

Preparation, Characterization and Photoreactivity of Methyl- and Methoxysalicylatocopper(II) Complexes

Zuzana Repická, Mário Izakovič, Milan Mazúr¹, Jozef Šima, Dušan Valigura

Department of Inorganic Chemistry, FCHPT STU, Radlinského 9, 812 37 Bratislava

¹*Department of Physical Chemistry, FCHPT STU, Radlinského 9, 812 37 Bratislava*

zuzana.repicka@stuba.sk

Abstract

The synthesis and characterization of complexes of stoichiometry $\text{Cu}(\text{Xsal})_2(\text{H}_2\text{O})_2$ for $\text{X} = 3\text{-MeO}$ and 4-MeO and $\text{Cu}(\text{Xsal})_2(\text{H}_2\text{O})$ for $\text{X} = 3\text{-Me}$ and 4-Me (where $3\text{-MeOsal} = 3\text{-methoxysalicylate}$, $4\text{-MeOsal} = 4\text{-methoxysalicylate}$, $3\text{-Mesal} = 3\text{-methylsalicylate}$ and $4\text{-Mesal} = 4\text{-methylsalicylate}$) are reported. The composition of all complexes has been determined by elemental analysis and their ligand coordination mode and stereochemistry have been determined by electronic, infrared and EPR spectroscopy. The photoreactivity of prepared complexes in DMSO (DMSO = dimethylsulfoxid) solutions at room temperature have been studied too. For complexes of composition $\text{Cu}(4\text{-MeOsal})_2(\text{H}_2\text{O})_2$ and $\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$ some spectral changes registered after irradiation with light ($\lambda_{\text{irr}} = 366 \text{ nm}$).

Keywords: copper complexes, salicylato ligand, EPR spectra, molecular structure, photoreactivity

Introduction

A great number of copper(II) complexes with various organic ligands have been a subject of intense study because of their biomedical activities, chemical and industrial versatility. It is well known, that in some cases copper(II) complexes could exhibit better biological activity, in comparison to their components (Ranford 1993), e.g. copper(II) aspirinate complex is a more effective anti-inflammatory agent than aspirine itself (Greenaway 1984, Sorenson 1978), or the copper complex of 3,5-dimethylpyrazol exhibits greater antimicrobial activity (tested on *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*) than 3,5-dimethylpyrazol (Sokolík 1998). Moreover, some by their constituents very similar complexes

exhibit very different antimicrobial activity (Vasková 2009) so the systematic approach to preparation and biological activity test is needed. Prevailing number of biological applications is somehow connected with solutions and that is the reason for obtaining information about equilibria (Szabo-Planka 2008, Šípoš 2008) and/or about photochemical reactivity/stability of such systems. In this paper we presents preparation and spectral properties of four new methyl- or methoxysalicylates of copper(II). Stemming from the known ability of Cu(II) compounds to undergo spontaneous, electrochemical and photochemical redox processes, part of the work was focused to follow photochemical reactivity of the investigated complexes.

Experimental

Preparation

Salicylatocopper(II) complexes under study were prepared by the reaction of an aqueous solution of copper(II) acetate (1 mmol) with appropriate methyl-, or methoxy-salicylic acid (2 mmol) in water ($V = 30 \text{ cm}^3$). The reaction mixture was stirred until the reaction finished and the color of products remains unchanged. The precipitated product was filtered off and mother liquid was left to crystallize at ambient temperature.

Anal. of $\text{Cu}(3\text{-MeOsal})_2(\text{H}_2\text{O})_2$ Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_{10}\text{Cu}$: Cu, 14.65; C, 44.30; H, 4.18 %.

Found: Cu, 14.56; C, 44.34; H, 4.22 %.

Anal. of $\text{Cu}(4\text{-MeOsal})_2(\text{H}_2\text{O})_2$ Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_{10}\text{Cu}$: Cu, 14.65; C, 44.30; H, 4.18 %.

Found: Cu, 14.68; C, 44.62; H, 4.29 %.

Anal. of $\text{Cu}(3\text{-Mesal})_2(\text{H}_2\text{O})$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_7\text{Cu}$: Cu, 16.56; C, 50.07; H, 4.20 %.

Found: Cu, 16.01; C, 50.53; H, 4.51 %.

Anal. of $\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_7\text{Cu}$: Cu, 16.56; C, 50.07; H, 4.20 %.

Found: Cu, 16.43; C, 50.56; H, 4.55 %.

Photolysis

The steady-state photolysis with monochromatized radiation ($\lambda = 366 \text{ nm}$) was carried out in 130 cm^3 DMSO solutions ($c = 0.007 \text{ mol dm}^{-3}$) at $20 \text{ }^\circ\text{C}$. Progress of the photolysis was monitored by UV – VIS spectrophotometry in 1cm cells before irradiation and after 2 min., 4 min., 6 min., 8 min., 10 min., 15 min. and 20 min. of irradiation.

Apparatus and equipment

Analysis for carbon and hydrogen contents were carried out on a CHNSO FlashEA™ 1112 Automatic Elemental Analyzer. Copper was determined by electrolysis of water solution obtained by sample mineralization with a mixture of sulphuric 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 (4000 – 400 cm⁻¹) were measured with a Nicolet 5700 FT-IR spectrometer using ATR techniques.

EPR spectra of powdered sample were recorded at room temperature on the spectrometer Bruker ESP 300, operating at X-band equipped with an ER 035M Bruker NMR gaussmeter and a HP 5350B Hewlett Packard microwave frequency counter. Photolysis was carried out in a three-compartment temperature-controlled (20 ± 1 °C) quartz photoreactor equipped with a high-pressure 150 W Hg-lamp (Applied Photophysics). Radiation of the lamp was monochromatized using a solution filter. The intensity of the incident radiation was determined using ferrioxalate actinometry (Šima 2002).

Results and Discussion

In spite of the same synthesis procedure described above, two stiochiometrically different types of product were obtained: Cu(X-sal)₂(H₂O)₂ for X = 3-MeO, 4-MeO, and Cu(X-sal)₂(H₂O) for X = 3-Me, 4-Me. All prepared complexes, prior to photolysis, were studied in solid state by spectral techniques.

Solid state properties of complexes

Both types of complexes differing in their Cu(II) : H₂O molar ratio were analysed separately.

Methoxysalicylatocopper(II) complexes Cu(X-sal)₂(H₂O)₂

The composition of studied complexes has been determined by elemental analysis, the results are presented above. The found stoichiometry suggests that the bonding mode of salicylato and water ligands needs to be analyzed to evaluate the mode of coordination of salicylato ligands. The information concerning the carboxylate bonding mode (Nakamoto 1997) are provided by $\Delta\nu(\text{COO}^-)$ – the difference between the antisymmetric stretch $\nu_{\text{as}}(\text{COO}^-)$ and symmetric stretch $\nu_{\text{s}}(\text{COO}^-)$. The IR spectra of this group of complexes are very similar and contain the bands attributed to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ at about 1604 cm^{-1} and 1441 cm^{-1} , respectively (Table 1). So, the differences $\Delta\nu(\text{COO}^-)$ for these complexes are much smaller than $\Delta\nu(\text{COO}^-)$ for the ionic form (Repická 2010), and that is consistent with bidentate chelating bonding mode of the carboxylate group. The hydroxo oxygen atoms do not form the bonds to the central atom. The broad complex bands in the region of OH vibrations ($3500 - 3100\text{ cm}^{-1}$) that are very similar for this group of complexes are symptomatic for the presence of coordinated water molecules in the complex molecule together with the O–H groups of salicylato ligands. The absence of bands at about 1750 cm^{-1} supports the conclusion that water molecules are coordinated too.

Table 1. Wavenumbers (cm^{-1}) of the (COO^-) stretches and the Δ values for the methoxysalicylatocopper(II) complexes, solid state electronic spectra (nm) and EPR spectra.

Compound	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\lambda (d \leftarrow d)$	g_i
Cu(3-MeOsal) ₂ (H ₂ O) ₂	1603	1442	161	696	2.10
Cu(4-MeOsal) ₂ (H ₂ O) ₂	1605	1440	165	657	2.10

The solid state UV electronic spectra of salicylatocopper(II) complexes under study exhibit intraligand (250 – 300 nm) and LMCT (300 – 350 nm) bands. In the ligand field region broad asymmetric absorptions bands with maximum in the range of 696 – 657 nm are present. This type of $d \leftarrow d$ transitions are typical (Lever 1984) for tetragonal bipyramidal arrangement around Cu(II) (Table 1.).

The EPR spectra of powdered samples measured at room temperature are of pseudoisotropic symmetry (Table 1.) (Hathaway 1970). This type of spectra suggests of a strong dipole – dipole interactions between unpaired electrons of neighbouring molecules.

All data given above are in good agreement with proposed tetragonal bipyramidal donor atoms organization of central atom.

Methylsalicylatocopper(II) complexes $Cu(X-sal)_2(H_2O)$

According to the composition determined by elemental analysis the presented pair of complexes differs from the group above. In spite of the identical stoichiometry, the results of used spectral methods indicated that these two complexes differ one from the other. The character of EPR spectrum of powdered samples of $Cu_2(3-Mesal)_4(H_2O)_2$ complex measured at room and liquid nitrogen temperatures are typical of paddle-wheel carboxylate type (Hathaway 1970) (Fig. 1) with bidentate bridging carboxylato group.

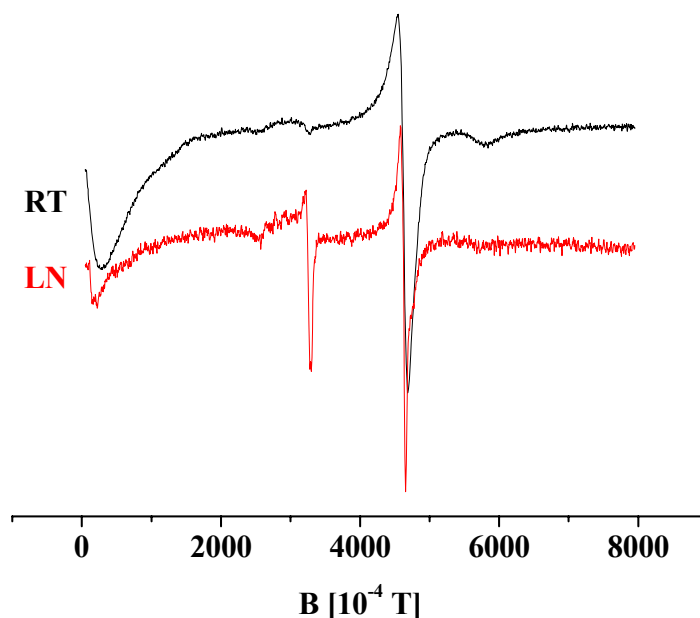


Fig. 1. Cu(II) EPR spectrum of complex $Cu_2(3-Mesal)_4(H_2O)_2$ measured at room and liquid nitrogen temperature

The difference between antisymmetric $\nu_{as}(COO^-)$ and symmetric vibrations $\nu_s(COO^-)$ (Table 2.) (Nakamoto 1997) supports this conclusion. The broad band localized in the region about 3200 cm^{-1} is in good agreement with presence of coordinated water molecules in dimeric complex. Finally, it could be concluded that all used spectral techniques for this complex are in good agreement with the $[Cu_2(3-Mesal)_4(H_2O)_2]$ formula.

Table 2. Wavenumbers (cm^{-1}) of the (COO^-) stretches and the Δ values for the methylsalicylatocopper(II) complexes, solid state electronic spectra (nm) and EPR spectra.

Compound	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\lambda (d \leftarrow d)$	g_i
$\text{Cu}(3\text{-Mesal})_2(\text{H}_2\text{O})$	1618	1440	178	699	2.10
$\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$	1610	1440	170	660	

The complex $\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$ is monomeric with probable square pyramidal Cu(II) coordination environment. The separation between the antisymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_{\text{s}}(\text{COO}^-)$ stretch (Table 2.) is consistent with assumed bidentate chelating bonding mode of the carboxylate group. The atypical width of (COO^-) bands could indicate slight difference in bonding of both salicylato anions – different distances of semicoordinated oxygen atoms (Vasková 2010).

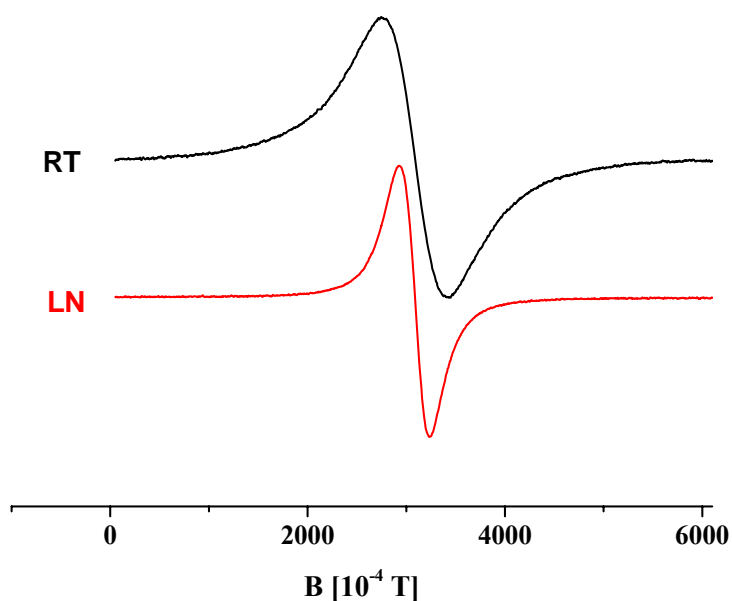


Fig. 2. Cu(II) EPR spectrum of complex $\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$ measured at room and liquid nitrogen temperature

The EPR spectra of powdered samples measured at room and liquid nitrogen temperature are of pseudoisotropic symmetry (Fig. 2.) (Hathaway 1970), which indicate strong dipole-dipole interactions between unpaired electrons of neighbouring molecules.

The solid state electronic spectra of both discussed complexes exhibit a broad asymmetric ligand field band with a maximum at 699 nm and 660 nm, respectively. Similarly as in case of methoxyderivatives, there are also intraligand charge transfer bands (250 – 300 nm) and LMCT band in the range of 300 – 350 nm.

Photolysis

Upon irradiation at $\lambda_{\text{irr}} = 366$ nm the spectral changes were observed in the case of $\text{Cu}(4\text{-MeOsal})_2(\text{H}_2\text{O})_2$ (Fig. 3.) and $\text{Cu}(4\text{-Mesal})_2(\text{H}_2\text{O})$. After irradiation of other complexes $\text{Cu}(3\text{-MeOsal})_2(\text{H}_2\text{O})_2$, $\text{Cu}(3\text{-Mesal})_2(\text{H}_2\text{O})$ these changes were not observed.

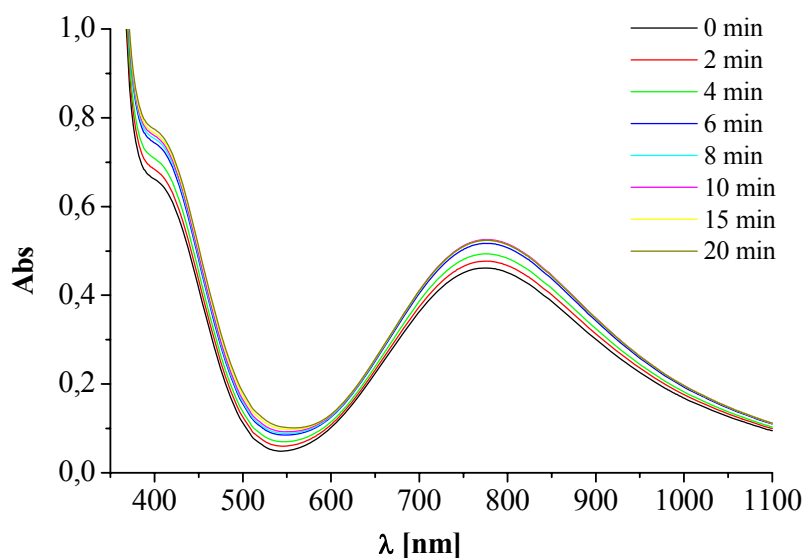


Fig. 3. Spectral changes during the photolysis at room temperature at $\lambda_{\text{irr}} = 366$ nm ($\text{Cu}(4\text{-MeOsal})_2(\text{H}_2\text{O})_2$)

At 366 nm irradiation of solutions of the mentioned complexes both IL and LMCT excited states are populated. As evidenced by time evolving spectral changes, the main deactivation modes are of photophysical nature. The observed absorbance increase in the entire monitored spectral region can be tentatively attributed to two chemical processes. One of them may lie in a shift in the equilibrium of Cu(II) species present in irradiated solutions in the direction to those characterized by a more intensive absorption of radiation (e.g. dimer – monomer equilibria). The other mode is photosubstitution of H_2O for DMSO molecule(s) yielding complexes with higher molar absorption coefficient in the visible region. Photoreduction of

Cu(II) to Cu(I) can be excluded based on the fact that the intensity of the LF bands did not decrease (in Cu(I) species no LF transitions are possible).

Acknowledgement

Financial support was provided by the Slovak Grant Agency (VEGA Grant No. 1/0353/08) and 1/0575/08).

References

- Greenaway FT, Pezesbk A., Gordes AW, Noble MC, Sorenson JRJ (1984) *Inorg. Chim. Acta* 93: 67-71
- Hathaway BJ, Billing DE (1970) *Coord. Chem. Rev.* 5: 143-207
- Lever ABP (1984) *Inorganic Electronic Spectroscopy* (2nd Ed.), Elsevier, Amsterdam
- Nakamoto K (1997) *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B* (5th Ed.), Willey, New York
- Ranford JD, Sadler PD, Tocher DA (1993) *J. Chem. Soc. Dalton Trans.:* 3393-3399
- Repická Z (2010) PhD Thesis, FCHPT STU Bratislava
- Sokolík J, Blahová M, Cukanová G, Kohútová M, Mišíková E, Mlynarčík D (1998) *Čes. Slov. Farm.* 47: 186-188
- Sorenson JRJ (1978) *Progr. Med. Chem.* 15: 211-260
- Szabo-Planka T, Gyurczik B, Nagy NV, Rockenbauer A, Šípoš R, Šima J, Melník M. (2008) *Journal Inorg. Biochem.* 102: 101-109
- Šima J, Brezová V (2002) *Coord. Chem. Rev.* 229: 27-35
- Šípoš R, Szabo-Planka T, Rockenbauer A, Nagy NV, Šima J, Melník M, Nagypal I. (2008) *Journal. Physical Chem.* 112: 10280-10286
- Vasková Z, Stachová P, Krupková L, Hudecová D, Valigura D (2009) *Acta Chimica Slovaca* 2: 77-87
- Vasková Z, Moncol' J, Korabik M, Valigura D, Švorec J, Lis T, Valko M, Melník M, (2010) *Polyhedron* 29: 154-163