NEW COORDINATION COMPOUND OF MN(II) WITH LIGAND DERIVED FROM MORPHOLINE-4-CARBODITHIOIC ACIDS

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The synthesis and characterization of some new complex of Mn (II) with organic ligands derived from morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester is reported in this paper. The morpholine-4-carbodithioic acid 2-(3, 5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester was utilized as solution, in an ethylic alcohol-water medium (1:1, v: v) while the Mn (II) as a fresh aqueous solution of $MnCl_2.4H_2O$. . The complex is insoluble in the reaction medium and was separated by filtering.

Elemental analysis, ESR, FTIR spectroscopy and thermal analysis performed the characterization of this complex compound. 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. Study of the IR spectra evidenced the functional groups of complex and the chemical analysis showed that the combination rate of M:L is 1:2 $(C_{13}H_{12}O_3S_2NI_2)_2Mn$. 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 five odd electrons in inner coordination sphere compound being paramagnetic.

The obtained precipitate was submitted thermogravimetric analysis using MOM Q -1500D derivatograph to 1000^OC. Until 85^0C, complex is stable but between 85^0C-270^0C there are three loss masses. One corresponding waters molecules loss and the second corresponding thermal degradation of parts from ligands. The last loss mass corresponding formation of manganese oxide. Up to 270^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 manganese ion is sp^3 type and the space configuration is thetraedrical, with two coordination liaisons from two oxygen atoms and two covalent liaisons between copper ion and other two oxygen atoms.

***Keywords**: Mn (II) complex; Organic Ligands; Synthesis; Characterization.*

A series of transition metal ions, such as Co(II), Mn(II), Ni(II), Fe(II) and Cu(II) form complexes with organic ligands having varied theoretical and practical applications[1].

In order of increasing the utilization of ligand derived from morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester, 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), Ni(II), Cr(III), U(VI) and Mn(II).

The present study discusses the results obtained in the characterization of the precipitation formed and suggests a possible method for gravimetric determination of Mn (II) with morpholine-4-carbodithioic acid.

The studies were making by using the methods: chemical analysis, ESR, IR spectroscopy and thermal analysis [2].

MATERIAL AND METHOD

10-20mL of 10^{-2}M, $MnCl_2.4H_2O$ solution (0.01-0.02gMn(II)) are diluted at 100mL and than treated with morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester solution in excess, under stirring. pH is corrected at 4.5 values with 0.1N NaOH solution (control with universal indicator paper). After 90 minutes, the yellow precipitate is filtered on a G_4 filtering crucible and washed with a mixture of C_2H_5OH-H_2O (1/1, v/v) until the filtrate becomes colorless. Then follows 105^0C drying up to constant weight and weighing in the form of $(C_{13}H_{12}O_3S_2NI_2)_2Mn$. It results a yellow precipitate, by reaction between mentioned ligand with Mn (II) at low acid pH, which are stable in time, at room temperature. [3-4]

The morpholine-4-carbodithioic acid 2-(3, 5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester was utilized as solution, in an ethylic alcohol-water medium (1:1, v: v) while the Mn (II) as a fresh aqueous solution of $MnCl_2.4H_2O$.

The IR spectra of the ligand and of the complexes have been recorded between 200-4000cm^{-1} by the method of KBr pelleting.

RESULTS AND DISCUSSIONS

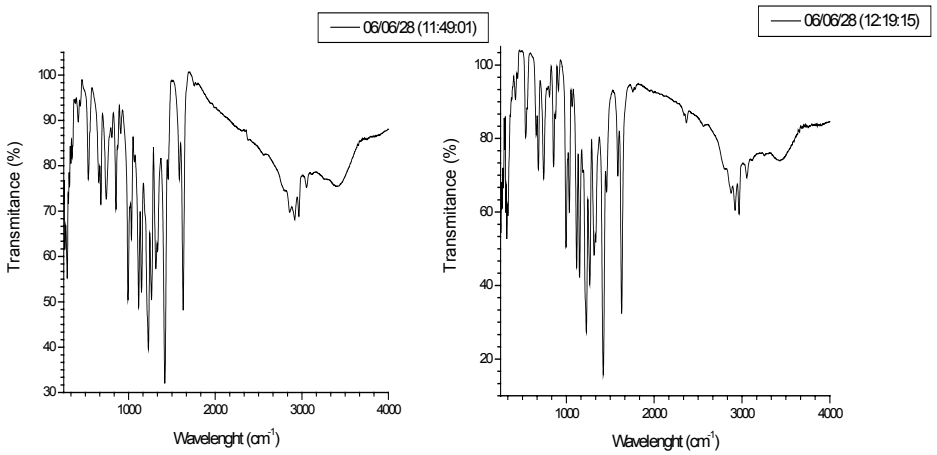
The IR-absorption and ESR spectra

The IR spectra of morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester have been compare with IR spectra of complex compound with Mn(II).

In the ligand's IR spectrum, a peak al 1730 cm^{-1} is observed, due to the C=O valence vibration, which also found in the spectrum of the precipitate formed, at 1710 cm^{-1}, although with a weaker intensity – which suggests the involvement of the oxygen atom from the >C=O group in the process of coordination. The higher modification, comparatively with the ligand, appears at the band from the 3300-3600 cm^{-1} domains attributed to the –OH phenolic group. The absence of this band in spectrum of the precipitation formed indicates involvement of the -OH group in the complexation reaction. More than that, in the complex compound spectrum, appears a peak at 460 cm^{-1}, attributed to the M-O bond.[5-7].

The ESR spectra were recorded on solid samples with a RES-IFA Bucharest Spectrometer. The intensity of the magnetic field was 3216.9 Gauss at a frequency of 9030 MHz. The compound with Mn(II) is paramagnetic because we have the signal ESR.

The spectra of molecular absorption in the IR domain are presented in figures 1(a, b).



a. **b.**

Figure 1. **The IR absorption spectrum of free ligand (a) and the complex compound of Mn(II) (b)**

Based on the spectroscopic data and chemical analysis the following structure was proposed: [8-9]

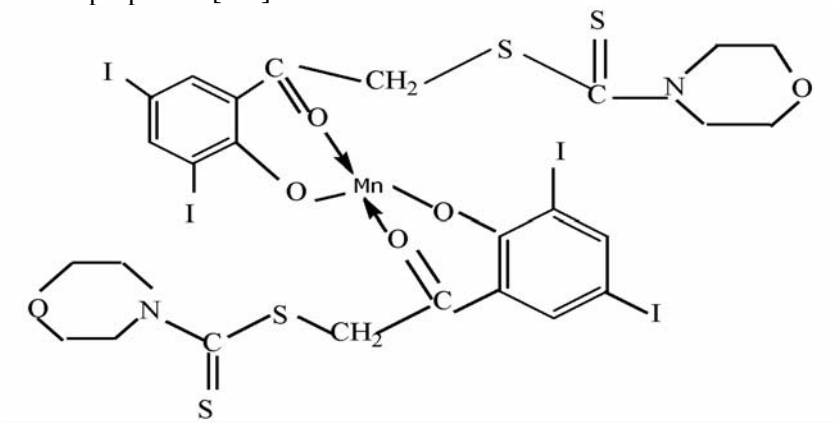


Figure 2. **Structure of $(C_{13}H_{12}O_3S_2NI_2)_2Mn$ complex**

Thermal analysis

Thermal stability of $(C_{13}H_{12}O_3S_2NI_2)_2Mn$ complex was studied with MOM Budapest Q-1500D derivatograph to 1000^OC. 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

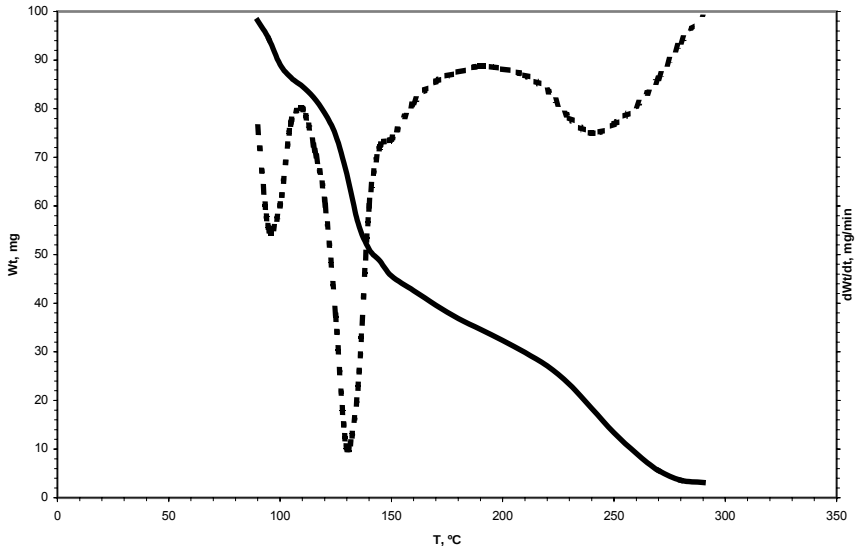


Figure 3. **Thermogram of $(C_{13}H_{12}O_3S_2NI_2)_2Mn$ complex (TG-uninterrupted line, DTG-interrupted line).**

Until 85^0C, complex is stable but between 85^0C-110^0C there is a loss mass corresponding to *n* water molecules (where *n* is about twelve). In this domain of temperatures take place the following chemical decomposition:

$$(C_{13}H_{12}O_3S_2NI_2)_2Mn \cdot nH_2O \xrightarrow{85^oC-110^oC} (C_{13}H_{12}O_3S_2NI_2)_2Mn + nH_2O$$

Second loss mass take place between 110^oC and 155^oC, corresponding formation of $(C_8H_4O_2I)_2Mn$ complex, parts of ligands transformed in volatile:

$$(C_{13}H_{12}O_3S_2NI_2)_2Mn \xrightarrow{110^0C-155^0C} (C_8H_4O_2I)_2Mn + \text{volatile}$$

Third loss mass take place between 155^oC and 270^oC, corresponding formation of manganese oxide:

$$(C_8H_4O_2I)_2Mn \xrightarrow{155^0C-270^0C} MnO + \text{volatile}$$

Up to 270^oC, the decomposition product is stable from thermal point of view.

In table 1 it presents both theoretical and practical loss mass in weight percentages.

Table 1

Domains of decomposition temperatures, theoretical and practical loss mass, relative errors for $(C_{13}H_{12}O_3S_2NI_2)_2Mn$ complex

Stage	Domain of temperature, °C	% Loss mass		$\varepsilon\%=100(\%W_p-\%W_t)/\%W_t$
		Theoretical, $\%W_t$	Practical, $\%W_p$	
I	85^oC-110^oC	15.80	15.21	3.73%
II	110^oC-155^oC	50.21	49.04	2.33%
III	155^oC-270^oC	87.61	90.37	3.05%

CONCLUSIONS

Morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester reacts with Mn(II) at low acid pH, and yellow complex compound resulting, with formula: $(C_{13}H_{13}O_3S_2NI_2)_2Mn$. A new complex compound was obtained by reaction between Mn(II) with morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester. The obtained precipitate will be used that a method for the gravimetric determination of Mn(II). Cu(II), Zn(II), Cr(III), U(VI) and Pd(II) precipitate in the same conditions that Mn(II) and with morpholine-4-carbodithioic acid 2-(3,5-diiodo-2-hydroxy-phenyl)-2-oxo-ethyl ester.

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