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Article

THE SYNTHESIS AND STUDY OF SOME COMPLEXES OF METHYLENEDISALICYLIC ACID

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ABSTRACT

The aim of this paper is the synthesis and characterization of the methylenedisalicylic acid (MDSA) and its complexes with Cu^{2+}, Pb^{2+} and Ag^{+}. In order to study these four compounds, the FT-IR spectrometry and thermal methods of analysis were used. The results of this study indicated different behaviors between these three cations, as expected according to their electronic structure and oxidation numbers.

Keywords: methylenedisalicylic acid, MDSA, complexes, study, characterization

1. INTRODUCTION

The coordination chemistry has become a field of high interest due to its wide range of possible applications. Metal complexes are used successfully in medicine, as active components of a variety of drugs [1]. Recently, researches were conducted using all the metals in the Periodic Table, with coordination numbers varying from 2 to 12. The new synthesis methods and physical methods for the study of structure have played an important role in the development of this branch of chemistry. The importance of catalysts and the role of metals in biochemistry have attracted the researchers' interest in towards the study of metal complexes [2].

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There are several studies presented in the literature involving the synthesis of methylenedisalicylic acid but all of them describe the same method for this synthesis: treatment of salicylic acid with formaldehyde using 40% sulphuric acid [3,4,6]. In this ligand there are two active groups: hydroxyl and carboxyl and this may be expected to act as a multidentate ligand [3]. But the presence of the inactivating CH_2-group can cause steric effects. Ahmed et al. stated that the structure of the methylenedisalicylic acid (MDSA) can consist of two salicylic acid molecules joined by a methylene bridge in the ortho- position [6].

Over the years, studies were conducted on methylenedisalicylic acid, as a ligand in complexes [5-7]. The reported metals used in the literature were rare earths (M= La, Ce, Pr, Nd, Sm, Gd, Ho, Yb, or Y) [5] and transitional metals (M= Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Fe(II), Fe(III)) [6]. Some of these studies revealed biological activity for some of the samples, illustrating a possible application as antimicrobial agents in medicine [6].

2. MATERIALS AND METHODS

2.1. Methods

The synthetized compounds were analyzed using the coupled techniques: TG-DTG-DTA, UATR (Universal Attenuted Transmitance Reflectance). These were assembled by a physical coupling of the two Perkin-Elmer units' software: a Diamond thermobalance and a Spectrum 100 FT-IR spectrometer.

2.2. The synthesis of the ligand

The ligand, MDSA, was prepared according to the literature [6], using the following: 13.8 g salicylic acid, 4.8 g formaldehyde (30% concentration) and 90 g sulphuric acid (50% concentration). The mixture was refluxed for 8 hours. Then the compound was cooled, filtered, washed with cold water and ethanol to remove any salicylic acid in excess. Afterwards, MDSA was recrystallized from acetone and a pale pink powder was obtained.

2.3. The synthesis of the complexes

The MDSA complexes were prepared using ethanolic solutions of MDSA (0.005 moles) with the following metal salts: Cu(II) and Pb(II) acetates and silver nitrate, $AgNO_3$ (0.01 moles). The compounds were refluxed for 1-2 hours, then they were filtered while still warm, washed with ethanol and dried in air [6].

3. RESULTS AND DISCUSSIONS

3.1. Solubility

The solubility of the synthetized complexes and ligand was determined using some common solvents. The results presented in Table 1 indicate that the MDSA is soluble in all the solvents that were used, while the complexes of MDSA with Cu^{2+}, Pb^{2+} and Ag^{+} are slightly soluble in methanol, ethanol and dimethylformamide (DMF) and insoluble in the other solvents.

Table 1: The solubility of the ligand and the complexes in different solvents

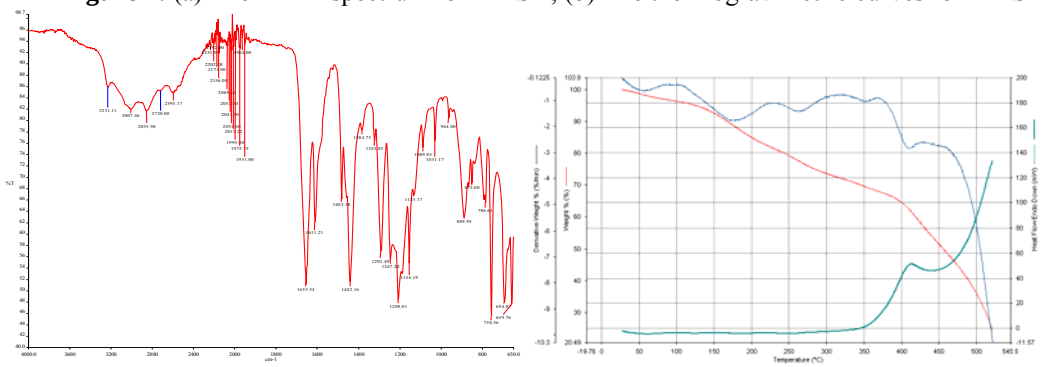
Compound	MeOH	EtOH	BuOH	Acetone	Ethyl acetate	DMF	Benzene	p-xylene
MDSA	S	S	S	S	S	S	S	S
Cu-MDSA	SS	SS	IS	IS	IS	SS	IS	IS
Pb-MDSA	SS	SS	IS	IS	IS	SS	IS	IS
Ag-MDSA	SS	SS	IS	IS	IS	SS	IS	IS

S = soluble, SS = slightly soluble, IS = insoluble

3.2. The study of MDSA

The FT-IR studies on the ligand suggested that the synthesis of MDSA was successful. Characteristic peaks are present in the spectrum: the C=O peak (in the carboxyl group) at 1655 cm^{-1} and the C=O stretch and in plane OH bending (specific for the COOH group) at 1442 cm^{-1} and 1292 cm^{-1} (Figure 1a). The results also indicate that two isomers of MDSA were obtained, due to the peaks for 1, 2, 3- and 1, 2, 4 - trisubstituted aromatic compounds at 1156 cm^{-1} and 1209 cm^{-1} respectively.

Figure 1: (a) The FT-IR spectrum for MDSA; (b) The thermogravimetric curves for MDSA



(a) (b)

The thermogravimetric studies for MDSA present the decomposition of the ligand between 25 and 530ºC in many steps, which can be hardly separated on the TG (Weight) and DTA (Heat flow) curves, but separable on the DTG (Derivative Weight). On the DTG curve,

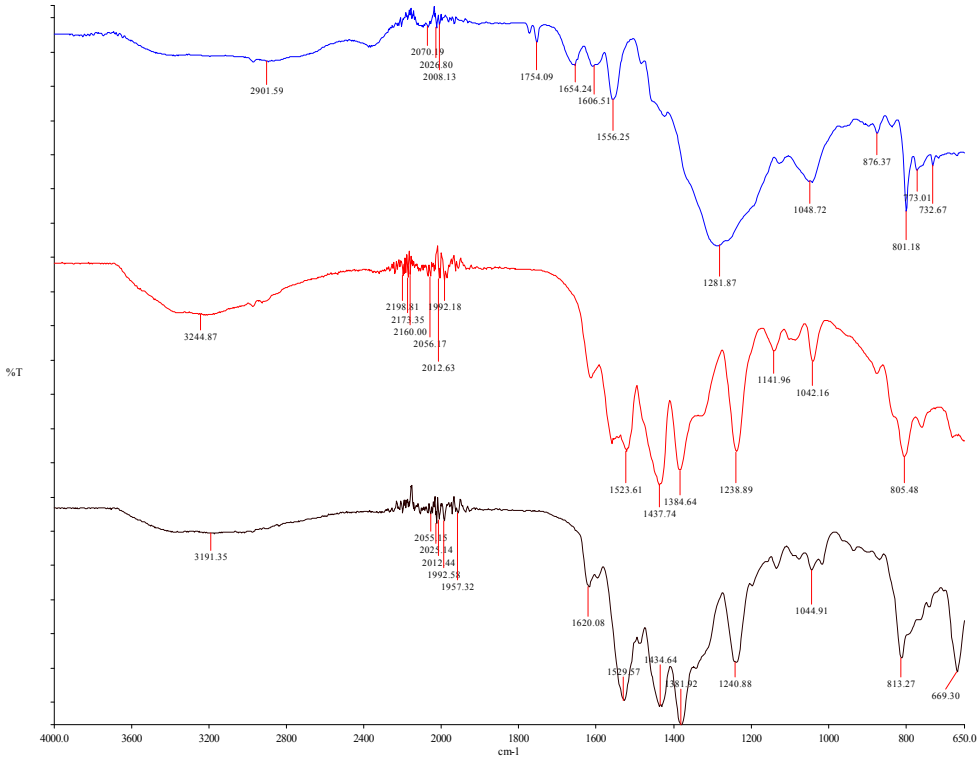
there are 6 maximums in the analyzed temperature interval (Figure 1b). The first four steps have very weak thermal effects, while the last two steps are exothermic processes. The first decomposition steps are due to the loss of the crystallization water and humidity. The last decomposition step does not end in the temperature interval that was studied.

3.3. The study of the three complexes

After the comparison of the FT-IR spectra of the MDSA and the metal complexes, specific peaks appeared for the carboxylate ion (around 1385 cm^{-1}) and for the bonded phenolic OH group (around 3150 cm^{-1}). The peak for the carboxyl group (C=O) around 1655 cm^{-1} disappeared, a first sign of the success of the reaction.

The comparative analysis of the FT-IR spectra for the three coordination compounds shows a similarity between the Cu^{2+} and Pb^{2+} complexes and a different coordination for the Ag^{+} complex.

Figure 2: The comparison of the FT-IR spectra for Ag-MDSA (blue), Cu-MDSA (red) and Pb-MDSA (black)



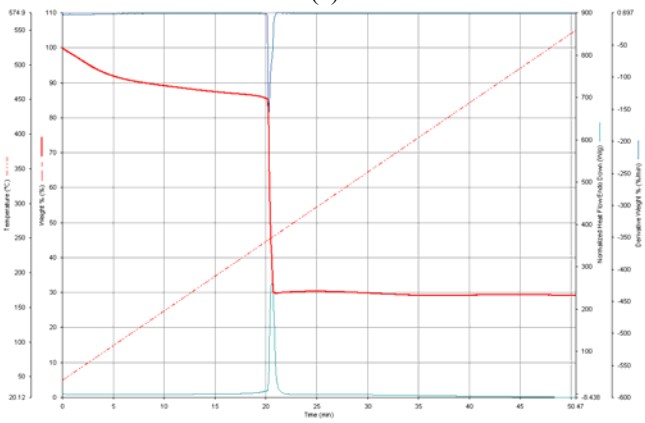
The thermogravimetric studies for the Cu^{2+} complex were conducted between 25 and 500ºC with a heating rate of 10ºC/min, in air atmosphere. The Cu-MDSA complex had two decomposition steps: the first, between 45 and 242ºC, due to the loss of two molecules of crystallization water and the second step, between 242 and 253 ºC, representing the decomposition of the complex, when the metal-complex bond was broken (Figure 3a).

The results of the TG studies for the Pb-MDSA complex were quite similar to the Cu^{2+} compound.

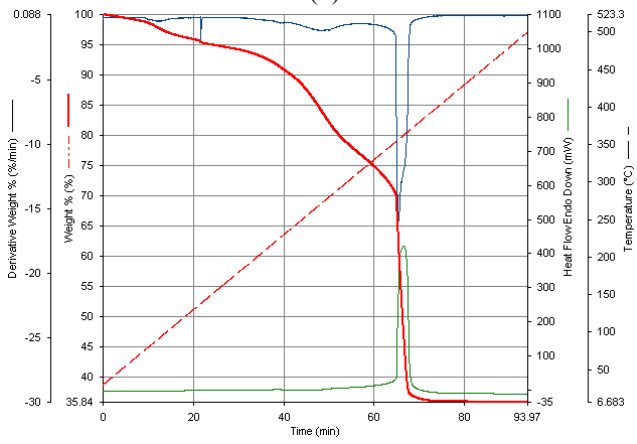
The results for the Ag^{+} complex were slightly different from the first two complexes. The thermogravimetric analysis was conducted between 25 and 523ºC, with a heating rate of 5ºC/min. A lower heating rate was necessary in order to separate some of the decomposition processes. This complex had four decomposition steps. The difference is the fact that Ag-MDSA has four interior coordination water molecules and the exothermic process appeared at a temperature higher with 100ºC than the others. This suggests a stronger metal-ligand bond (Figure 3b). The thermal effects of the decomposition reaction for the three complex compounds vary in the following order: Pb-MDSA < Ag-MDSA < Cu-MDSA and the thermal stability varies as following: Cu-MDSA < Pb-MDSA < Ag-MDSA.

Figure 3: The thermogravimetric curves for (a) Cu-MDSA and (b) Ag-MDSA

(a)



(b)



4. CONCLUSION

The purpose of this paper was the synthesis of the methylenedisalicylic acid (MDSA) and some complex compounds with Cu^{2+}, Pb^{2+}, Ag^{+}. This ligand and its complexes were analyzed using FT-IR spectrometry and thermogravmetric analysis. The results indicate that these synthesis reactions were successful.

A different behavior can easily be noticed between the Cu^{2+} and Pb^{2+} cations and Ag^{+} from the FT-IR spectra, as well as from the thermoanalytical curves for the three compounds. This was expected to happen due to the electronic structure and the oxidation numbers of the three cations. For Cu^{2+} and Pb^{2+} complexes, an octahedral geometry is expected, however Ag^{+} usually prefers a linear geometry. Therefore, it can be deducted that $[Ag_2(MDSA\text{-}4H)\cdot(H_2O)_4]\cdot 2H_2O\cdot(NO_3^-)$ has four molecules of water in the interior coordination sphere, as well as two molecules in the exterior sphere of coordination. In contrast, the other two complexes, $[Cu_2(MDSA\text{-}4H)]\cdot 2H_2O$ and $[Pb_2(MDSA\text{-}4H)]\cdot 5H_2O$ present coordinated water molecules only in the exterior coordination sphere.

These studies will be continued in the future with other investigation methods to assure the stability and the geometry of these complex compounds.

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