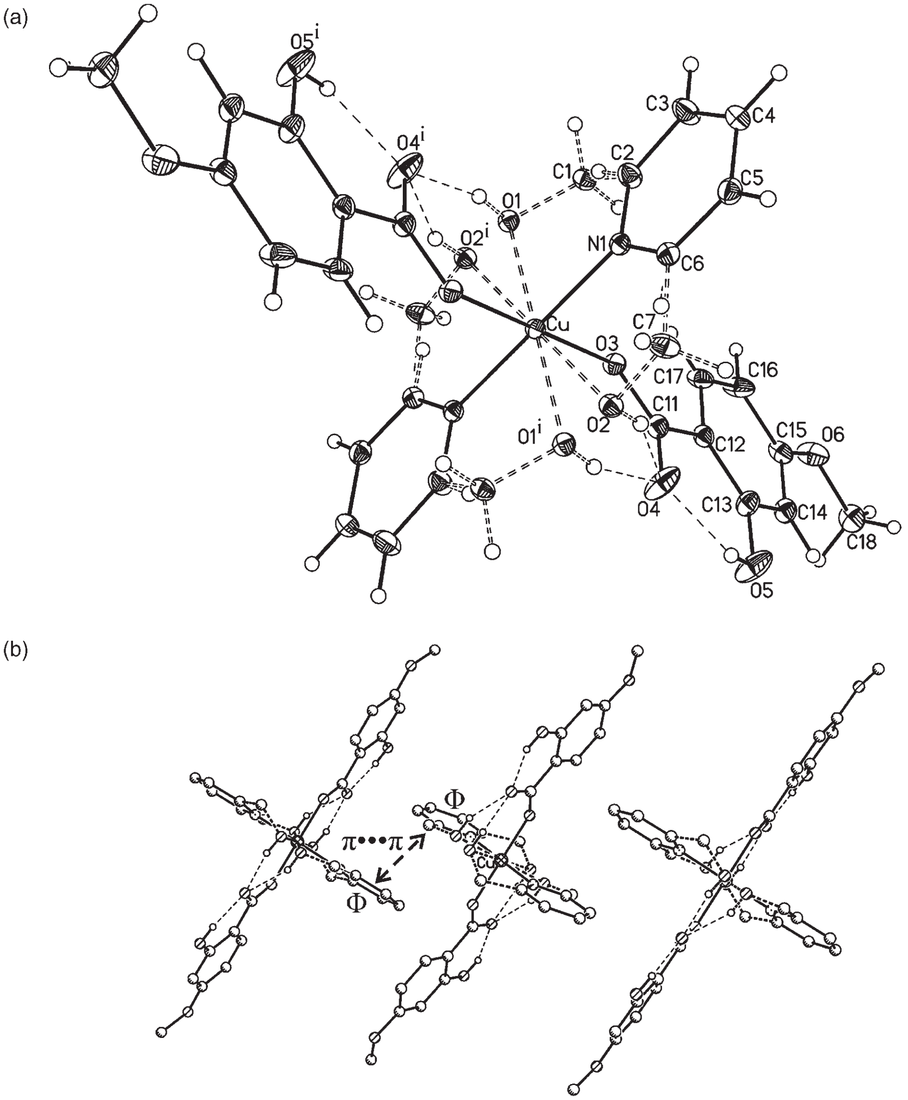

Figure 1. (a) Perspective view of [Cu(4-MeOsal)$_2$(2-pyme)$_2$] (**1**), with the atom numbering scheme [symmetric code (*i*): $-x+1/2$, $-y+3/2$, $-z+1$]. Thermal ellipsoids are drawn at the 50% probability level. Dashed open lines indicate disordered hydroxymethyl groups; (b) the $\pi\cdots\pi$ stacking in packing diagram of [Cu(4-MeOsal)$_2$(2-pyme)$_2$] (**1**).

atom of the 4-MeOsal anions to the uncoordinated carboxylate oxygen atoms O5–H5O$\cdots$O4 with interatomic distance O5$\cdots$O4 of 2.564(2) Å, also create six-membered rings (O_2C_3H), and stabilize the structure. The molecules in **1** have offset $\pi\cdots\pi$ stacking interactions [15] between two symmetrical adjacent pyridine rings N1–C6 (Φ) ($-x+1$, y, $-z+3/2$) of 2-pyridylmethanol molecules (figure 1b), [centroid$\cdots$centroid distance = 4.22 Å, distances between two planes range from 3.33–4.42′, normal-normal angle α [16, 17] is 23.5° and the distance between the normal and the ring centroid, offset [16, 17] is 1.68 Å].

Table 1. Crystallographic data for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{28}H_{28}CuN_2O_{10}$	$C_{28}H_{28}CuN_2O_8$
M	616.06	584.06
T (K)	100(2)	100(2)
Crystal size (mm^3)	$0.13 \times 0.25 \times 0.55$	$0.35 \times 0.35 \times 0.50$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P21/c$
a (Å)	14.178(6)	12.044(3)
b (Å)	12.160(5)	8.238(2)
c (Å)	17.211(7)	13.841(3)
β (°)	114.36(3)	107.33(3)
V (Å^3)	2703.1(19)	1310.9(5)
Z	4	2
D_c (Mg m^{-3})	1.514	1.480
μ (Mo-Kα) (mm^{-1})	0.87	0.89
F(000)	1276	606
θ Range (°)	2.9–33.0	3.0–35.0
$T_{\min}/T_{\max}$	None	0.662/0.784
$h/k/l$	−21, 21/−18, 14/−26, 26	−15, 19/−12/13/−21/21
Reflections collected	19570	20166
Unique reflections (R_{int})	5004 (0.059)	5623 (0.033)
Data/restraints/parameters	5004/2/214	5623/1/183
S	1.12	1.07
R_1, wR_2 (observed reflections)	0.050, 0.130[a]	0.034, 0.092[b]
R_1, wR_2 (all reflections)	0.072, 0.139[a]	0.046, 0.096[b]
$-\Delta_\rho/\Delta_\rho$ (e^{-1} Å^{-3})	−0.81/0.58	−0.39/1.06

Calculated weights: [a]$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.9422P]$; [b]$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

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

	1	**2**
Cu–N1	1.986(2)	1.9881(9)
Cu–O1	2.312(2)	2.314(1)
Cu–O2	2.329(3)	
Cu–O3	2.004(2)	2.025(1)
N1–Cu–O3	88.80(6)	87.16(4)
N1–Cu–O1	78.56(8)	78.68(3)
N1–Cu–O2	77.52(10)	
O3–Cu–O1	85.51(7)	88.69(3)
O3–Cu–O2	91.23(9)	

The principal structural features of $[Cu(3\text{-Mesal})_2(2\text{-pyme})_2]$ (**2**) are illustrated in figure 2 and selected bond distances and angles are shown in table 2. Complex **2** has a similar structure to **1**. Copper is at the centre of symmetry and exhibits a square-bipyramidal coordination polyhedron with a pair of salicylato ligands monodentately coordinated *via* carboxylate O atoms (Cu–O2 = 2.025(1) Å). The other two positions of basal plane are occupied by two nitrogen atoms of 2-pyridylmethanol ligands (Cu–N1 = 1.9881(9) Å). The axial positions of the polyhedron are occupied by two oxygen atoms (Cu–O3 = 2.314(1) Å) of hydroxymethyl groups of two 2-pyridylmethanol ligands. The value of the T parameter in **2** is 0.867.

Intramolecular hydrogen bonds O1–H1O···O4 (table 3) between coordinated hydroxyl O1–H1O in axial position and carboxylato oxygen O4 of 3-Mesal anion

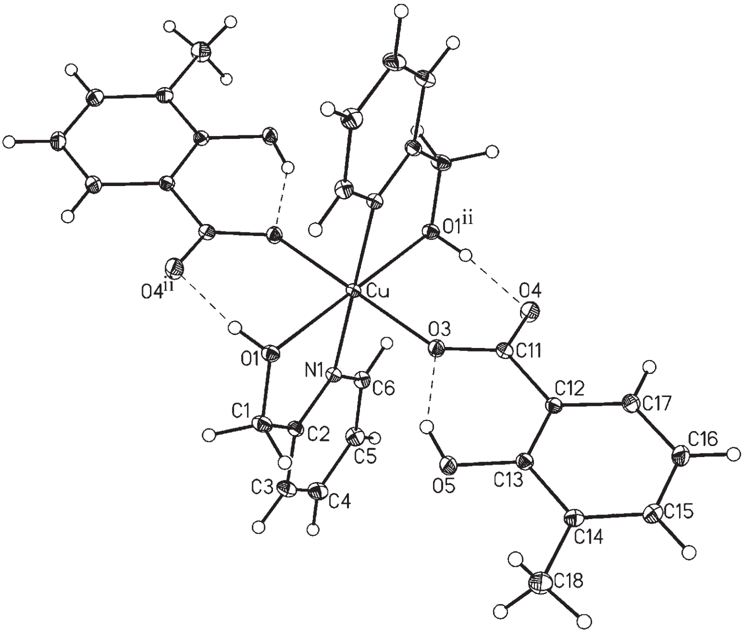

Figure 2. Perspective view of [Cu(3-Mesal)$_2$(2-pyme)$_2$] (**2**), with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Parameters in (Å) and (°) of hydrogen bonds within the structure.

D–H···O		d(D–H) (Å)	d(H···O) (Å)	d(D···O) (Å)	∠(DHO) (°)
1					
O5–H5O···O4		0.84	1.83	2.564(2)	145
O1–H1O···O4	$-x+1/2, -y+3/2, -z+1$	0.84	1.81	2.629(3)	164
O2–H2O···O4		0.84	1.91	2.702(4)	156
2					
O5–H5O···O3		0.84	1.79	2.534(1)	146
O1–H1O···O4		0.84	1.77	2.595(2)	169
C4–H4···O5	$-x+1, -y, -z+1$	0.95	2.60	3.546(2)	174
C6–H6···O4	$x, -y+1/2, z-1/2$	0.95	2.53	3.302(2)	139
C16–H16···O5	$x, -y+1/2, z+1/2$	0.95	2.40	3.226(2)	145

is similar in arrangement (six-membered metallocycle) to those in **1**, but is stronger giving O1···O4 of 2.595(4) Å. The intramolecular hydrogen bond of salicylato O5–H5O group is linked to the coordinated O3 oxygen atom of carboxylato group different from **1**, but the bond strength of this hydrogen bond is very similar to those in complex **1** (O5–H5O···O3, interatomic distance O5···O3 of 2.534(1) Å). Comparing the O–H···O hydrogen bonds in structures of **1** and **2**, show differences in position of hydroxyl group on benzene rings of salicylates anions. In complex **1**, the hydroxyl group lies *trans* to coordinated oxygen atom of carboxylate group, but in **2**, *cis*. Additional intermolecular hydrogen bonding interactions in **2** (figure 3) are between hydrogen atoms of aromatic rings and hydroxyl oxygen atoms of 3-methylsalicylate anions (O5) [C4–H4···O5 ($-x+1$, $-y$, $-z+1$) and C16–H16···O5 (x, $-y+1/2$,

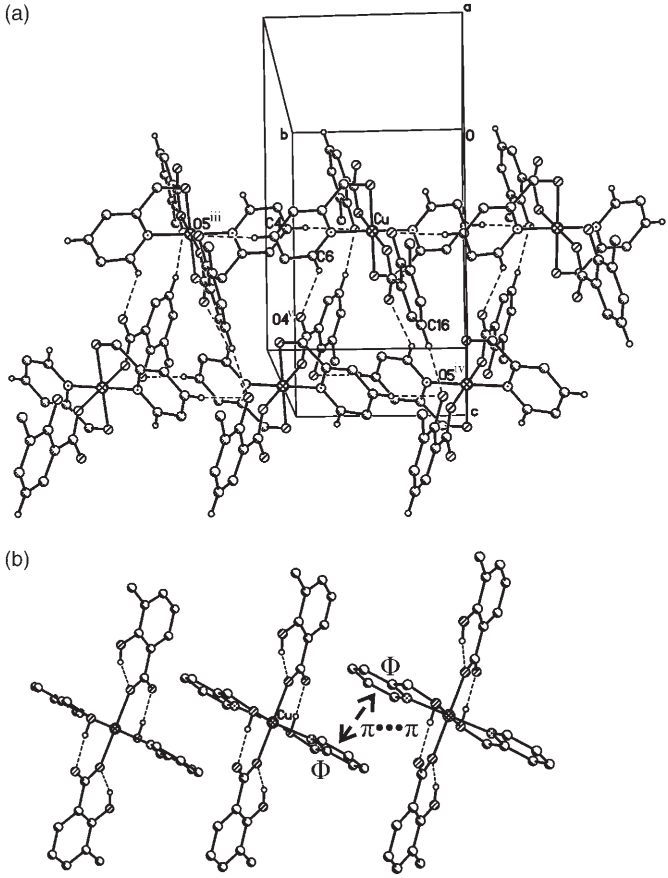

Figure 3. (a) The crystal packing of [Cu(3-Mesal)$_2$(2-pyme)$_2$] (**2**), viewed approximately along the *a* axis. Dashed lines indicate C–H $\cdots$ O hydrogen bonds; (b) the $\pi \cdots \pi$ stacking in [Cu(3-Mesal)$_2$(2-pyme)$_2$] (**2**).

$z-1/2$)] with interatomic distances C4 $\cdots$ O5 of 3.546(2) Å and C16 $\cdots$ O5 of 3.226(2) Å; and between hydrogen atoms of aromatic rings and uncoordinated carboxylate oxygen atoms of 3-methylsalicylate anions (O4) [C6–H6 $\cdots$ O4 ($1-x$, $1/2+y$, $3/2-z$)] with interatomic distances C6 $\cdots$ O4 of 3.302(2) Å. The additional slipped $\pi \cdots \pi$ stacking interactions [17] along *b* are between two symmetrically adjacent pyridine rings N1–C6 (Φ) ($-x+1$, $-y$, $-z+1$) of 2-pyridylmethanol molecules (figure 3), [centroid $\cdots$ centroid distance = 3.87 Å with distances between two planes 3.43 Å]. In the crystal structure of **1**, the hydrogens of benzene are linked to one oxygen of methanolic groups [C14–H14 $\cdots$ O1 ($-x+1/2$, $y-1/2$, $-z+1/2$) or C14–H14 $\cdots$ O2 (x, $-y+1$, $z-1/2$)] with C $\cdots$ O distances of 3.365(3) and 3.382(4) Å, respectively.

The structures of both complexes can be compared with other complexes of general formula [CuX$_2$(2-pyme)$_2$], where X is salicylate [18], clofibriate [19], 2-bromopropionate [20] and mefenamate [21]. The Cu–O$_{eq}$ (O atom of carboxylate group), Cu–N$_{eq}$ (N pyridine atom of 2-pyme) and Cu–O$_{ax}$ (O atom of 2-pyme hydroxyl group) bond lengths are 1.981(1), 1.981(1) and 2.331(2) Å for salicylate [18] 1.997(2), 1.978(2) and 2.388(2) Å for clofibriate [19] 2.003(2), 1.984(2) and 2.404(2) Å for 2-bromopropionate [20] 1.966(2), 1.990(2) and 2.415(2) Å for mefenamate [21]. The corresponding bond lengths in the present structure are consistent with these values. The tetragonality parameter T ($T = R_S/R_L$; where R_S is mean Cu–L bond length within equatorial plane and R_L is mean Cu–L bond length in axial positions) [22], decreases in the order of X: 0.867 (X = 3-Mesal) > 0.860 (X = 4-MeOsal) > 0.850 (X = sal [18]) > 0.832 (X = clof [19]) > 0.822 (X = 2-Brprop [20]) > 0.819 (X = mef [21]), indicating that the degree of tetragonal distorsion, as the consequence of Jahn–Teller effect, increases in the same order. This class of compounds displays structures with axially elongated tetragonal bipyramidal geometry about each Cu(II) atom of the [$CuO_2N_2O'_2$] chromophore. In the square-bipyramidal coordination polyhedron of complexes with formula [$Cu(NO_3)_2$(2-pyme)$_2$] [23] and [Cu(sac)$_2$(2-pyme)$_2$] (sac = saccharinate anions) [24] both donor atoms of 2-pyme ligands are localized in the equatorial plane with bond lengths Cu–N_{eq}(2-pyme) = 1.952(1) and 1.967(1) Å, respectively, and Cu–O_{eq}(2-pyme) = 1.971(1) and 2.139(1) Å, respectively. However, a completely different [$CuO_2N_2O'_2$] chromophore of tetragonal pyramidal geometry was found for [CuY(2-pyme)$_2$]Y (where Y = 3,5-dinitrobenzoate anion) [25], but 2-pyme molecules are chelating as well.

The IR spectrum of **1** shows the band at 1607 cm^{-1} assigned to the antisymmetric stretch $\nu_{as}(COO^-)$. The band at about 1440 cm^{-1} can be assigned as $\nu_s(COO^-)$. Similar antisymmetric and symmetric (COO^-) vibrations are in the IR spectrum of the **2** ($\nu_{as} = 1609\,cm^{-1}$ and $\nu_s = 1434$). The differences between the antisymmetric and symmetric stretch give information about carboxyl bonding, $\Delta\nu$ [26] ($\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$) of compounds with ionic carboxyl groups. The value of $\Delta\nu = 167\,cm^{-1}$ for **1** is higher than for sodium 4-methoxysalicylate ($\Delta\nu = 149\,cm^{-1}$), and similarly the $\Delta\nu = 175\,cm^{-1}$ is greater than $\Delta\nu$ for sodium 3-methylsalicylate ($\Delta\nu = 147\,cm^{-1}$), consistent with unidentate bonded carboxyl group determined by X-ray analysis in both complexes.

The solid-state electronic spectra of the complexes exhibit a broad asymmetric ligand field band with a maximum at about 634 nm **1** and 653 nm **2**. This type of d ← d spectra is typical for a tetragonal bipyramidal arrangement around Cu(II). There are also charge transfer bands at about 226, 266 and 298 nm in **1** and 255 nm in **2**. The g values $g_\perp = 2.085$, $g_\parallel = 2.410$ for **1** and $g_\perp = 2.094$, $g_\parallel = 2.305$ for **2** are also in good agreement with a tetragonal bipyramidal arrangements about Cu(II) atom.

Molar magnetic susceptibility of polycrystalline samples of **1** and **2** between 1.8 and 300 K (figure 4) obey the Curie–Weiss law

$$\chi_m = \frac{C}{T - \Theta}$$

where

$$C = \frac{Ng^2\beta^2 S(S+1)}{3k}$$

with $S = ½$. The values of Curie and Weiss constants obtained by linear regression were $C = 0.436\,cm^3\,mol^{-1}\,K$, $\Theta = -0.5\,K$ for **1**, and $C = 0.451\,cm^3\,mol^{-1}\,K$, $\Theta = -0.8\,K$ for **2**, respectively. These values of Curie constant correspond well with g_{av} values ($g_{av} = 2.19$ for **1**, and $g_{av} = 2.16$ for **2**) obtained from EPR spectra (figure 5). Small, but not negligible negative values of Weiss constants indicate very weak antiferromagnetic interaction in both complexes (figure 6). The $\chi_m T$ value for **1** at 300 K is $0.437\,cm^3\,mol^{-1}\,K$ ($\mu_{eff} = 1.87$ BM) and at 1.8 K $\chi_m T = 0.417\,cm^3\,mol^{-1}\,K$ ($\mu_{eff} = 1.83$ BM).

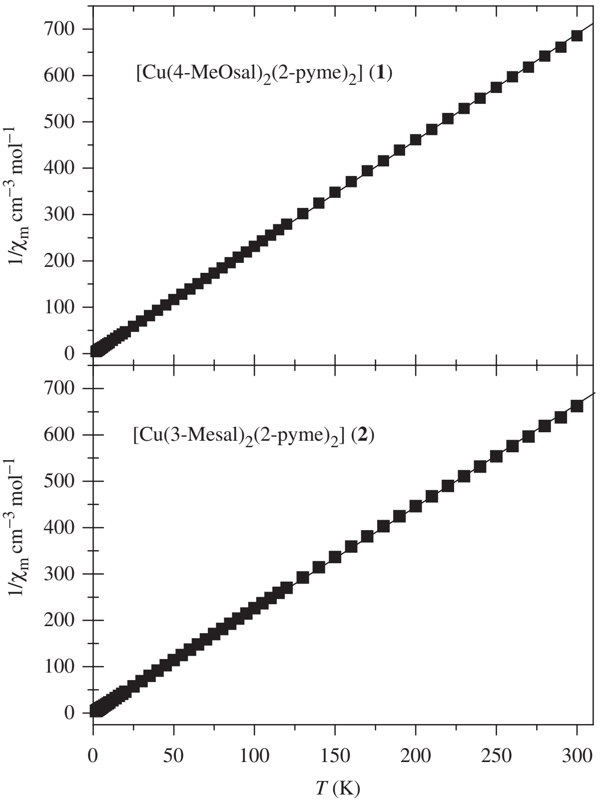

Figure 4. Plot of $1/\chi_m$ *vs.* T for complexes **1** and **2**. Straight lines are obtained by linear regression giving Curie constant $C = 0.436\,\mathrm{cm^3\,mol^{-1}\,K}$ and Weiss constant $\Theta = -0.5\,\mathrm{K}$ for **1**, and $C = 0.451\,\mathrm{cm^3\,mol^{-1}\,K}$ and $\Theta = -0.8\,\mathrm{K}$ for **2**.

Complex **2** exhibits the $\chi_m T$ value at 300 K equal to $0.453\,\mathrm{cm^3\,mol^{-1}\,K}$ ($\mu_{\mathrm{eff}} = 1.90\,\mathrm{BM}$) and at 1.8 K $\chi_m T = 0.430\,\mathrm{cm^3\,mol^{-1}\,K}$ ($\mu_{\mathrm{eff}} = 1.86\,\mathrm{BM}$). These small effective magnetic moment decreases are in good agreement with the obtained value of Weiss constant and confirm that there are very weak interactions between neighbouring Cu(II) atoms in both structures (see discussion above). This was analyzed by application of molecular field model into the calculation of the presented magnetic data of both complexes which have been fit using magnetic centres ($S = ½$) in the molecular field model of magnetic interactions [27]:

$$\chi_m = \frac{N\beta^2 g^2}{3kT} S(S+1), \quad \chi_m^{\mathrm{corr}} = \frac{\chi_m}{1 - (2zJ'\chi_m/Ng^2\beta^2)}$$

where zJ' is the molecular exchange parameter, z is number of the nearest neighbours. The R is the agreement factor defined as:

$$R = \sum_{i=1}^{n} \frac{(\chi_i^{\mathrm{exp}} T - \chi_i^{\mathrm{calcd}} T)^2}{(\chi T_i^{\mathrm{exp}})^2}$$

The magnitude of the magnetic exchange between ions obtained from these calculations, $zJ' = -0.099\,\mathrm{cm^{-1}}$, $R = 6.25 \times 10^{-6}$ for **1**, and $zJ' = -0.093\,\mathrm{cm^{-1}}$,

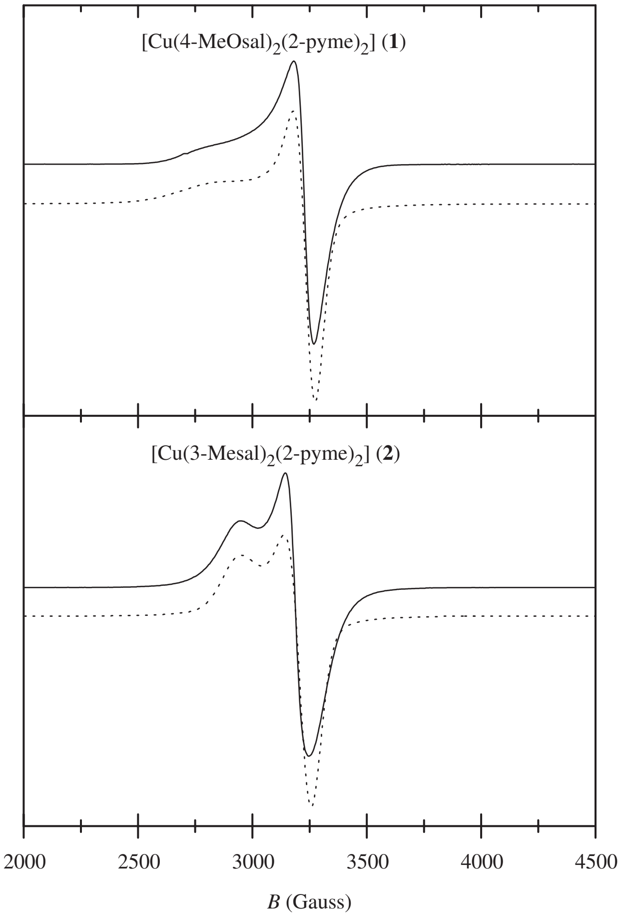

Figure 5. EPR spectra of powdered samples of complexes under study (—— measured at room temperature, and …… simulated).

$R = 1.13 \times 10^{-4}$ for **2** are for both complexes in good agreement with very weak interaction between magnetic centres. The shortest pathway linking each Cu^{2+} ion to its neighbours (Cu–Cu contact is similar for both complexes, about 8.20 Å) is *via* aromatic stacking interaction (figure 1b, and/or figure 3b) and it could be taken as confirmation that $\pi \cdots \pi$ stacking interactions offer a route for the transmission of magnetic effects. Although the observed magnetic effects were small, their characterizations were important because the weak $\pi \cdots \pi$ interactions were not mixed or overlapped with stronger covalent interactions. Noncovalent bondings, like $\pi \cdots \pi$ stacking interactions, are intensively studied because they play a major role in the structure of biological macromolecules and in magnetic molecular materials [28, 29]. The g values obtained ($g = 2.15$ for **1** and $g = 2.17$ for **2**) are similar to those obtained from EPR. Somewhat lower value of magnetic moment of **1** corresponds well with larger tetragonal distortion ($T = 0.860$) about the Cu(II), than **2** ($T = 0.867$). Greater tetragonal distortion leads to a lower magnetic moment. This is in good agreement with the ligand field band as well as with the G values ($G = 4.82$ for

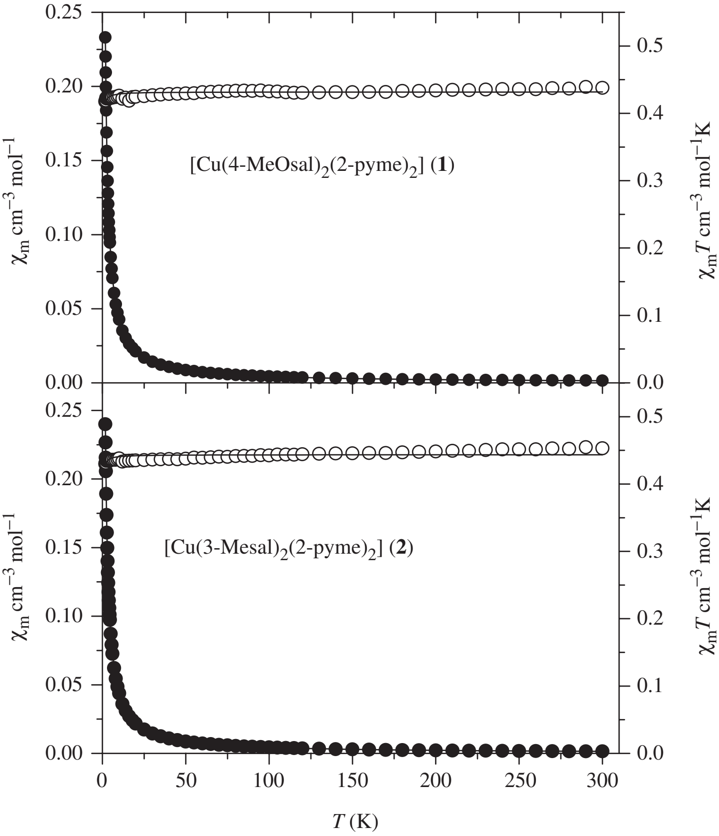

Figure 6. Plots χ_m (●) and $\chi_m T$ (○) values *vs.* T for **1** and **2**. The full lines represent the best fit (see text).

complex **2**, and $G = 3.24$ for complex **2**, respectively) calculated from EPR spectra ($G = (g_{\parallel} - 2)/(g_{\perp} - 2)$) [30].

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-297132 **1** and CCDC-297133 **2**. 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; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

We thank Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences (1/2452/05), Research and Development Support

Agency (APVT-20-005504) and the Polish Ministry of Science and Computerization for financial support.

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