COORDINATION COMPOUND OF CU(II) WITH N,N'-BIS(SALYCILIDENE) – METHYLENEDIAMINE(SALMEN)

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The bis-Schiff base, N, N' (salicylidene)-methylenediamine, known as Salmen, forms together with Cu (II) at pH=4.5 a dark green precipitate, which is stable at room temperature. The Salmen was utilized as solution, in an ethylic alcohol-water medium (1:1, v:v) while the Cu (II) - as a fresh, aqueous solution of $CuCl_2$. The complex is insoluble in the reaction medium and was separated by filtering.

The compound was studied by chemical analysis, IR-absorption spectra, ESR spectroscopy and thermal analysis. Chemical analysis showed that the precipitation formed is a complex and the combination rate of M: L is 1:1.The IR spectra were recorder between 200 cm^{-1} and 4000 cm^{-1} using a spectrometer FTIR 660 Plus by the method of KBr pelleting. The ESR spectra were recorder on solid samples with RES-IFA Bucharest spectrometer. Intensity of magnetic field was 3216.9 Gauss at 9030 MHz frequency. ESR spectra evidenced one odd electron in inner coordination sphere compound being paramagnetic. Thermal stability of the complex was studied with MOM Budapest Q-1500D derivatograph to 1000^oC. Until 70^0C, complex is stable but between 70^0C-280^0C there are two loss masses. One corresponding waters molecules loss and the last corresponding thermal degradation complex until copper oxide. Up to 280^oC, the decomposition product is stable from thermal point of view. Based on experimental data and literature indications the structural formula of this compound is assigned. Hybridization of copper ion is dsp^2 type and the space configuration is square plane, with two coordination liaisons from both nitrogen atoms and two covalent liaisons between copper ion and oxygen atoms.

***Keywords**: Cu(II), Salmen, coordination compound, ESR, IR, thermal analysis.*

The bis-Schiff bases of the o-hydroxycarbonylic compounds are employed in the complexation of transitional metals cations, however all bases discussed in literature possess- between the two nitrogen atoms a hydrocarbonated chain with at least two carbon atoms [1,2]. A bis-Schiff base, N,N'-bis(salicylidene)-methylenediamine, Salmen has been synthesized and further utilized for the obtaining of a complex combination with Co(II), for the reversible fixing of the molecular oxygen[1].

In order of increasing the utilization of Salmen, their complexation capacity towards certain metallic ions has been tested, the first results obtained permitting the conclusion of its possible application as an analytical agent of precipitation for Cu(II), Zn(II), Mn(II), Pd(II), Cr(III), U(VI) and Ni(II).

The present study discusses the results obtained in the characterization of the precipitation form Cu (II) with Salmen and their thermal stability.

MATERIAL AND METHOD

Salmen was obtained through condensation of salicylic aldehyde with ammonia, in the presence of formic aldehyde [2]. In the reaction between Salmen and Cu (II) at pH= 4.5 results a dark green precipitate which is stable in time, at room temperature. The Salmen was utilized as solution, in an ethylic alcohol-water medium (1:1, v:v) while the Cu (II) - as a fresh, aqueous solution of $CuCl_2$.

The synthesis of the presented compound was accomplished by mixing and stirring two solutions at room temperature for 90 minutes. The 100 mL solutions presented both the concentration of 0.1M. The first solution contained $CuCl_2$ -water and the second is Salmen in ethylic alcohol – water (1:1, v: v).

The obtained compound presented dark green colour, insoluble in the reaction medium and was separated by filtering and was washed in a mixture of ethylic alcohol – water (1:1, v:v). Then it was dried at 105^0C temperature till constant weight. The reaction yield in the mentioned conditions is 100%.

RESULTS AND DISCUSSIONS

Elementary analysis

The results of chemical analysis of reaction product are presented in table 1, where the calculated values are in concordance with experimental found values.

Table 1

The elementary analysis, colour and molecular formula of the complex compound

Compound	Formulae	Calculated values (%)				Found values (%)				Yield (%)
		Cu	C	H	N	Cu	C	H	N	
Cu-Salmen	$C_{15}H_{12}O_2N_2Cu$	20.25	56.96	3.79	8.86	20	55.7	2.83	8	100

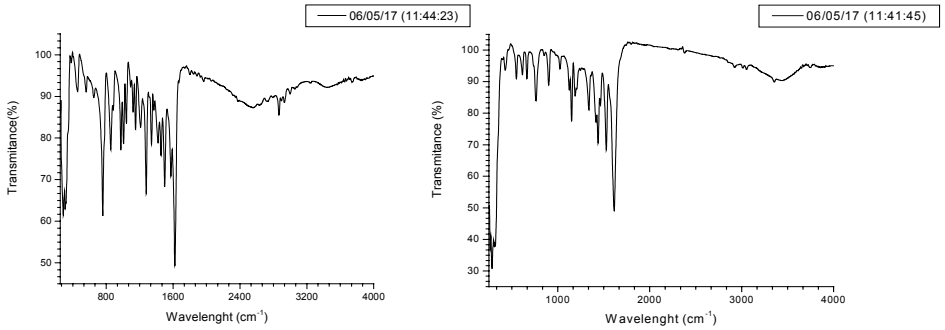
The IR-absorption spectra

The IR spectra of free ligand Salmen and of complex compound of Cu (II) with Salmen have been recorded in the 200-4000 cm^{-1} domain on a spectrometer FT IR 660 Plus, by the method of KBr pelleting.

The IR spectra have been correlated between Salmen and complex compound with Salmen.

In the ligand's IR spectrum, a peak at 1630 cm^{-1} may be observed, due to the C=N valence vibration, which may be also found in the spectrum of the precipitation form at 1610 cm^{-1}, although with a weaker intensity- which suggests the involvement of the nitrogen atom from the >C=N group in the process of coordination. The higher modification, comparatively with the ligand, appears at

the band from the 3300-3600 cm^{-1} domain, attributed to the –OH phenolic group. Lowering of the intensity if this band in spectrum of the precipitation form indicates involvement of the –OH group in the reaction of complexation. More than that, in the complex spectrum there appears a peak at 592 cm^{-1}, which may be attributed to the M-N bond, and another at 530.42 cm^{-1} attributed to the M-O bond, in according with the literature data [5-7].



a. **b.**

Figure 1. **The IR spectrum of the free ligand-Salmen (a) and of the complex compound Cu-Salmen (b)**

The IR – absorption spectra justified the fact that oxygen and nitrogen atoms of ligand are bonded to the central atom Cu (II).

The ESR spectra

The ESR spectrum of the studied compound was recorded for solid samples with an I.F.A. – Bucharest spectrometer. From experimental data, the paramagnetic properties of the studied compound were determined. This fact confirmed that the central atoms of Cu(II) have one odd electron , resulting that the hybridization type is ,, dsp^2''.

Based on the ESR spectra data and chemical analysis of the Cu (II)-Salmen complex, the following structure was proposed: [8-10]

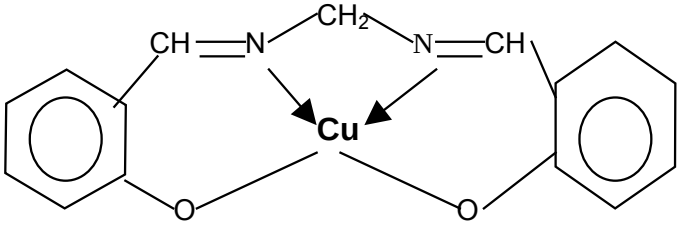


Figure 2. **The structure of the Cu (II)-Salmen complex**

Thermal analysis

Thermal stability of Cu-Salmen complex was studied with MOM Budapest Q-1500D derivatograph to $1000^{O}C$. Sensitivity of thermobalance was 100, rate of

heating 10^0C/min and recorder sensitivities were: T=500 μV, TG=500 μV, DTG=2.5 mV. The loss mass and the rate of loss mass are presented in figure 3.

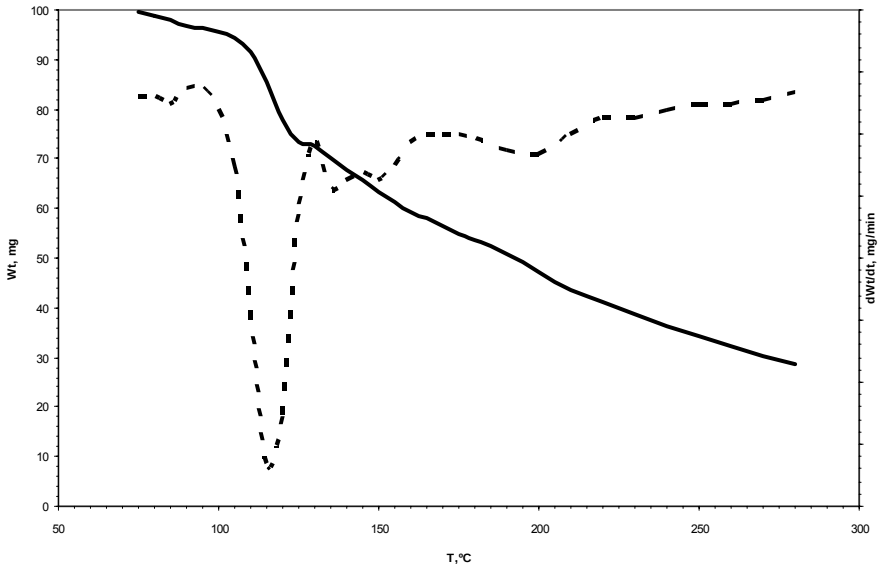


Figure 3. **Thermogram of the Cu (II)-Salmen complex (TG-uninterrupted line, DTG-interrupted line)**

Until 70^0C, complex is stable but between 70^0C-130^0C there is a loss mass corresponding *n* water molecules (where *n* is about seven). In this domain of temperatures take place the following chemical decomposition:

$$C_{15}H_{12}O_2N_2Cu \cdot nH_2O \xrightarrow{70^oC-130^oC} C_{15}H_{12}O_2N_2Cu + nH_2O$$

Other loss mass take place between 130°C and 280°C, corresponding formation of copper oxide:

$$C_{15}H_{12}O_2N_2Cu \xrightarrow{130^oC-280^oC} CuO + \text{volatile}$$

Up to 280°C, the decomposition product is stable from thermal point of view.

In table 2 it presents both theoretical and practical loss mass in weight percentages.

Table 2

Domains of decomposition temperatures, theoretical and practical loss mass, relative errors for Cu (II)-Salmen complex

Stage	Domain of temperature, °C	% Loss mass		ε%=100(%Wp-%Wt)/%Wt
		Theoretical, %Wt	Practical, %Wp	
I	70°C-130°C	28.54	28.44	0.35%
II	130°C-280°C	74.80	72,36	3.26%

CONCLUSIONS

Salmen reacts with Cu (II) at pH= 4.5 and result a dark green complex, insoluble in water, with formula $C_{15}H_{12}O_2N_2Cu$. A method for synthesis was elaborated, based a reaction between Cu (II) salt and Salmen. The precipitate is thermal stable to 280^oC and present one odd electron.

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