

Synthesis and Characterization of Some Coordination Compounds of Mn(II), Co(II) and Fe(III) with 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone

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This study presents the synthesis and characterization of solid-state coordination compounds resulted from the interaction between Mn(II), Fe(III) and Co(II) with 1-(2 bromine, 2 hydroxy, 3 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone ligand. The synthesized compounds were characterized by using the following methods: elemental chemical analysis, derivatographic thermogravimetry, IR absorption spectroscopy, Electron Spin Resonance (ESR) spectroscopy, Mössbauer spectroscopy and X-ray diffraction. The study of the obtaining reactions of these novel compounds supports the author suggestion that might be applied in gravimetric determination of Mn(II), Fe(III) and Co(II).

Keywords: 1-(2 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone, Mn(II), Fe(III), Co(II), gravimetric determination

Coordination compounds formed from the interaction of Mn(II), Fe(III) and Co(II) with 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone ligand can be classified in the category of coordination compounds achieved by coordinating >C=O and $O(H)$ bound to the benzene ring in α position.

In this field of study were also reported other works [1-7] where are discussed the synthesis and characterization of new compounds underlining their applications in the gravimetric determination of metal ions.

Also, the compounds presented in this paper can be applied in gravimetrical determination of Mn(II), Fe(III) and Co(II).

Herein further is described a study of synthesis and characterization of solid-state complex compounds resulted from 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone and cations such as Mn(II), Fe(III) and Co(II) in the reactants combination ratio of 2:1 for Mn(II), Co(II) and 3:1 for Fe(III) respectively.

The obtained coordination compounds were studied applying methods such as chemical analysis, IR absorption spectroscopy, thermogravimetry, ESR and Mössbauer spectroscopy and diffraction X-ray.

Based on the performed studies, it is shown that central atoms of Mn(II), Fe(III) and Co(II) coordinate with oxygen atoms from groups of >C=O and $O(H)$ of $C_{15}H_{12}O_2SBr_2$ ligand.

The investigated coordination compounds present a relatively high thermal stability because they start to decompose at temperatures very close to 200°C.

These reactions can be applied to determine quantitatively the respective cations. Moreover, their reactions take place under normal conditions with 100% efficiency, and the resulted precipitates can be easily separated by filtration.

ESR and Mössbauer spectra show that all the investigated compounds contain central atoms having a maximum number of odd electrons.

By indexing the X-ray diffractograms it can be shown that Mn and Co compounds crystallize in monoclinic

system, while Fe(III) compound presents an amorphous state.

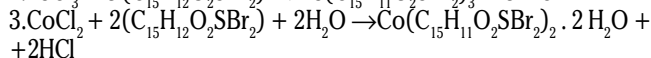
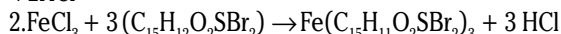
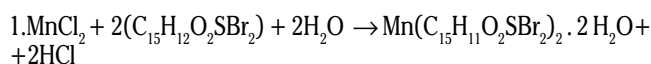
Experimental part

The experimental determinations were carried out using 10^{-1} M $MnCl_2 \cdot 4H_2O$, $FeCl_3$, $CoCl_2 \cdot 6H_2O$ (Merck A.R.) and a ligand from 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone.

The synthesis of the coordination compounds presented in this work was performed according to the method described in literature [8,9] using as solvent a mixture of ethylic alcohol and water in the ratio of 1:1 (in volumes) for inorganic salts, and dimethyleformamide (DMF) solvent for 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone.

The obtaining reactions of the new compounds were performed by mixing and stirring the mixtures of inorganic salts and ligand at room temperature, for 75 min. These mixtures were composed of 100 mL from one of each 10^{-1} M solutions of $MnCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ respectively, and 200 mL of 10^{-1} M solution of 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone ligand. In case of Fe(III) cation, the mixture was composed of 100 mL of 10^{-1} M solution of $FeCl_3$ and 300 mL of 10^{-1} M solution of ligand.

The reaction products are precipitates separated by filtration, washed on a funnel vacuum nozzle, and then dried at 105°C until a constant weight is reached. Under the specified conditions, efficiencies of 100% were achieved.



The contents of C, H, S, Br and Mn(II), Fe(III), Co(II) respectively were determined for each obtained compound using proper conventional methods [1,2].

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Table 1
ELEMENTAL COMPOSITION OF THE INVESTIGATED COMPOUNDS %

Compounds	C		H		S		Br		M(II)	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
MnL ₂ ·2H ₂ O	29.03	29.15	2.09	2.15	5.16	5.05	51.54	51.68	4.43	4.52
FeL ₃	28.21	28.34	2.27	2.39	5.01	5.11	50.63	50.75	4.37	4.46
CoL ₂ ·2H ₂ O	28.93	29.11	2.08	2.19	5.14	5.23	51.37	51.48	4.73	4.84

The thermal stability of the synthesized compounds was carried out using a Q1500D (MOM Budapesta) derivatograph, following the procedure described in the previous works [10].

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 and the electronic spin resonance (ESR) spectra were recorded by means of an IFA Bucharest spectrometer, according to the procedure described in [10].

Mössbauer spectra of the compound FeL₃ were recorded by means of an electrodynamic spectrometer with a uniform accelerated motion of the source, based on ⁵⁷Co isotope in Cr matrix according to the procedure described in the previously works [10].

The structural analyses of the synthesized compounds was carried out by XRD methods, according to the procedure described also in [10].

Results and discussions

Based on the synthesis reactions and chemical analysis of the investigated compounds, it results that to each central atom of Mn(II) and Co(II) correspond two anions of the 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone ligand, while to each Fe(III) central atom correspond three anions of the same ligand.

Determined with an error of ±0.25%, the elemental composition of the studied compounds is presented in table 1 and corresponds to the formula: M(C₁₅H₁₂O₂SBr₂)₂.

These experimental data lead to the conclusion that the new compounds presented in this work have the following formulae: Mn(C₁₅H₁₂O₂SBr₂)₂ · 2H₂O, Fe(C₁₅H₁₂O₂SBr₂)₃,

Co(C₁₅H₁₂O₂SBr₂)₂ · 2H₂O abbreviated as MnL₂, FeL₃ and CoL₂.

The temperatures of characteristic stages of thermal decomposing of the investigated compounds are presented in table 2. Water in the studied compounds is eliminated at the following temperatures: MnL₂ – 220°C, FeL₃ – 180°C and CoL₂ – 230°C.

The Freeman-Carroll method was used in order to determine the reaction order and activation energy [12].

In table 3 are presented the values of the reaction order and activation energy of the thermal decomposing of MnL₂·2H₂O, FeL₃ and CoL₂ · 2H₂O. In the case of thermal decomposing of the coordination compounds presented in this paper, reaction order values ranged between 0.4 and 1.5 were recorded [1,4,12,13].

The fractional values of reaction appear due to the fact that the proper chemical reaction is unfavored by transport phenomena of the volatile compounds through the solid layer, interphase phenomena or “vaporization” phenomena of volatile components at the free surface of the solid compound. In case of multi-stage thermal decomposition of the investigated compounds, the augmentation of the dispersion degree is achieved by the chemical reaction itself, after the elimination of the volatile component, which means, a decreasing of the layer the gases will pass through [3, 4, 7, 13].

IR absorption spectra of the studied compounds give important information on the chemical bonds of the central atoms Mn(II), Fe(III) and Co(II) with ligand atoms.

In the IR absorption spectra of the investigated compounds, the main purpose was to establish whether there are absorptions corresponding to bonds such as O-M, > C=O → M and M ← OH₂, originating from the

Table 2
CHARACTERISTIC TEMPERATURES OF THERMAL DECOMPOSITION STAGES OF THE INVESTIGATED COMPOUNDS

Compound	Range temperatures of thermal decomposition stages (°C)		
	Stage I	Stage II	Stage III
MnL ₂	220 - 300	310 - 390	400 - 590
FeL ₃	180 - 360	370 - 590	-
CoL ₂	230 - 290	300 - 500	510 - 600

Table 3
VALUES OF REACTION ORDER AND ACTIVATION ENERGY OF INVESTIGATED COMPOUNDS

Compound	Reaction order		Activation energy (kJ/mol)	
	Stage II	Stage III	Stage II	Stage III
MnL ₂	0.8	1.5	39.124	40.696
FeL ₃	1.7	-	28.291	-
CoL ₂	0.7	1.4	11.084	15.918

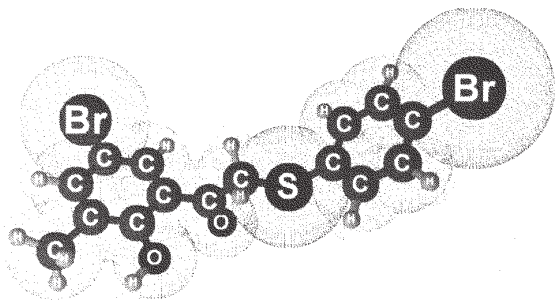


Fig. 1. Structure of ligand 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphonyl)-ethanone

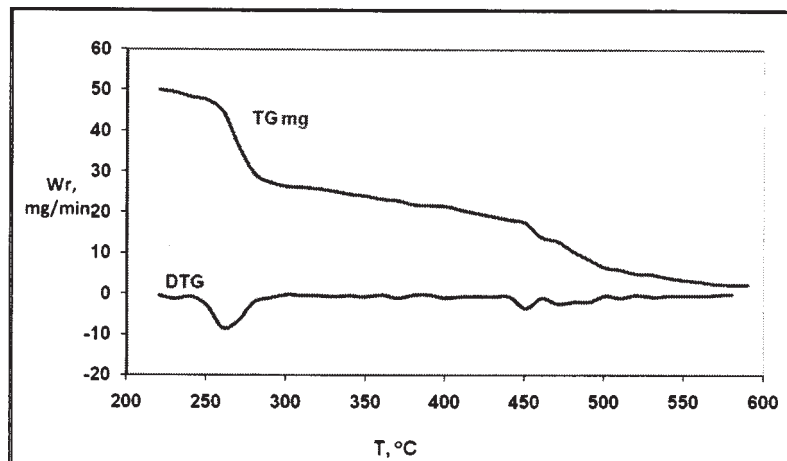
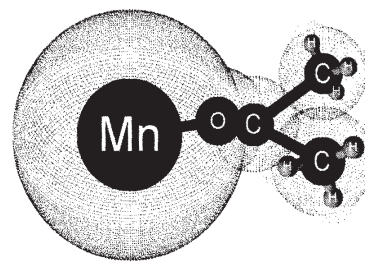


Fig. 2. Thermogram of $MnL_2 \cdot 2H_2O$ compound

interaction of functional groups $-O(H)$ and $>C=O$ in ligand and respectively due to the coordination water.

In the low frequency range ($450-1500\text{ cm}^{-1}$) occur both bands corresponding to the valence vibrations of simple bonds: $C-C$, $C-O$, $Mn-O$, $Fe-O$, $Co-O$, and bands corresponding to the deformation vibrations of other bonds. The bands with frequencies of 475 cm^{-1} , 470 cm^{-1} and 436 cm^{-1} are designated to the corresponding stretch frequencies: ν_{Mn-O} , ν_{Co-O} and ν_{Fe-O} respectively. The bands of vibration frequency of $C-O$ group observed in the region $1277-1297\text{ cm}^{-1}$ in the spectrum of ligand are shifted towards higher wavelengths and become less intense in the spectra of the investigated compounds.

The stretch (valence) vibrations of carbonyl groups, occurring in case of ligand at 1705 cm^{-1} , in the case of the studied compounds occur at 1667 cm^{-1} , 1647 cm^{-1} and 1627 cm^{-1} for MnL_2 , FeL_3 and CoL , respectively. This supports the assumption that the central atoms $Mn(II)$, $Fe(III)$ and $Co(II)$ coordinate with the oxygen atom in carbonyl group, $M = Mn, Fe, Co$.



IR adsorption spectra of the compounds MnL_2 , FeL_3 and CoL , respectively are presented in figure 3. The absorption of OH phenol group in ortho position is located in the range $3277-3275\text{ cm}^{-1}$, but it disappears in the investigated compounds.

In case of phenols, the most important band [14-15] is located between $1147-1237\text{ cm}^{-1}$ (ν_{C-OH}). By substituting the hydrogen atom with a central atom ($Mn(II)$, $Fe(III)$ or $Co(II)$), the peaks in IR spectra of the investigated compounds corresponding to OH group disappear.

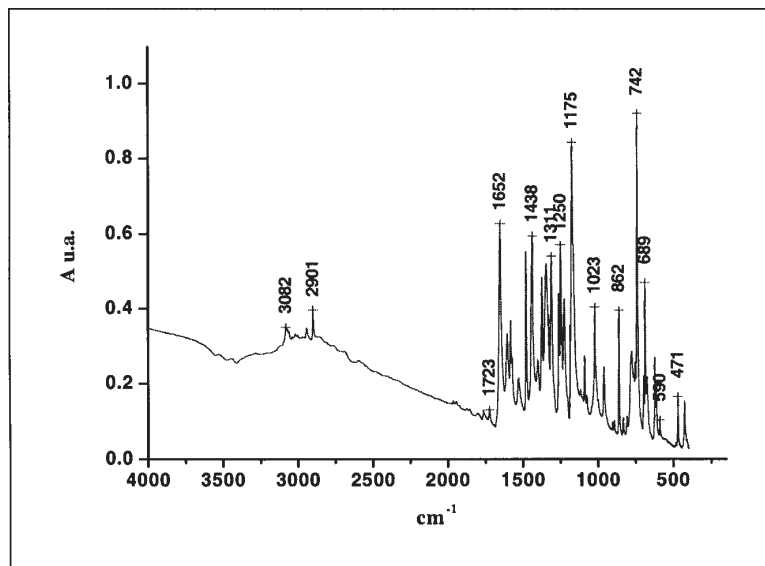


Fig. 3. IR absorption spectrum of $MnL_2 \cdot 2H_2O$ compound

Hence, it can be stated that each central atom binds to an oxygen atom from the phenol group where, in fact, a hydrogen atom is substituted with Mn(II), Fe(III) and Co(II) respectively.

Processing the ESR spectra, it results that the studied compounds of Mn(II) and Co(II) present paramagnetic properties. The spectroscopic splitting factor takes values between 2.0240-2.0217, hence higher than that of the free electron (2.0023) due to the contribution of the orbital momentum and covalence degree of bonds where central atoms such as Mn(II) and Co(II) are involved (table 4). This is in agreement with the works reported in literature [4,5,7] in relation to similar central atoms and ligand type.

Table 4
VALUES OF THE SPECTROSCOPIC SPLITTING FACTOR (G), INTENSITY OF THE MAGNETIC FIELD CORRESPONDING TO THE SPECTRUM CENTER OF THE SAMPLE (H_x , GAUSS) AND ODD ELECTRON NUMBER OF THE CENTRAL ATOM (n) FOR EACH STUDIED COMPOUND

Compound	g	H_x	n
MnL ₂	2.0219	3243.1	4.90
FeL ₃	2.0194	3239.1	4.89
CoL ₂	2.0199	3246.8	2.92

The value of g splitting factor of odd electrons decreases with the increase of the stability of investigates compounds in the following order: MnL₂ · 2H₂O < CoL₂ · 2H₂O.

Based on the performed analyses such as chemical analysis, IR absorption spectra, derivatographic analysis, electron spin resonance and Mössbauer spectra and X-ray diffraction, it can be concluded that the central atoms of investigated compounds present coordination 6 in octahedral structures. Each central atom is coordinated by four oxygen atoms provided by two molecules of ligand, and two oxygen atoms provided by two water molecules as shown in case of MnL₂ · 2H₂O and CoL₂ · 2H₂O.

Mössbauer spectrum of FeL₃OH · 3H₂O recorded at 80 K is shown in figure 4, and the values of Mössbauer parameters are shown in table 5.

The interpretation of the Mössbauer spectra recorded at the temperature of 300K and 80K (fig. 4.), and Mössbauer parameters show that in the investigated compound the iron central atom is in the IIIrd oxidation state with high spin (S=5/2) which pinpoints a weak character of Fe-ligand bond as in other compounds [15, 16].

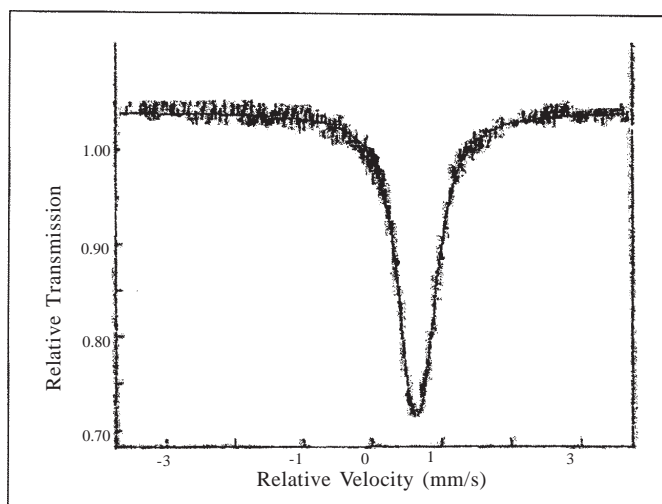


Fig. 4. Mossbauer spectrum of FeL₃ recorded at 80 K temperature

Table 5
VALUES OF MÖSSBAUER PARAMETERS OF FeL₃ COMPLEX

T (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
300	0.90	0.85	0.72
80	0.64	0.24	0.54

The parameter of isomer shift, δ , shows a similarity of s-type electron density around the central atom nucleus. The value of ΔE_Q leads to the conclusion that Fe(III) central atom present octahedral encompassment.

For this compound, it was observed a dependence on the temperature of the isomer shift that is higher than that obtained in case of Fe(III). This phenomenon is in agreement with the second-order Doppler effect.

It is probable that as the temperature increases from 80 to 300 K, at the same time as the oscillations of Fe(III) atoms in the crystalline network increase, it takes also place a shift of the electronic density of spin s within the ligand-central atom bond.

Mössbauer spectra of FeL₃ present a particularity as regards Γ lines. Thus, the values of Γ parameter increase with lower temperatures, which can be due to the relaxation effect.

By indexing the X-ray diffractograms of the ligand and investigated compounds, it results that only FeL₃ is amorphous.

The compounds CoL₂ · 2H₂O and MnL₂ · 2H₂O and 1-(2 bromine, 2 hydroxy, 3 methyl-phenyl)-2-(4 bromine-phenyl-sulphanyl)-ethanone ligand have coordinated structure, classified in the monoclinic system having the elemental cell parameters presented in table 6.

The coordination of ligand by central atoms Co(II) and Mn(II) is achieved in the ac plane of the elemental cell accompanied by its volume compression. In the same time it can be noted a slight distortion of an angle that leads to the conclusion that water molecules coordinate with the central atoms of Co(II) and Mn(II) above and beneath the ab plane accompanied by volume compression of compound elemental cell due to coordination.

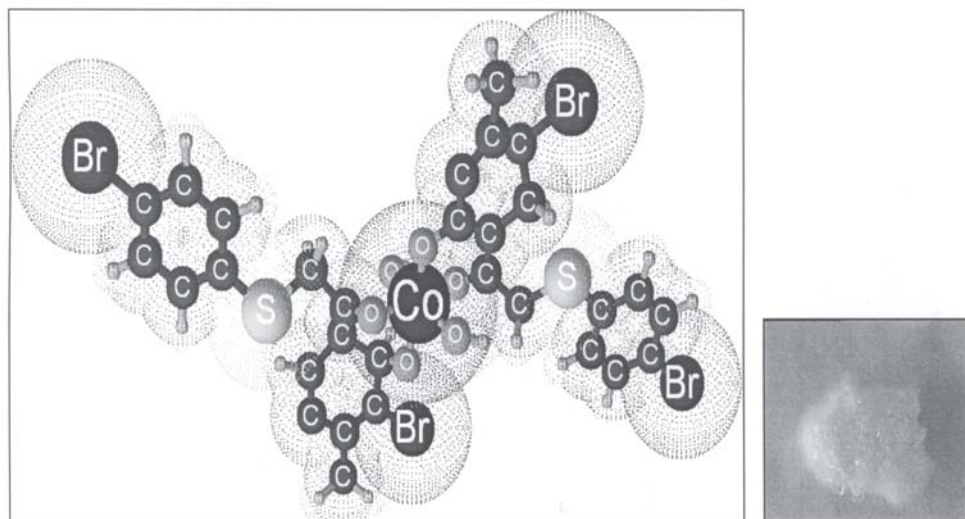
It must be mentioned that in the preparation process of CoL₂ · 2H₂O and MnL₂ · 2H₂O compounds, the ligand was completely consumed due to its characteristics peaks cannot be found in these compounds.

These experimental data and their interpretation are in good agreement with results reported in other works [17,18].

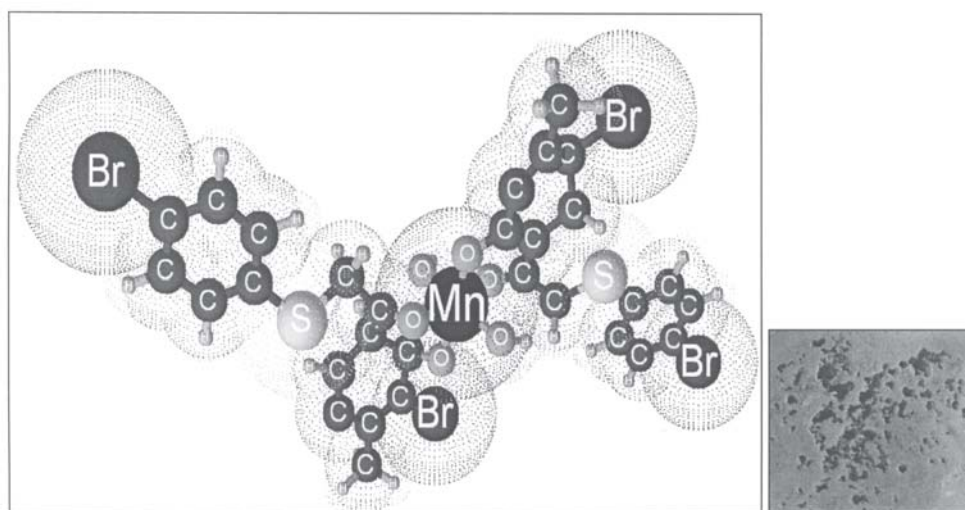
Based on the experimental data acquired through chemical analysis, thermal analysis, IR absorption and ESR spectroscopy and X-ray diffraction the structures of the

Table 6
PARAMETER VALUES OF ELEMENTAL CELLS OF INVESTIGATED COMPOUNDS

Elemental cell parameter	Value determined by indexation		
	HL	MnL ₂ ·H ₂ O	CoL ₂ ·H ₂ O
a (Å)	14.229	14.500	14.788
b (Å)	9.108	6.502	6.711
c (Å)	11.486	13.801	14.015
α	94°	102°	98°10'
β	90°	90°	92°
γ	90°	90°	90°



CoL₂



MnL₂

Fig. 5. Structures of CoL₂·2H₂O and MnL₂·2H₂O compounds

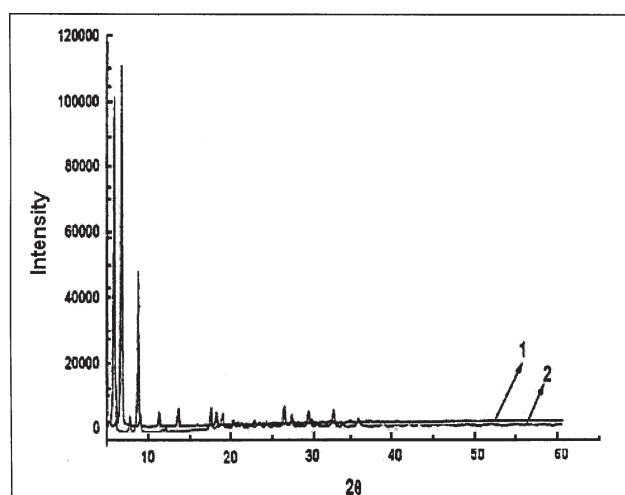


Fig. 6. Diffractograms of HL(1) ligand and CoL₂·2H₂O compound

investigated compounds were suggested as shown in figure 5, 6.

Conclusions

In this paper were presented the synthesis and study of several new compounds Mn(II), Fe(III) and Co(II) with 1-(3 bromine, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromine-phenyl-sulphonyl)-ethanone ligand, in the central atom-ligand molar ratio of 1:2 in case of Mn(II), Co(II) and respectively 1:3 in case of Fe(III).

The investigated compounds were characterized by means of modern technical methods such as elemental chemical analysis, thermogravimetry, IR absorption spectroscopy, ESR spectroscopy and Mössbauer spectroscopy and X-ray diffraction. Thus, it was shown that the investigated compounds are of high spin having hexacoordinated central atoms, only MnL₂·2H₂O and CoL₂·2H₂O present crystalline structure of monoclinic symmetry, FeL₃ being amorphous.

The obtaining reaction of the new synthesized compounds can be used in order to determine gravimetrically the ions Mn(II), Fe(III) and Co(II) with a maximum error of $\pm 0.27\%$.

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