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Dimeric and different polymeric copper(II) salicylates – Crystal structure and spectral properties

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ABSTRACT

The small differences in synthesis condition led to formation of four new copper(II) salicylatocomplexes – two differently polymeric $[Cu(4\text{-}MeOSal)_2(\mu\text{-}H_2O)_2]_n$ **1,** $[Cu(\mu\text{-}3,5\text{-}Br_2Sal)_2(H_2O)_2]_n$ **2** and two dimeric $[Cu(5\text{-}MeSal)_2(MeOH)]_2{\cdot}2MeOH$ **3** $[Cu(4\text{-}MeSal)_2(EtOH)_2]_2$ **4** compounds, where 4-MeOSal = 4-methoxysalicylate, 3,5-Br_2Sal = 3, 5-dibromsalicylate, 5-MeSal = 5-methylsalicylate, and 4-MeSal = 4-methoxysalicylate monoanion. Complexes were characterized by elemental analysis, UV–Vis, infrared, EPR spectra and single crystal X-ray analysis. Spectral properties are in good agreement with structural information. Intermolecular interactions are responsible for building supramolecular structure. The complexes **1** and **2** build up 2D supramolecular structures by the O–H···O hydrogen bonds formation while the complexes **3** and **4** are forming 1D supramolecular chain of paddle wheel units and coordinated solvent molecules.

1. Introduction

Salicylic acid is used in agriculture, cosmetics and recently in new drugs development. The importance this substance is well known for its different biological properties. It is not only a significant signal molecule for modulating plant responses to environmental stress [1–3], but its derivatives are biologically very potent: some of them exhibited cytotoxicity against tumor cell lines, some showed antioxidant properties [4,5]. Thus the salicylic acid is one of the most studied substances in wide variety of aspects including complex formation and structure of complexes because some salicylate complexes have shown better material and pharmacological properties than the parent ligand. Most popular are those metal complexes, which have shown practical application as precursors in the synthesis of novel compounds [6] and are also used in the search for new biologically active substances [7,8]. Many copper(II) complexes belong to this group of pharmacologically active compounds which have been shown to be more effective in treatment diseases [9], for example the copper(II) aspirinate exhibits enhanced anti-inflammatory activity in comparison to aspirin itself [10]. The copper(II) salicylates and aspirinates can be used as anti-cancer drugs [11,12], radio-protectants [13] and for treatment of inflammatory diseases [14]. Some copper(II) salicylates exhibit also DNA cleavage activity [15].

The specific feature of salicylic acid structure is that this carboxylate ligand posses hydroxyl functional –OH group which can participate in coordination or in building of H-bond system and the intramolecular H-bond makes carboxylate group of most salicylates strictly coplanar with aromatic ring. It is well known that the salicylic acid and its anions (monoanion or diaanion) can behave as mono-, bi-, or tridentate ligands, literature provides a lot of evidences [16–22] and our previous study of copper complexes with salicylate derivatives shows monodentate [23,24], chelating [15,25], combination of chelating and bridging [15,26] bonding mode of salicylate anion. Different binding modes of anion can influence significantly properties of synthesized complexes. Therefore, our attention is here focused to four new salicylatocopper complexes without any additional ligand except the used solvent molecules. We refer preparation, structure and spectral properties of two polymeric complexes $[Cu(4\text{-}MeOSal)_2(\mu\text{-}H_2O)_2]_n$ **1** $[Cu(\mu\text{-}3,5\text{-}Br_2Sal)_2(H_2O)_2]_n$ **2** and moreover two dimeric complexes $[Cu(5\text{-}MeSal)_2(MeOH)]_2{\cdot}2MeOH$ **3** $[Cu(4\text{-}MeSal)_2(EtOH)_2]_2$

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4 where 4-MeOSal = 4-methoxysalicylate, 3,5-Br_2Sal = 3,5-dibromsalicylate, 5-MeSal = 5-methylsalicylate and 4-MeSal = 4-methoxysalicylate monoanion.

2. Experimental

2.1. Synthesis

Appropriate derivative of salicylic acid (1 mmol) was added to aqueous solution of copper(II) acetate (5 ml, 0.5 mmol) under stirring and then was added a solvent (ethanol, water, methanol). The reaction mixture was stirred at room temperature until the reaction finished. The green precipitate was filtered and dried in air at ambient temperature. Mother liquid was left to crystallize at laboratory temperature. The obtained crystals were suitable for X-ray structure determination.

Anal Calc for $[Cu(4\text{-}MeOSal)_2(H_2O)_2]_n$ (**1**): C, 44.29; H, 4.18. Found: C, 44.3; H, 4.22.

Anal Calc for $[Cu(3,5\text{-}Br_2Sal)_2(H_2O)_2]_n$ (**2**): C, 24,26; H, 1,75. Found: C, 24.30; H, 1.40.

Anal Calc for $[Cu(5\text{-}MeSal)_2(MeOH)]_2\cdot MeOH$(**3**): C, 50.8; H, 4.78. Found: C, 50.6; H, 4.34.

Anal Calc for $[Cu(4\text{-}MeSal)_2(EtOH)]_2$ (**4**): C, 52.5; H, 4.89 Found: C, 52.04; H, 4.74.

2.2. Analysis and physical measurements

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 infrared spectra (4000–400 cm^{-1}) were measured with a NICOLET 5700 FT-IR (Nicolet) spectrophotometer at room temperature using ATR technique.

The electronic spectra (190–1100 nm) of the complexes were measured in nujol suspension with a SPECORD 250 (Carl Zeiss Jena) spectrophotometer at room temperature.

2.3. X-ray crystallography

Intensity data for structural analysis were collected by Bruker-Nonius KappaCCD diffractometer at 150 K, and the multi-scan absorption correction was applied by SADABS program [27]. The structures were solved by direct or charge-flipping methods using the programs SHELXT [28] or SUPERFLIP [29], and refined by the full-matrix least squares method on all F^2 data using the program or SHELXL (ver. 2015/1) [30]. Geometric analyses were performed using SHELXL. The structures were drawn using OLEX2 software [31].

The crystal structure of complex **4** shows positional disorders of both 4-methylsalicylate anions as well as ethanol ligand. The disordered 4-methylsalicylate anion of **4** has been modelled using SAME, EADP and RIGU commands. The crystal data and final parameters after refinement are summarized in Table 1. Selected atom distances and bond angles are given in Table 2.

2.4. EPR measurements

The first-derivative Cu(II) EPR spectra of polycrystalline copper(II) complexes (**1**–**4**) were measured on an EPR spectrometer EMX series (Bruker, Germany) operating at X-band (≈9.4 GHz) with 100 kHz field modulation in the standard TE_{102} (ER 4102 ST) rectangular cavity at room temperature. A special procedure was used for sample packing and precisely positioning the thin-walled quartz EPR tubes (Bruker) within the microwave cavity [32]. The experimental EPR spectra were processed using original Bruker software WinEPR [33]. The spin Hamiltonian parameter values, which were obtained from the experimental EPR spectra, were then further refined by computer simulation. The EPR spectra of: a) doublet-state systems ($S = 1/2$) were calculated using Bruker program SimFonia [34], whereas b) triplet-state systems ($S = 1$) were computed by an original program "Triplet" (A.Ozarowski, National High Magnetic Field Laboratory Florida, USA) [35].

3. Results and discussion

Four new green compounds have shown three different bonding modes of monoanion depending on the reaction conditions. The polymeric complex with 3,5-dibromsalicylate monoanion $[Cu(\mu\text{-}3,5\text{-}Br_2Sal)_2(H_2O)_2]_n$ **2** was prepared using 3,5-dibromosalicylic acid in water as solvent. The small change of condition (concentration of reactants, or solvent volume) and of course using

Table 1
Crystallographic data for **1**–**4**.

	MP249 ml	KS49 ml	MP276 ml	MP80 ml
Chemical formula	$C_{16}H_{18}CuO_{10}$	$C_{14}H_{10}Br_4CuO_8$	$C_{34}H_{36}Cu_2O_{14}\cdot 2(CH_4O)$	$C_{36}H_{40}Cu_2O_{14}$
M_r	433.84	689.40	859.79	823.76
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\overline{1}$	$P\overline{1}$
T/K	150(1)	150(1)	150(1)	150(1)
a/Å	14.6330(12)	32.417(7)	8.6920(7)	6.7560(4)
b/Å	3.7290(3)	4.5160(9)	10.1980(6)	11.0640(6)
c/Å	14.7880(15)	13.126(3)	10.9980(6)	12.4890(7)
α/°	90	90	70.426(4)	85.105(4)
β/°	96.575(6)	106.75(3)	89.352(5)	75.151(4)
γ/°	90	90	83.732(5)	87.164(5)
V/Å^3	801.62(12)	1840.2(7)	912.71(11)	898.70(9)
Z	2	4	1	1
λ (Mo–$K\alpha$)/Å	0.71,037	0.71,037	0.71,037	0.71,037
μ/mm^{-1}	1.422	9.914	1.240	1.252
Crystal size/mm	0.15 × 0.08 × 0.05	0.37 × 0.12 × 0.08	0.28 × 0.19 × 0.10	0.42 × 0.30 × 0.15
ρ_{calc}/g.cm^{-3}	1.797	2.488	1.564	1.522
S	1.048	1.059	1.114	1.083
R_1 [$I > 2\sigma(I)$]	0.0356	0.0279	0.0376	0.0292
wR_2 [all data]	0.0806	0.0612	0.0917	0.0758
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$/e Å^{-3}	0.38, −0.33	0.44, −0.80	0.32, −0.41	0.18, −0.19
CCDC	1,449,408	1,449,409	1,449,410	1,449,411