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Supramolecular structure formation of molecular copper(II)methylsalicylate complexes with nicotinamide or methylnicotinamide – Crystal structure and spectral properties

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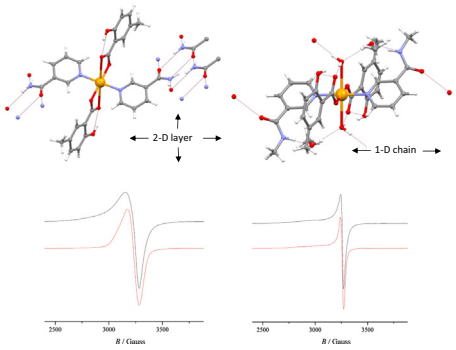
HIGHLIGHTS

- Four new molecular complexes prepared and characterized.
- X-ray diffraction, structure description and supramolecular structure.
- Complexes with nicotinamide form different 2-D supramolecular networks through H-bonds.
- Complexes with *N*-methylnicotinamide form 1-D supramolecular chains through H-bonds involving alcohol molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

As the systematic investigation of salicylatocopper complexes with nicotinamide derivatives the preparation, characterization and X-ray structure determination of four new molecular copper(II) complexes with *x*-methylsalicylate anion (*x*-Mesal$^-$) and nicotinamide (nia) or *N*-methylnicotinamide (mna) are reported. The molecular complexes $[Cu(5\text{-Mesal})_2(nia)_2]$ (**1**), $[Cu(3\text{-Mesal})_2(nia)_2]$ (**2**) build up 2-D supramolecular structures of different character. The ladder-type supramolecular structure of (**1**) is formed by the head-to-head H-bonds of neighbouring carboxamide groups, while the supramolecular structure of (**2**) is formed by N—H···O H-bonds of carboxamide groups into 1-D chain that are by the additional H—H···O H-bonds of N—H carboxamide and the carboxylate group oxygen atoms linked to 2-D layers. The centrosymmetrical crystal molecular structure of $[Cu(4\text{-Mesal})_2(mna)_2(H_2O)_2]\cdot 2EtOH$ (**3**) or $[Cu(5\text{-Mesal})_2(mna)_2(H_2O)_2]\cdot 2MeOH$ (**4**) are forming 1-D supramolecular chains that involve the methylcarboxamide N—H group, the crystalosolvate alcohol O—H group, the coordinated water molecule O—H bond and oxygen atom of neighbouring complex molecule. The coordination polyhedron symmetry corresponds with the isotropic character of EPR spectra of (**1**) and (**2**) while the EPR spectrum of (**4**) is of axial symmetry.

Introduction

Nicotinamide, (abbreviated as nia), is an essential for many metabolic processes as one form of the vitamin B_3 and is present

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in different types of food [1,2] and one of the nicotinamide major primary metabolite is 1-methylnicotinamide which together with nicotinamide-N-oxide, endogenously present in human plasma, both are potent anti-inflammatory agents [3]. Nicotinamide is frequently used by coordination chemists as ligand allowing them to prepare coordination compounds of the wide structural variety due to its three donor atoms of very different coordination ability. Moreover the carboxamide group represents a potential donor and acceptor for hydrogen bond formation and the nicotinamide as versatile reagent in crystal engineering of the supramolecular frameworks have been intensively studied [4–7]. On other hand, the reduction of the suitable carboxamide hydrogen atoms number by substitution with methylgroup has been already used for the comparative study in the case of nitrobenzoatocomplexes and it was shown that one amido hydrogen atom in *N*-methylnicotinamide (mna) enables 1-D structure formation in [Cu(4-NO_2bz)$_2$(mna)$_2$(H_2O)] while the extended 2-D structure were observed in [Cu(3,5-(NO_2)$_2$bz)$_2$(nia)$_2$(H_2O)] (where 4-NO_2bz and 3,5-(NO_2)$_2$bz are 4-nitrobenzoate and 3,5-dinitrobenzoate anion, respectively) [8].

Salicylic acid and its derivatives have been used for many years as anti-inflammatory, antipyretic and analgesic drugs [9–12]. The methyl- or methoxysalicylic acid derivatives are recently used for their antioxidant properties as active substances in some drugs [13,14].

In this paper, our attention is focused on molecular methylsalicylatocopper complexes with nicotinamide or metylnicotinamide their preparation, spectral and structural properties and supramolecular organization in relation to nitrogen donor atom ligand (nicotinamide and *N*-methylnicotinamide). We are presenting four molecular complexes of composition [Cu(5-Mesal)$_2$(nia)$_2$] (**1**), [Cu(3-Mesal)$_2$(nia)$_2$] (**2**), [Cu(4-Mesal)$_2$(mna)$_2$(H_2O)$_2$]·2EtOH (**3**) and [Cu(5-Mesal)$_2$(mna)$_2$(H_2O)$_2$]·2MeOH (**4**) (where *x*-Mesal = *x*-methylsalicylate anionic ligand).

Experimental

Preparation

Analytical grade (Aldrich, or Sigma) chemicals were used without further purification.

*Complex (**1**)*

Copper acetate (0.5 mmol) was dissolved in ethanol under stirring. The nicotinamide (1 mmol) was added under stirring to the reaction mixture and than it was followed by washing down the 3-methylsalicylic acid (1 mmol) with some amount of ethanol. The dark green product was filtered off, and the mother liquid was left to crystallize at ambient temperature. Blue crystals formed were separated and dried at room temperature. The obtained crystals were suitable for X-ray structure determination.

[Cu(5-Mesal)$_2$(nia)$_2$]

Anal Calc: C, 55.13; H, 4.29; N, 9.18. Found: C, 54.88; H, 4.21; N, 9.13.

*Complex (**2**)*

Copper acetate (0.5 mmol) was dissolved in ethanol and was left under vigorous stirring with nicotinamide (5 mmol) and then 3-methylsalicylic acid (1 mmol) was washed down to the reaction mixture with some amount of solvent. The green–blue product precipitated within few minutes, it was filtered off, and the mother liquid was left to crystallize at ambient temperature. Blue crystals formed, were separated and dried at room temperature. The obtained crystals were suitable for X-ray analysis.

[Cu(3-Mesal)$_2$(nia)$_2$]

Anal Calc: C, 55.13; H, 4.29; N, 9.18. Found: C, 55.13; H, 4.10; N, 9.17.

*Complex (**3**)*

N-methylnicotinamide (1 mmol) was added to an aqueous solution (5 mL) of copper acetate (0.5 mmol) and after few minutes 4-methysalicylic acid (1 mmol) was washed down with ethanol (about 20 mL). The reaction system was heated about one hour using water bath. The dark green precipitate was formed during heating, it was filtered off and the mother liquid was left to crystallize at room temperature. Green crystals were then separated and they were suitable for X-ray structure determination.

[Cu(4-Mesal)$_2$(mna)$_2$(H_2O)$_2$]·2EtOH

Anal Calc: C, 53.29; H, 6.05; N, 7.31.

*Complex (**4**)*

The complex was prepared similarly as above with 5-methylsalicylic acid and methanol as reactant and solvent, respectively.

[Cu(5-Mesal)$_2$(mna)$_2$(H_2O)$_2$]·2MeOH

Anal Calc: C, 52.60; H, 5.7; N, 7.91. Found: C, 52.00; H, 5.60; N, 7.66.

Apparatus and physical measurements

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 Plus (Carl Zeiss Jena) spectrophotometer at room temperature.

The EPR spectra were measured at room temperature in the polycrystalline form with a spectrometer Bruker EMX series operating at X-band (≈9.4 Ghz).

Crystallography

Data collection for single crystal crystallography and cell refinement were carried out using kappa-axis four-circle diffractometers Bruker Kappa APEXII (**2**) [15] or Bruker-Nonius KappaCCD (**1**,**3** and **4**) [16] with graphite monochromated Mo Kα radiation. The diffraction intensities were corrected for Lorentz and polarization factors. The structures were solved by the direct methods with SHELXT [17] or SIR-2011 [18], and refined by the full-matrix least squares procedure with SHELXL [17] (version 2014/6) or CRYSTALS [19] (version 14.60 using SHELX weighting scheme). The semi-empirical absorption corrections were made by multi-scans methods using SADABS [15]. Geometrical analysis were performed using SHELXL or CRYSTALS and the structures were drawn using the OLEX2 [20] programs. Final crystal data and structure refinement parameters are given in Table 1. The selected bond distances are given in Tables 2 and 3.

The positions of all hydrogen atoms have been constrained for all compound using AFIX (SHELXL) or RIDE (CRYSTALS) commands. Discrete positional disorder of the 5-methylsalicylate ligand [C9A–C15A/O4A] and [C9B–C15B/O4B] (methyl group, hydroxyl group and benzene ring) of **3** is observed with site occupancy factors 0.584(7) and 0.416(7), respectively. The disordered groups of **3** are restrained using AFIX66/AFIX65 (benzene rings), SADI and EADP commands of SHELXL program. The carboxamide group of **2** is also disordered in two discrete positions for oxygen atom [O3A] and [O3B] with site occupancy factors 0.31(6) and 0.69(6), respectively.