Compounds of Mn(II), Co(II) and Ni(II) with Ligand Derived from Morfolin-4 Carboditioic Acid-2(3,5 Diiod, 4 Methyl 2 Hydroxiphenyl) 2-Oxoethylesther

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In order to obtain new compounds of transitional metals having applications in analytical chemistry, we synthesized and studied compounds of Mn(II), Co(II) and Ni(II) with ligand derived from morfolin-4 carboditioic acid-2(3,5-diiod, 4 methyle 2-hydroxiphenyl) 2-oxoethylesther in the molar ratio of 2:1 (ligand to central atom). The characterization of new compounds was performed by means of chemical analysis, derivatographic thermogravimetry, IR absorption spectroscopy, ESR spectroscopy and X-ray diffraction. The investigated compounds are paramagnetic and crystallize in monoclinic system with central atoms Mn(II), Co(II) or Ni(II) hexacoordinated in octahedral structures. The study of the obtaining reactions of these new compounds supports their use in gravimetric determination of Mn(II), Co(II) and Ni(II).

Keywords: Manganese(II), Cobalt(II), Nickel(II), precipitating reagent, gravimetric determination

In this paper are presented novel compounds of Mn(II), Co(II) and Ni(II) with a new ligand synthesized with the aim of obtaining coordination compounds of transitional metals with uses in gravimetric determination [1,2].

The compounds presented in this paper are from the category of compounds containing central atoms of metals in different oxidation states coordinated by oxygen atoms of >C=O and OH groups bound to the benzene ring in α position, and being applied in gravimetry [3,4].

Compared to compounds having similar chelatizant groups, the obtaining reactions of the new compounds present the advantages takeing place at room temperature in relative short times (maximum 45-50 min), 100% efficiencies and being easily separated using a filter washed on a funnel vacuum nozzle.

New compounds were obtained in aqua medium from the reactions of morfolin-4 carboditioic acid-2(3,5-diiod, 4 methyle 2-hydroxiphenyl) 2-oxoethylesther ligand with ions like Mn(II), Co(II) and Ni(II) in the molar ratio of 2:1 (ligand:central:atom). Their characterization was carried out employing methods like: chemical analysis, derivatographic thermogravimetry, IR absorption spectroscopy, ESR spectroscopy and X-ray diffraction.

All the compounds described in this paper are paramagnetic and crystallize in monoclinic system with values of elemental cell parameters a and c very close one to another but much different than the values of b parameter.

Experimental part

In order to synthesize the coordination compounds, solution of 10^{-1} M concentration of $MnCl_2 \times 6H_2O$, $CoCl_2 \times 6H_2O$, $NiCl_2 \times 6H_2O$ (Merck A.R.) and morfolin-4 carboditioic acid-2(3,5-diiod, 4 methyle 2-hydroxiphenyl) 2-oxoethylesther (HL) were prepared using as solvents a mixture of ethylic alcohol and water in a ratio of 1:1 (in volumes) for inorganic salts, and dimethyl formamide for the organic ligand.

The synthesis of the novel coordination compounds was performed according to the method described in [3,4] by mixing and stirring at room temperature, for 60 min , the mixtures composed of 150 mL from one of each 10^{-1} M solutions of above-mentioned inorganic salts and 300 mL of 10^{-1} M solution of HL_2.

Obtained precipitates containing the novel coordination compounds of Mn(II), Co(II) and Ni(II) were separated by filtration and washing with 1:1 (in volumes) solutions of ethylic alcohols (98%) and water, and then dried at 105°C until a constant weight is reached.

The contents in C, H, S, I and divalent cations of Mn, Co and Ni metals of the compounds obtained with 100% efficiencies were determined for each obtained compound by using the appropriate chemical method.

The thermal stability of the synthesized compounds was carried out using a Q1500D (MOM Budapesta) derivatograph, following the procedure described in the previously works [6].

ESR (Electronic spin resonance) spectral curves of all the investigated compounds and reference employed are of the Lorentz type, being recorded on an IFA Bucharest spectrometer, according to the procedure described in the previous works [6].

The absorption spectra in the IR range (200 and 4000 cm^{-1}) were recorded by means of a Perkin Elmer FT-IR 100 spectrometer with KBr pellet technique.

The structural analyses of the synthesized compounds was carried out by XRD methods, according to the procedure described in the previously works [6].

Results and discussions

The experimental results on the content of carbon, hydrogen, sulphur, iodine and divalent metals Mn, Co, and Ni respectively, shown in table 1, lead to the following formula of the synthesized compounds: $Mn(C_{14}H_{15}O_3S_2I_2)_2 \times 2H_2O$, $Co(COS_2I_2) \times 2H_2O$ and $Ni(COS_2I_2) \times 2H_2O$. These

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compounds are mentioned herein further as $MnL_2 \times 2H_2O$, $CoL_2 \times 2H_2O$ and $NiL_2 \times 2H_2O$ respectively, whilst the ligand is noted HL_2.

In table 2 are listed temperatures corresponding to thermal decomposing stages together with the reaction order and activation energy values calculated according to Freeman-Carrol method [7].

It is worth to be mentioned that thermal decomposing stages listed in table 2 refer to thermal decomposing that follows the elimination of coordinated water.

Water in the investigated compounds is removed at the following temperatures:

$$MnL_2 . 2\,H_2O \xrightarrow{190 - 205\ ^oC} MnL_2 + 2\,H_2O$$

$$CoL_2 . 2\,H_2O \xrightarrow{180 - 200\ ^oC} CoL_2 + 2H_2O$$

$$NiL_2 . 2\,H_2O \xrightarrow{180 - 210\ ^oC} NiL_2 + 2\,H_2O$$

The elimination of coordinated water is followed by two successive stages of thermal decomposing that yield as final solid product MO metal oxides. Gaseous products derived from thermal decomposing of the two stages could not be analyzed.

The thermal stability of investigated coordination compounds decreases with the increase of central atom basicity: $MnL_2 > CoL_2 > NiL_2$, which is in agreement with other experimental results reported in literature [8-10].

Yielding solid and gaseous reaction products, thermal decomposing reactions of studied compounds are gas-solid systems generally characterized by reaction orders with values ranged between 0 and 1. In this kind of reaction, thermal decomposition is hindered by the transport of volatile compounds through the heated solid layer. If the layer of compound undergoing thermal decomposition had the thickness of a molecule, gases yielded from the reactions would not encounter any resistance to their evaporation, and the reaction order would be 1. In fact, the layer of substance subjected to thermal decomposing has a few millimeters, and it gets thinner and thinner as the reaction takes place. It should also be mentioned that as the thermal decomposition advances, the dispersion degree increases due to the chemical reaction generates volatile products. This generates thinner layers through which the gases pass. Therefore, the reaction order increases tending to unity in agreement with the data presented in this paper (table 2) and by other authors [11-14].

The main purpose of IR adsorption spectra interpretation was to note whether there are bends corresponding to bonds like O-M, $>C=O \rightarrow M$ and $M \leftarrow OH_2$ originated from the interaction of functional groups -O (H) and $>C=O$ existing in ligand and respectively due to coordinated water.

According to literature and experimental results presented here, the frequency range of 450-1500 cm^{-1} is specific to the bends corresponding[15-19] to valence and deformation vibrations of bonds such as *C-C*, *C-O*, *Mn-O*, *Co-O*, *Ni-O*.

In case of phenols (OH group) the most important bend is located between 1140 and 1265 cm^{-1} (ν_{C-OH}). This bend disappears when hydrogen atom is substituted with Mn(II), Co(II) and Ni(II), which is in agreement with other works [20].

The bends with frequencies , 485, 475and 478 cm^{-1} are assigned to the stretch frequencies ν_{Mn-O}, ν_{Co-O} and ν_{Ni-O} respectively (table 3).

The bends of vibration frequencies of *C-O* group observed in the region 1220-1295 cm^{-1} on the ligand spectrum are shifted to higher wavelengths and become less intense in the spectra of the studied compounds.

In IR absorption spectra of HL_2 ligand, the stretch (valence) vibrations of the carbonyl corresponds to an intense characteristic bend with a maximum located at 1725 cm^{-1}, while in the studied compounds occurs at 1680-1650 cm^{-1}. This represents an argument on the coordination of central atoms Mn(II), Co(II) and Ni(II) respectively with the oxygen atom in carbonyl group: $>C=O \rightarrow M$ (fig. 1), in agreement with other papers [11,17].

According to IR absorption spectra of investigated compounds ($MnL_2 \times 2H_2O$, $CoL_2 \times 2H_2O$ and $NiL_2 \times 2H_2O$),

Table 1

ELEMENTAL COMPOSITION OF THE INVESTIGATED COMPOUNDS (%)

Compound	C		H		N		S		I		M	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$MnL_2 \cdot 2H_2O$	27.85	27.67	2.32	2.16	2.32	2.38	10.60	10.39	41.74	41.68	4.55	4.68
$CoL_2 \cdot 2H_2O$	27.75	27.69	2.31	2.14	2.31	2.22	10.57	10.68	41.60	41.45	4.86	4.58
$NiL_2 \cdot 2H_2O$	27.76	27.63	2.31	2.20	2.31	2.20	10.57	10.40	41.61	41.75	4.86	4.63

Table 2

CHARACTERISTIC TEMPERATURES OF THERMAL DECOMPOSING STAGES, REACTION ORDERS AND ACTIVATION ENERGIES (KJ/mol) OF THE STUDIED COMPOUNDS

Compound	Temperatures of thermal decomposing stages (°C)							
	Stage I				Stage II			
	Ti ^{0}C	Tf ^{0}C	n	E	Ti ^{0}C	Tf ^{0}C	n	E
MnL_2	205	345	0,80	160,2	345	580	0,90	210,10
CoL_2	200	340	0,85	145,6	340	600	0,93	205,7
NiL_2	210	350	0,82	170,1	350	520	0,95	241,6

Table 3

VALUES OF THE REACTION ORDER AND ACTIVATION ENERGY OF THE STUDIED COMPOUNDS.

Compound	ν_{H2O}	$\nu_{C=O}$	$\delta_{\Phi OH}$	ν_{Φ}	ν_{M-O}
HL_2	-	1725	1265	1585	-
MnL_2	3420-3380	1680	-	1570	485
CoL_2	3385-3360	1680	-	1560	475
NiL_2	3375-3285	1650	-	1565	478

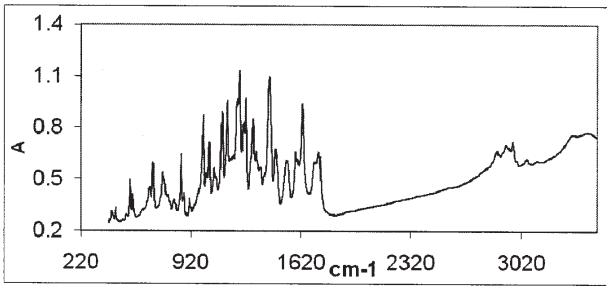

Fig. 1. IR absorption spectrum of $NiL_2 \times 2H_2O$

central atoms are coordinated with water molecules having symmetric and asymmetric stretch vibrations at 3400-3380, 3380-3360 and 3370-3230 cm^{-1} respectively, and deformation vibrations [16,17] at 1620-1600, 1615-1605 and 1610-1600 cm^{-1} respectively, in agreement with literature [18,22].

Processing the ESR spectra of the studied compounds, it results that central atoms of Mn(II), Co(II) and Ni(II) are paramagnetic. Calculated according to directions given in literature [5], the spectroscopic splitting g factor takes values between 2.019-2.0315, which are higher than that of the free electron (2.0023). This is due to the contribution of the orbital momentum and covalence degree of the respective bond where the central atoms Mn(II), Co(II) and Ni(II) are involved (table 4) [9,10,15].

The value of g factor of odd electrons decreases with the increase of the stability of investigated compounds in the following order: $NiL_2 \times 2H_2O < MnL_2 \times 2H_2O < CoL_2 \times 2H_2O$.

Processing the X-ray diffractogram of HL ligand and $MnL_2 \times 2H_2O$, for $CoL_2 \times 2H_2O$ and $NiL_2 \times 2H_2O$ compounds,

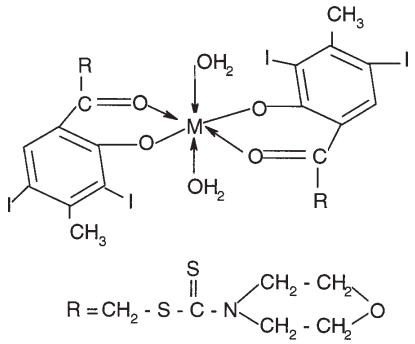

Fig.2 Structures of $ML_2 \times 2H_2O$ compounds (M = Mn^{2+}, Co^{2+} and Ni^{2+})

it results that all the synthesized compounds crystallize in monoclinic system with parameters of crystalline cells as shown in table 5.

Based on chemical analysis, derivatographic analysis, IR absorption spectra, ESR spectra, it was established that the structures of synthesized compounds are classified in the octahedral structures with hexacoordinated central atoms. Each central atom is coordinated to four oxygen atoms from two molecules of ligand and other two oxygen atoms from two water molecules (fig.2)

An important conclusion can be drawn from the difractogramms of ligand and synthesized compounds. (fig. 3,4).This is related to the coordination process of central atoms of Mn(II), Co(II) and Ni(II), which was determined by crystallographic characteristics of the ligand. It was noticed a similarity between two of the elemental cell parameters of compounds in relation to those of the ligand. The central atoms of Mn(II), Co(II) and Ni(II), bind to two

Table 4
VALUES OF g FACTOR, MAGNETIC FIELD INTENSITY H_x (GAUSS) AND ODD ELECTRON NUMBER CORRESPONDING TO A CENTRAL ATOM(n) IN THE INVESTIGATED COMPOUNDS

Compound	g	H_x	Odd electron number to central atom
$MnL_2 \cdot 2H_2O$	2.0242	3187.2	4.93
$CoL_2 \cdot 2H_2O$	2.0315	3175.8	2.88
$NiL_2 \cdot 2H_2O$	2.0190	3195.5	1.92

Table 5
PARAMETER VALUES OF ELEMENTAL CELLS OF HL_2 LIGAND AND $MnL_2 \times 2H_2O$, FOR $CoL_2 \times 2H_2O$ AND $NiL_2 \times 2H_2O$ COMPOUNDS.

Elemental cell parameters	Values obtained by indexation			
	HL_2	$MnL_2 \cdot 2H_2O$	$CoL_2 \cdot 2H_2O$	$NiL_2 \cdot 2H_2O$
a (Å)	17.0126	17.9528	18.1210	18.2065
b (Å)	12.3386	9.2713	9.3661	9.4486
c (Å)	8.6898	10.1215	10.3150	10.4098
α	90°	90°	90°	90°
β	90°	93.30°	92.50°	93.10°
γ	90°	90°	90°	90°
Elemental cell volume ($Å^3$)	1824.09	1684.68	1750.69	1790.75

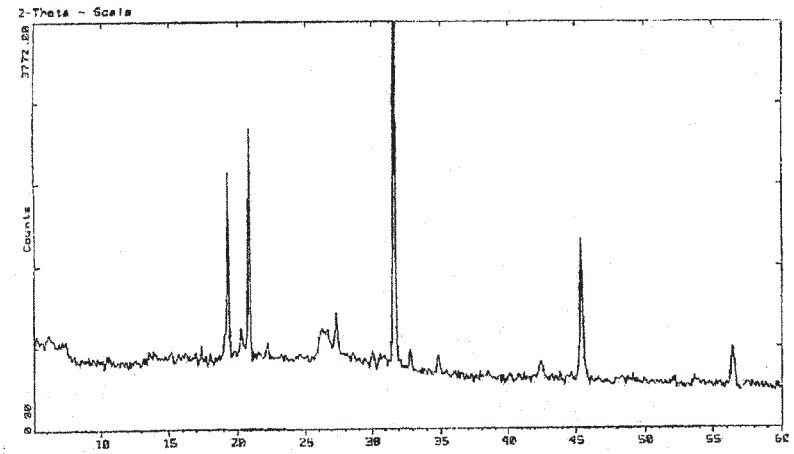

Fig. 3 The X-ray diffractogram of $NiL_2 \times 2H_2O$ compounds

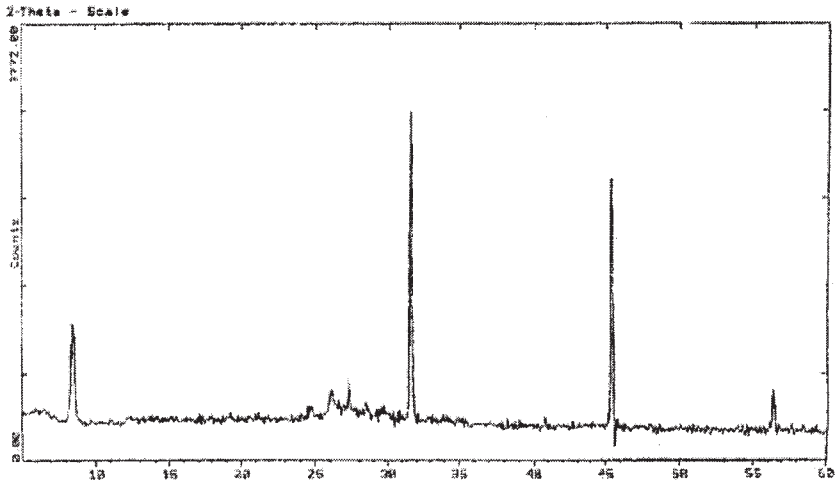

Fig. 4 The X-ray diffractogram of $MnL_2 2H_2O$ compounds

water molecules in ab plan, though on the crystallographic direction b accompanied by the volume compressing of the respective coordination compounds.

It is noted a slight decreasing of β distortion angle due to a probable disposal of the two molecules of water coordinated to the central atoms, one above and the other beneath the plan were are placed the ligands. However, it is preserved a slightly deformed octahedral symmetry of the central ion.

Conclusions

This work continues our studies on compounds obtained through the interaction of transitional metal ions with ligands derived from organic ligands with complexant groups -OH phenolic and >C=O bound to benzene ring. Thus, new coordination compounds with central atoms such as Mn(II), Co(II) and Ni(II) were synthesized and characterized.

Three new compounds were synthesized through the interaction of morfolin-4 carboditioic acid-2(3,5-diiod, 4 methyle 2-hydroxiphenyl) 2-oxoethylesther with Mn(II), Co(II) and Ni (II) in the molar ratio of 2:1 in reaction medium composed of dimethylformaldehide, ethylic alcohol (98%) and water in volumetric ratio of 1:1:1.

Using modern methods, such as chemical analysis, derivatographic analysis, IR absorption spectroscopy, ESR spectroscopy, and X-ray diffraction, it was established that to each central atom of Mn(II), Co(II) and Ni(II) respectively correspond two anions derived from morfolin-4 carboditioic acid-2(3,5-diiod, 4 methyle 2-hydroxiphenyl) 2-oxoethylesther and two water molecules.

The new compounds are paramagnetic and crystallize in monoclinic system with the central atom hexacoordinated in octahedral structures.

Practical application of this work lies in the use of the obtaining reaction of new synthesized compounds to dose Mn(II), Ce(II) and Ni(II) by gravimetrical method with a maximum error of ± 0.20%.

Reference

1.GAVRIS, G., STANASEL, O., PODE, R., STOIA, M., CHITAC, V., Rev. Chim.(Bucharest), **59**, no. 1, 2008, p. 61

2.LAZAR, GH., CAPATANA ,C., SIMIONESCU, C.M., Rev. Chim.(Bucharest), **59**, no. 8, 2008, p. 939

3.POPA, GR., MOLDOVEANU, S., Reactivi organici în chimia analitică, Ed. Acad. Române, Bucureşti, 1976

4.POPA, GR., CROITORU, V., Chimie analitică cantitativă, Ed. Didactică şi Pedagogică, Bucureşti, 1977

5.POLIVAN,C.G., Studii de rezonanţă paramagnetica electronică a structurii unor combinaţii complexe de interes biologic, Ed. Acad. Române, Bucureşti, (1995)

6. SIBIESCU, D., TURCUMAN, (ANTIGHIN) S., TUTULEA, D., ROSCA, I., CRETESCU ,I., SECULA M., Rev. Chim. (Bucharest), **61,** no. 3, 2010, p.311

7.FREEMAN, S.E., CARROLL, B., J.Phys.Chem.1958, 62, p.394 Introduction to Thermal Analysis Ed. Springer, 2001

8.SEGAL, E., FĂTU, D., Introducere în cinetica reacţiilor neizoterme, Ed. Acad. Române, Bucureşti, 1983.

9.FLONDOR, M., ROŞCA, I., SIBIESCU, D., Rev. Chim.(Bucharest), **59**, no. 12, 2008, p. 1330
10.FLONDOR, M., ROŞCA, I., SIBIESCU, D., SUTIMAN D., CAILEAN A., CRETESCU I., Rev. Chim. (Bucharest), **60**, no. 2, 2009, p 119
11.FLONDOR, M. Compusi coordinativi ai cationilorunor metale tranziţionale- Teză de doctorat. Univ.Tehnică „Gh.Asachi" Iaşi, 2007
12.ROŞCA I., FOCA N., SUTIMAN D., CĂILEAN A., SIBIESCU D., VIZITIU M ., J. Termal Analisys and Colorymetry, **56,** 1999, p.401
13.ROŞCA I., SUTIMAN D., SIBIESCU D., VIZITIU M., CĂILEAN A., OPREA J., Serbien Chem. Soc., **67**, no. 8-9, 2002, p.617
14.MAHON M., Mc GINLEZ J., ROONAY, A. D., Inorganica Chimica Acta, 2009, **362** p.2353
15.ROCKDIFFE., D.A., MARTELL A.E., J. Molecular Catalysis A. Chemical, 1996, **106**, p.211
16.ROCCHICCIOLI, C., Chimie Analytique 1964 **48,** nr.9, p.454
17.LECONTE, J., Spectroscopie dans l'infrarouge, Ed. Dumond Paris, 1995
18.FOCA N., SIBIESCU D., OANCEA D., Metode fizico-chimice aplicate în studiul combinaţiilor complexe Ed. Tehnopress Iaşi 2006
19.WELLS, F.A., Structural inorganic chemistry Oxford Univ. Press 1999
20.BALABAN, T. A., BANCIU, M., POGANY, I., Aplicaţii ale metodelor fizice în chimia organică, Ed. Ştiinţifică şi Enciclopedică Bucureşti , 1983
21.BROWN, M.E., Introduction to Thermal Analysis Ed. Springer, 2001
22.SIBIESCU, D., Chimia compuşilor coordinativi Ed. Tehnopress Iaşi 2005

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