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Ferenc, Wiesława; Dariusz, Osypiuk; Sarzy#ski, Jan; Głuchowska, Halina
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Complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand formed by condensation reaction of isatin with glutamic acid

Wiesława Ferenc+, Dariusz Osypiuk, Jan Sarzyński, Halina Głuchowska
Maria Curie-Skłodowska University, Institute of Chemical Sciences, Faculty of Chemistry, Department of General and Coordination Chemistry and Crystallography, 20-031 Lublin, Poland

+Corresponding author: Wiesława Ferenc, Phone: +48 81 537 57 65, Email address: wetafer@poczta.umcs.lublin.pl

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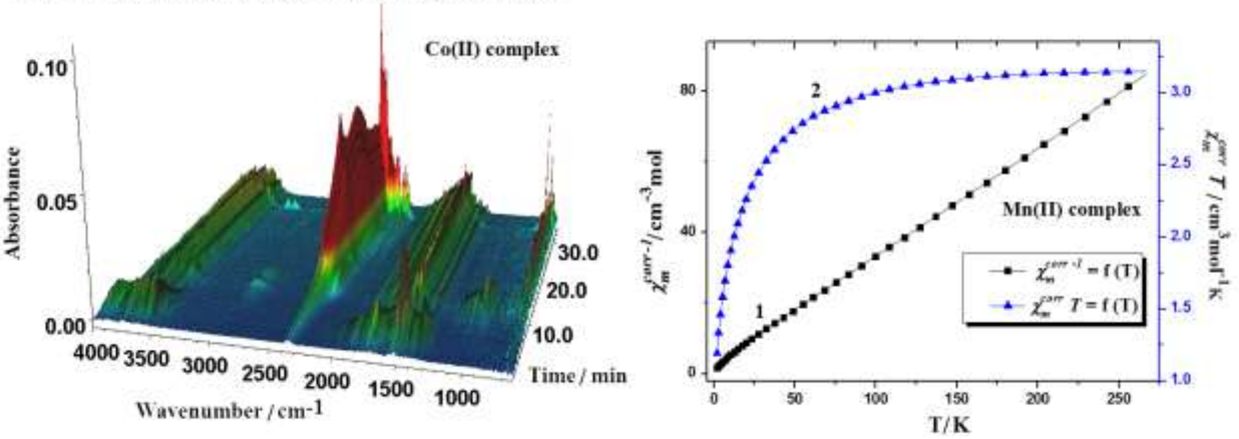
ABSTRACT: The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand ($H_2L=C_{13}H_{12}N_2O_5$) formed by condensation reaction of isatin and glutamic acid were synthesized. Their physico-chemical properties were characterized using elemental analysis, XRF, XRD, FTIR, TG–DSC and TG–FTIR methods and magnetic measurements (Gouy's and SQUID-VSM methods). The complexes were obtained in crystalline forms (monoclinic or triclinic) with the formulae: $M(LH)_2{\cdot}nH_2O$ for Mn(II), Ni(II) and Zn(II) and $ML{\cdot}nH_2O$ for Co(II) and Cu(II), where $LH=C_{13}H_{11}N_2O_5^{-}$, $L^{-}=C_{13}H_{10}N_2O_5^{2-}$, n = 1 for Mn(II), Cu(II) and Zn(II), n = 2 for Co(II) and n = 3 for Ni(II). In air at 293–1173 K they decompose in three steps forming finally the oxides of the appropriate metals. The gaseous decomposition products were identified as: H_2O, CO_2, CO, hydrocarbons and N_2O. The magnetic moment values for complexes (except Zn(II) complex) show their paramagnetic properties with the ferro- and antiferromagnetic interactions between central ions. The compounds of Mn(II) and Co(II) are high spin complexes with weak ligand field. In Co(II) and Cu(II) complexes two carboxylate groups take part in the metal ion coordination while in those of Mn(II), Ni(II) and Zn(II) only one carboxylate anion coordinates to central ion.

The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand (H_2L, $L=C_{13}H_{10}N_2O_5^{2-}$) formed by condensation reaction of isatin and glutamic acid were synthesized and their physico–chemical properties studied.



1. Introduction

A type of ligand such as isatin (1H-indole-2,3-dione) creates an interesting basis of current research in inorganic and coordination chemistry due to its wide applications and diverse biological properties. It plays an important role such as: antibacterial, antifungal, anticonvulsant, anti-HIV and antiviral[1-7]. From literature survey, it appears that isatin heterocycles exhibit manifold importance in the field of medicinal chemistry. It is used for the design and development of anticancer drugs[1,2]. There are over ten thousand biologically active compounds containing indole core. More of them are approved as commercially available drugs or are undergoing clinical trials. Antioxidant potential of the thiosemicarbazone derivatives was analysed by *in vitro* free radical scavenging assay[8]. Therefore, derivatives of isatin based on the thiosemicarbazone are potential compounds with wide range of promising biological properties which may be explored further for the treatment of several diseases. Likewise, isatin structural scaffold could act as DNA inhibitors. The isatin compound hybrids have the potential to overcome the drug resistance[9].

Isatin and its derivatives are one of the most important and broadly occurring structural units in several natural compounds. As a natural substance it occurs in plants while as metabolite in the human body[10-16].

Isatin is sparingly soluble in ether. From water, alcohol and acetic acid it crystallizes in red needles form that melt at 200 – 201ºC[17]. Its structure may cause the electrophilic substitution or nucleophilic addition on the carbonyl group carbon atom.

The metal complexes of isatin were found to have pharmacological properties and some of them, especially Co(II) compounds, can form the interesting group of single–molecule magnets (SMMs) with special magnetic applications[18-22]. They show magnetization hysteresis at low temperature occurring the special property of macroscopic magnets and possess a finite magnetization that can be frozen in the absence of an applied magnetic field. At low temperatures, these systems can be considered as a magnet since the relaxation of the magnetization becomes significantly slow[22].

Isatin metal compounds with amino acids are little known. Only a few information about the synthesis of isatin and amino acid ligands are available in the literature[23,24]. Therefore, their studies are important for understanding the relationship between chemical structure and biological macrocycle activities that may indicate their practical use as models in biochemistry systems. Thus, the chemistry of metal complexes with multidentate ligands as isatin with amino acids can gain much interest. The toxicity towards various bacteria, the cytotoxic and inhibitory effects of the obtained compounds on some cells and examination of their impact on living organisms seem interesting.

The aim of our investigations was to synthesize the complexes of new ligand synthesized in reaction of condensation of isatin and glutamic acid, 2-(2-oxoindolin-3-ylideneamino)pentanedioic acid ($C_{13}H_{12}N_2O_5$) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions and to characterize them by various physico-chemical measurements.

2. Experimental

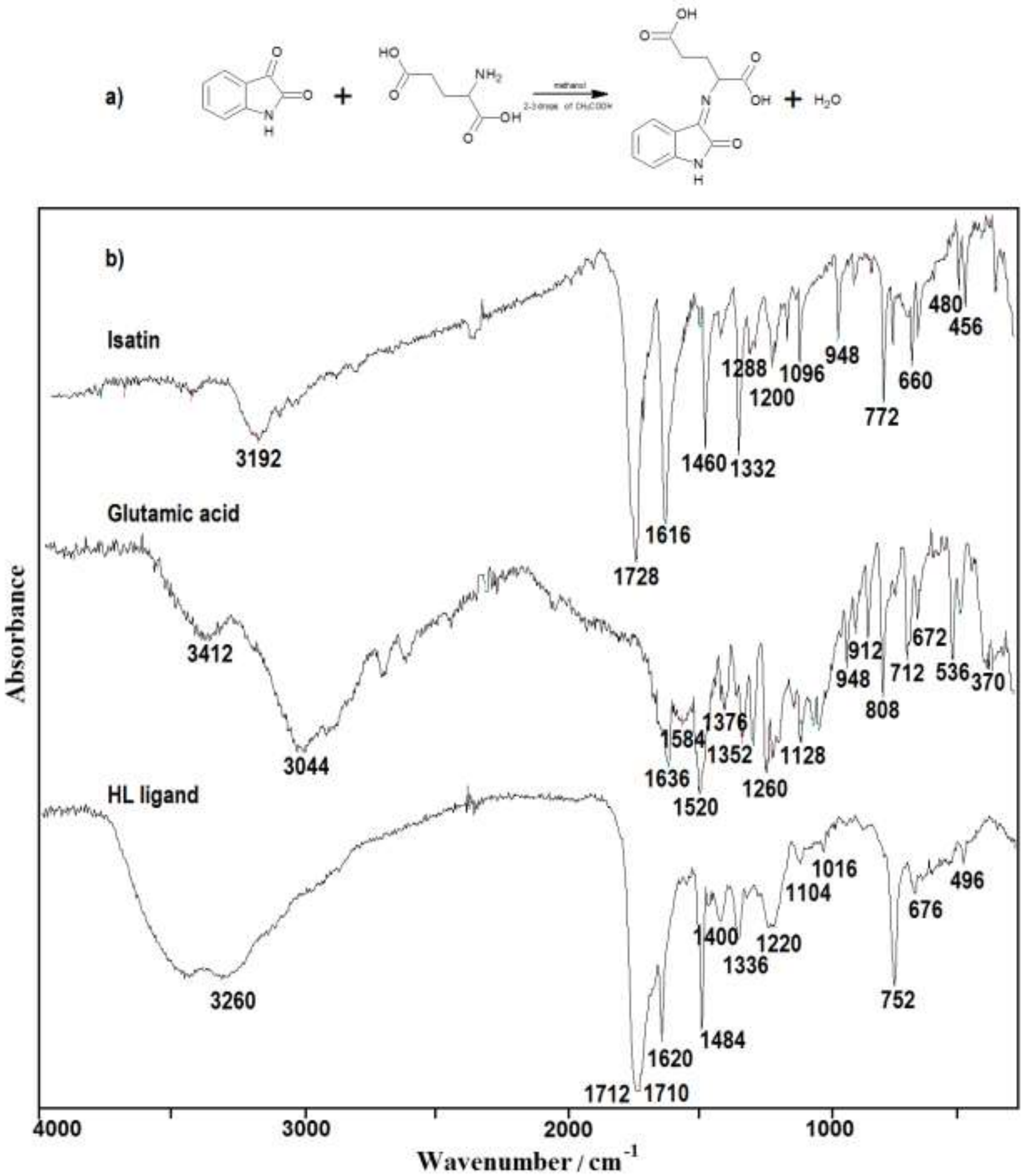
2.1. Materials

All chemicals and solvents used for the syntheses were of commercially available reagent grade and applied without further purification.

2.1.1. Synthesis

Ligand (Scheme 1) was synthesized by refluxing glutamic acid (0.01 mol L^{-1}) (1.47 g) with isatin (0.01 mol L^{-1}) (1.47 g) in 100 mL methanol aqueous solution (99% pure, Aldrich Chemical Company). For the reaching of equilibrium state the solids in solutions were constant heating for 2–3 h in the presence of three drops of glacial acetic acid. They were filtered off, washed with water and methanol and dried at 303 K to constant masses.

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) with ligand were prepared by adding the equivalent quantities of methanol solutions of metal chlorides (3.6 mmol): $MnCl_2 \cdot 4H_2O$ (710 mg), $CoCl_2 \cdot 6H_2O$ (860 mg), $NiCl_2 \cdot 6H_2O$ (860 mg), $CuCl_2 \cdot 2H_2O$ (610 mg) and $ZnCl_2$ (490 mg) (analytically pure, Polish Chemical Reagents in Gliwice – Poland) to a warm methanol solution of H_2L (3.6 mmol, 1000 mg) in the round bottom flask. The pH of solution was adjusted by water ammonia solution dropwise to pH value about 6.5 – 7. Then the reaction mixture was refluxed for 6 – 8 h. It was cooling at room temperature and after partial evaporation filtered off, washed with water and methanol and dried at 303 K to constant mass.



Scheme 1. a) Ligand synthesis, b) FTIR spectra of components used for the synthesis.

2.2. Methods and apparatus applied

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The amounts of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metals were established by X-ray fluorescence XRF method with the use of spectrophotometer of X-ray fluorescence with energy dispersion EDXRF-1510 (Canberra-Packard).

The FTIR spectra of complexes and the products of the intermediate and final complex decompositions were recorded over the range of 4000 – 400 cm^{-1} using an M-80 Perking-Elmer spectrometer. The samples were prepared as KBr discs.

The ^{1}H-NMR spectrum for ligand and Zn(II) compound in DMSO-d_6 was recorded on a Bruker Avance 300 MHz NMR spectrometer at 298.1 K.

The X-ray diffraction patterns of compounds and of their residues after final decomposition processes were taken on a HZG-4 (Carl-Zeiss. Jena) diffractometer with Ni filtered CuK_α radiation. The measurements were made within the range of $2\theta = 4^o – 80^o$ by means of Bragg-Brentano method.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow rate of 20 mL min^{-1} in the range of 297 – 1173 K at a heating rate of 5 K min^{-1}. The initial masses of samples used for measurements changed from 7.85 to 4.09 mg and were heated in Al_2O_3 crucibles.

The TG–FTIR measurements of Mn(II), Co(II) and Zn(II) complexes were performed to identify their gaseous decomposition products on the Q5000 TA apparatus coupled with the Nicolet 6700 spectrophotometer. The experiments were carried out under a dynamic nitrogen atmosphere in flowing nitrogen of 20 mL min$^{–1}$ in open platinum crucibles. The complexes were heated up to 1273 K at a heating rate of 20 K min$^{–1}$. The gaseous decomposition products were analysed over the range of 4000 – 400 cm^{-1} using the Nicolet 6700 spectrophotometer.

Magnetic susceptibility of polycrystalline samples of transition metal compounds was investigated at 76 – 303 K and for some of them at 2 – 300 K. The measurements in the range of 76 – 303 K were carried out using the Gouy's method. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrate employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5}$ cm^3 g^{-1}. The measurements were made at a magnetic field strength of 9.9 kθe. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants[25].

The effective magnetic moment values were calculated from the Eq. 1:

$$\mu_{eff} = 2.83\ (\chi_m \cdot T)^{1/2} \quad (1)$$

where: μ_{eff} - effective magnetic moment, χ_m – magnetic susceptibility per molecule and T - absolute temperature.

The measurements in the range of 2 – 300 K were carried out with the use of Quantum Design SQUID – VSM magnetometer at magnetic field 0.1 T. The superconducting agent may generally operate at a field strength ranging from 0 to 7 T. The SQUID magnetometer was calibrated with the palladium rod sample.

3. Results and Discussion

All synthesized compounds were obtained as powders with the different colours changing from brownish pink, via brown to brick-red ones. Elemental analysis, XRF and thermogravimetric experimental data confirmed them to be hydrated. The molar conductance, magnetic and infrared spectroscopy measurements were made to estimate their structure. The compounds were obtained with general formulae $M(LH)_2 \cdot nH_2O$ for Mn(II), Ni(II) and Zn(II) and $ML \cdot nH_2O$ for Co(II) and Cu(II), where $LH = C_{13}H_{11}N_2O_5^{–}$, $L = C_{13}H_{10}N_2O_5^{2–}$, n = 1 for Mn(II), Cu(II) and Zn(II), n = 2 for Co(II) and n = 3 for Ni(II). Some predictions about the compositions of compounds may be compatible with those in literature[26-30]. In the cited papers the ways of Cu(II) and Pd(II) ion coordination with ligand formed by the glutamic acid and various organic compound condensation reactions are presented. Not having identical compositions to those used by us, these arrangements show that one deprotonated glutamic carboxylic acid group may coordinate to metal ions. As we did not determine the complex structures this fact let us also state the formulae of compounds, especially for Cu(II) and Co(II) ones.

The results of elemental and XRF analyses are as follows:

Ligand $C_{13}H_{12}N_2O_5$, Yield: 78.98% as a brown solid. Anal. Calc. for ligand (%): C, 56.52; H, 4.38; N, 10.14. Found: C, 57.42; H, 4.60; N, 9.85.

$Mn(LH)_2 \cdot H_2O$, Yield: 75.63% as a light brown solid. Anal. Calc. for $MnL_2 \cdot H_2O$ (%): C, 50.09; H, 3.89; N, 8.99; Mn, 8.81. Found: C, 50.82; H, 4.08; N, 8.83; Mn, 7.87. IR: 3384 (ν_{OH}), 3216 ($\nu_{N–H}$), 1724 $(\nu_{C=O})_{ket.}$, 1712 (ν_{COOH}), 1690 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 (ν_{HC-N}), 1408 (δ_{C-H}), 1296 ($\nu_{sCOO–}$), 1196 (ν_{C-N}), 1104 (ν_{Ar}), 752 (δ_{CH}), 580 ($\nu_{M–O}$) cm^{-1}, 416 ($\nu_{M–N}$) cm^{-1}.

$CoL \cdot 2H_2O$, Yield: 83% as a brownish pink solid. Anal. Calc. for $CoL \cdot 2H_2O$ (%): C, 42.41; H, 3.57; N, 7.61; Co, 16.01. Found: C, 41.82; H, 4.06; N, 7.07; Co, 16.19. IR: 3340 (ν_{OH}), 3230 ($\nu_{N–H}$), 1725 $(\nu_{C=O})_{ket.}$, 1692 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468

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($\nu_{HC\text{-}N}$), 1400 ($\delta_{C\text{-}H}$), 1336 (ν_{sCOO-}), 1196 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 752 (δ_{CH}), 644 (ν_{M-O}) cm^{-1}, 460 (ν_{M-N}) cm^{-1}.

$Ni(LH)_2 \cdot 3H_2O$, Yield: 73.11% as a brown solid. Anal. Calc. for $NiL_2 \cdot 3H_2O$ (%): C, 47.07; H, 4.26; N, 8.45; Ni, 8.88. Found: C, 47.30; H, 4.26; N, 7.96; Ni, 9.20. IR: 3376 (ν_{OH}), 3200 (ν_{N-H}), 1704 ($\nu_{C=O})_{ket.}$, 1692 (ν_{COOH}),1680 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1404 ($\delta_{C\text{-}H}$), 1328 (ν_{sCOO-}), 1196 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 752 (δ_{CH}), 580 (ν_{M-O}) cm^{-1}, 456 (ν_{M-N}) cm^{-1}.

$CuL \cdot H_2O$, Yield: 84.87% as a brown solid. Anal. Calc. for $CuL \cdot H_2O$ (%): C, 43.89; H, 3.41; N, 7.87; Cu, 17.86. Found: C, 42.96; H, 3.80; N, 7.28; Cu, 17.50. IR: 3440 (ν_{OH}), 3340 (ν_{N-H}), 1724 ($\nu_{C=O})_{ket.}$, 1696 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1408 ($\delta_{C\text{-}H}$), 1328 (ν_{sCOO-}), 1216 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 756 (δ_{CH}), 680 (ν_{M-O}) cm^{-1}, 488 (ν_{M-N}) cm^{-1}.

$Zn(LH)_2 \cdot H_2O$, Yield: 60.50% as a brick-red solid. Anal. Calc. for $ZnL_2 \cdot H_2O$ (%): C, 49.27; H, 3.82; N, 8.84; Zn, 10.32. Found: C, 49.43; H, 4.12; N, 9.35; Zn, 10.03. IR: 3332 (ν_{OH}), 3248 (ν_{N-H}), 1724 ($\nu_{C=O})_{ket.}$, 1688 (ν_{COOH}), 1680 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1396 ($\delta_{C\text{-}H}$), 1340 (ν_{sCOO-}), 1220 ($\nu_{C\text{-}N}$), 1088 (ν_{Ar}), 748 (δ_{CH}), 640 (ν_{M-O}) cm^{-1}, 460 (ν_{M-N}) cm^{-1}.

The complexes are insoluble in most of the organic solvents except methanol and acetonitrile.

The ^1H-NMR spectrum for H_2L was recorded in DMSO-d_6. The experimental results were not suitable for fair interpretation due to their poor quality, high ratio of background noise to signals and d-electron nature so the results were not presented in this article.

In order to estimate the electrolytic properties of these compounds dissolved in methanol their molar conductance were measured and they were found to be in the range of 8.23 – 33.67 S cm^2 mol^{-1} indicating the analysed complex solutions not to be electrolytes since their molar conductance worths are less than 70 S cm^2 mol^{-1} [23,24].

3.1. Thermal analysis

The thermal stability of complexes was studied in air at 293 – 1173 K (Tab. 1, Fig. 1). When heated to 1173 K they decompose in three stages. First they dehydrate in one step and next being gradually decomposed form ultimately the oxides of appropriate metals with the intermediate formations of oxycarbonates, M_2OCO_3 or their mixtures with the metal oxides.

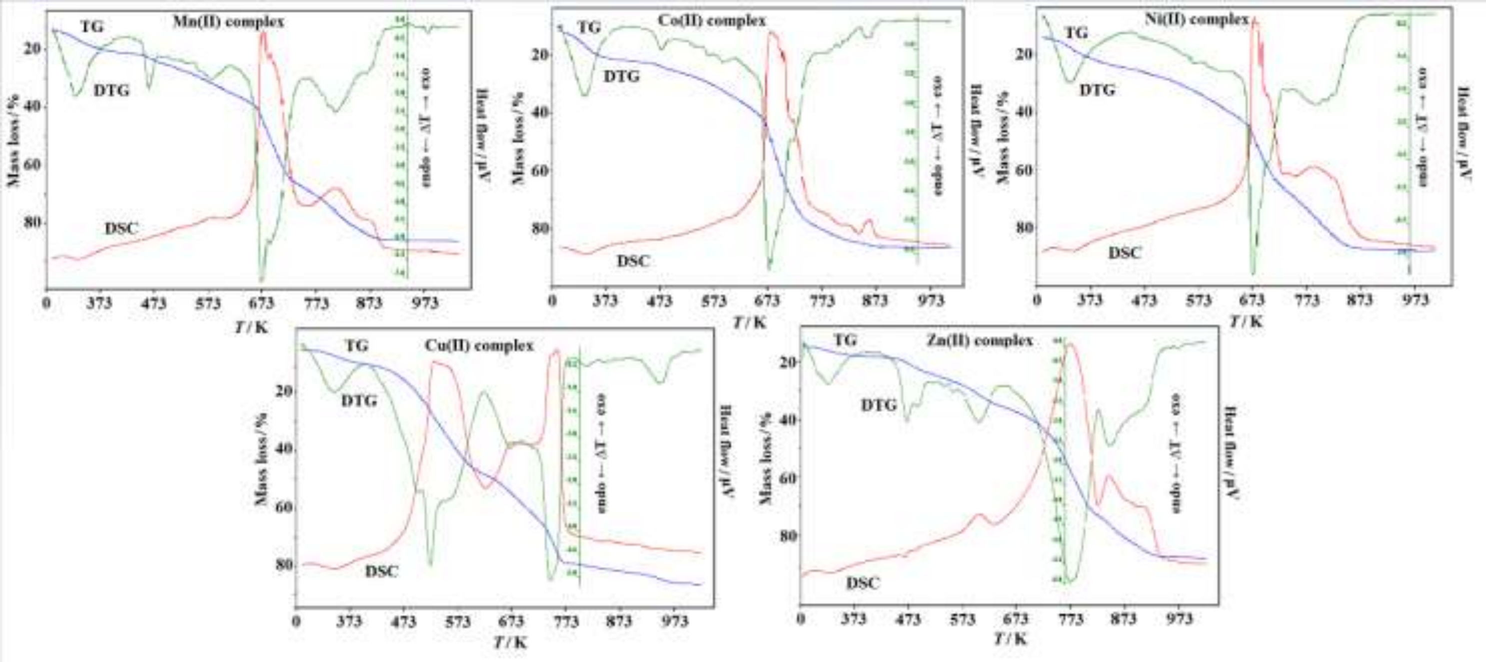


Figure 1. TG, DTG and DSC curves for analysed complexes.

Table 1. Temperature ranges of thermal stability for analysed complexes in air at 293 – 1173 K, their dehydration process and enthalpy values.

Complex	ΔT_1 / K	Mass loss / %		n°	ΔT_2 / K	Mass loss / %		Residue mass / %		T_K/ K	ΔH /	ΔH^o /
		calc.	found			calc.	found	calc.	found		kJ mol^{-1}	kJ mol^{-1}
$Mn(LH)_2{\cdot}H_2O$	310-394	10.40	10.09	4	419-900	86.37	86.36	13.63	13.64	906	52.88	13.22
$CoL{\cdot}2H_2O$	310-390	11.70	12.00	2	423-873	88.85	88.27	11.15	11.73	893	51.40	25.70
$Ni(LH)_2{\cdot}3H_2O$	323-414	12.82	12.45	3	436-970	88.98	89.90	11.01	10.10	973	30.93	10.31
$CuL{\cdot}H_2O$	323-404	5.07	5.02	1	413-1013	85.47	85.02	14.53	14.98	1023	37.78	37.78
$Zn(LH)_2{\cdot}H_2O$	323-388	4.45	4.46	1	423-903	87.44	88.25	12.56	11.75	923	17.74	17.74

$HL^{-}=C_{13}H_{11}N_2O_5^{-}$, $L=C_{13}H_{10}N_2O_5^{2-}$, ΔT_1 - temperature range of dehydration process, n – number of water molecules lost in one step, ΔT_2 - temperature range of anhydrous complex decomposition, T_K – final temperature of decomposition process, ΔH^o - enthalpy value for one molecule of water.

The complexes are stable up to 310–323 K. In the range of 310 – 414 K they dehydrate with an endothermic effect losing all water molecules. The found enthalpy values for one water molecule of dehydration process change from 10.31 to 37.78 kJ mol^{-1}. On further heating of compounds at 413 – 1013 K the oxycarbonates, M_2OCO_3 of the corresponding metals were formed[31] but in the case of Ni(II) and Zn(II) complexes the mixtures of Ni_2OCO_3 and Zn_2OCO_3 with NiO and ZnO were identified. The final products of complex decompositions were following oxides: MnO_2, CoO, NiO, CuO and ZnO. They were identified by X-ray analysis data. For example Fig. 2 presents the diffractogram of the final product of Ni(II) compound decomposition.

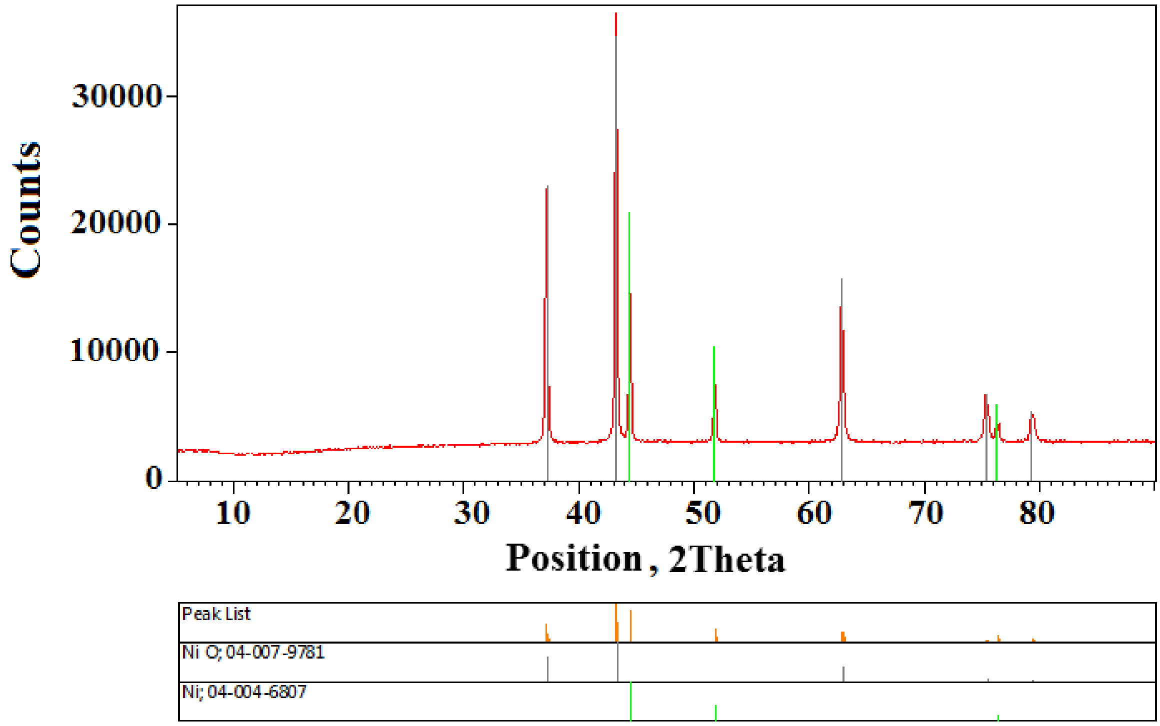


Figure 2. The X-ray powder diffractogram of the final product of decomposition for Ni(II) compound.

The residue masses calculated from TG curves are equal to 10.10–14.98%, while those theoretical were 11.01–14.53%.

The coordination number values of central ion depend mainly on the kind of cation[32,33]. In order to determine them it is necessary to estimate the positions of water molecules in analysed compounds. Not having monocrystal structure data of compounds we can only estimate them taking into account their initial dehydration process temperature values. If water molecules are lost in one step below 423 K they may form outer sphere water[32]. However, if they are coordinated weakly with central atom, they may be released also at low temperature indicating this way their outer sphere character. Then in the presented complexes it is difficult to state if water molecules are in outer or inner coordination positions.

3.2. TG–FTIR Analysis

The TG–FTIR coupled technique was applied for analysed complexes of Mn(II), Co(II) and Ni(II) to identify their gaseous decomposition products. For example the FTIR spectra of the volatile components of mixture evolved during destruction of Co(II) complex are presented in Figs. 3 and 4. Their interpretations reveal that H_2O, CO_2, CO and hydrocarbons are released during heating to 1173 K[34,35]. The heating of Co(II) complex leads to the release of water molecules up to about 393 K. The FTIR spectra show characteristic bands in the regions: 4000–3600 and 1700–1400 cm^{-1} (Fig. 3) due to stretching and deformation vibrations of water molecules[34]. Next, the intensity of gases evolved during heating increases. It is connected with the great liberation of CO_2 molecules. The FTIR spectra show bands at 3800 – 3500 cm^{-1}, 2400 – 2300 cm^{-1} and at about 900 cm^{-1} coming from stretching and deformation vibrations of carbon dioxide. The maximum amounts of CO_2 are observed after 20 minutes of heating at about 580 K. The FTIR spectra show as well the characteristic bands derived from N_2O at 1250 – 1100 cm^{-1} and ammonia molecules at about 1000 – 800 cm^{-1}. Additionally, the bands at 1200 and

1000 cm^{-1} derived from the rocking vibrations of C–H resulting from the $(CH_3)_2N$ moiety are observed[34,35]. Another volatile products of Co(II) compound thermal decomposition in nitrogen are hydrocarbons. Therefore FTIR spectrum contains the bands at 3300 – 3100 cm^{-1}, 1700 – 1650 cm^{-1} and 1500 – 1400 cm^{-1} coming from their molecule stretching vibrations[34,35]. Above 700 K the bands at 2200 – 2100 and 800 cm^{-1} resulting from carbon monoxide vibrations occur. Their highest intensities appear after 30 minutes of heating[34].

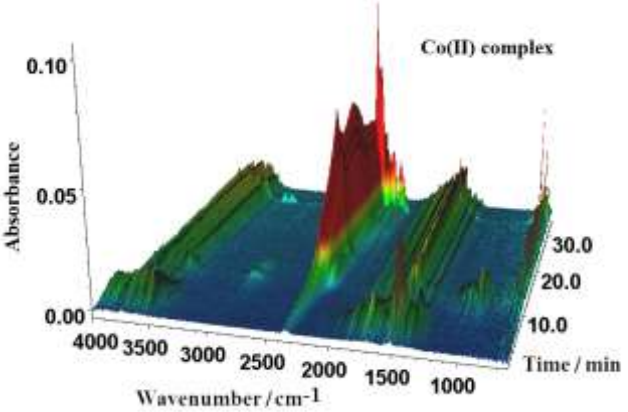


Figure 3. The FTIR spectrum of gaseous products evolved during the decomposition of Co(II) compound.

3.3. X-Ray powder diffraction

X–Ray powder diffraction of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes indicated them to be a crystalline compounds. A number of crystallization trials to obtain the single crystals of analysed complexes with several different solvents (such as H_2O, alcohols, DMSO, DMF and acetonitrile) have been carried out. The compounds were dissolved in pure solvent as well as in solvent mixture. Crystallization test were performed both at room temperature and at 8 °C.

Due to the lack of monocrystals of analysed compounds suitable for measurements, estimation of the unit cell parameters was carried out applying the Dicvol06 programme[36,37] (Tab. 2) using the X–ray powder diffraction data. According to the obtained results all analysed complexes were found to form low symmetry compounds. The complexes of Mn(II), Co(II), Cu(II) and Zn(II) crystallized in monoclinic system while that of Ni(II) in triclinic one[36,37]. All experimental data (angular values and lattice constants of primitive cell) are showed in Tab. 2. The X-ray diffraction patterns and dependences of I/I_0 *vs.* 2θ of analysed complexes are presented in Figs. 5 and 6.

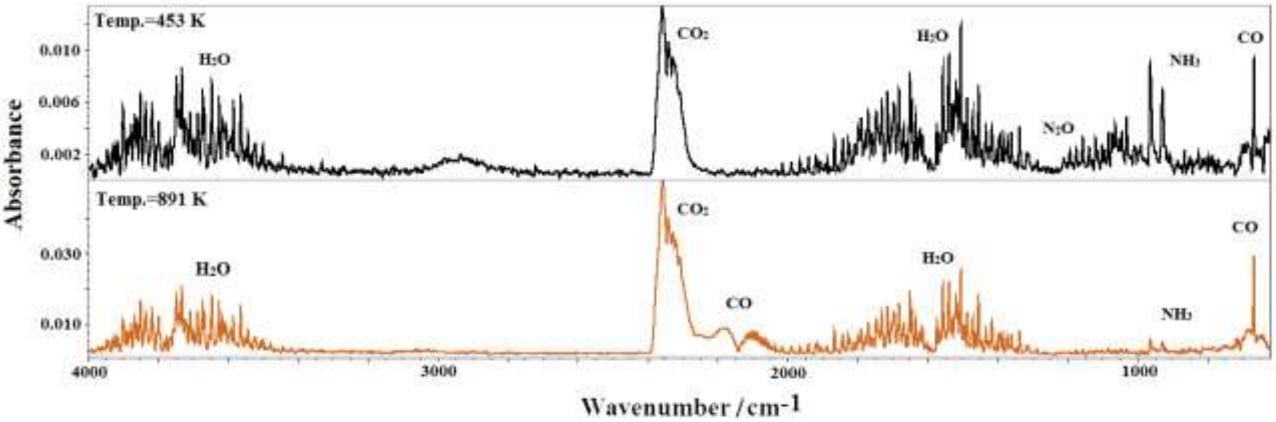
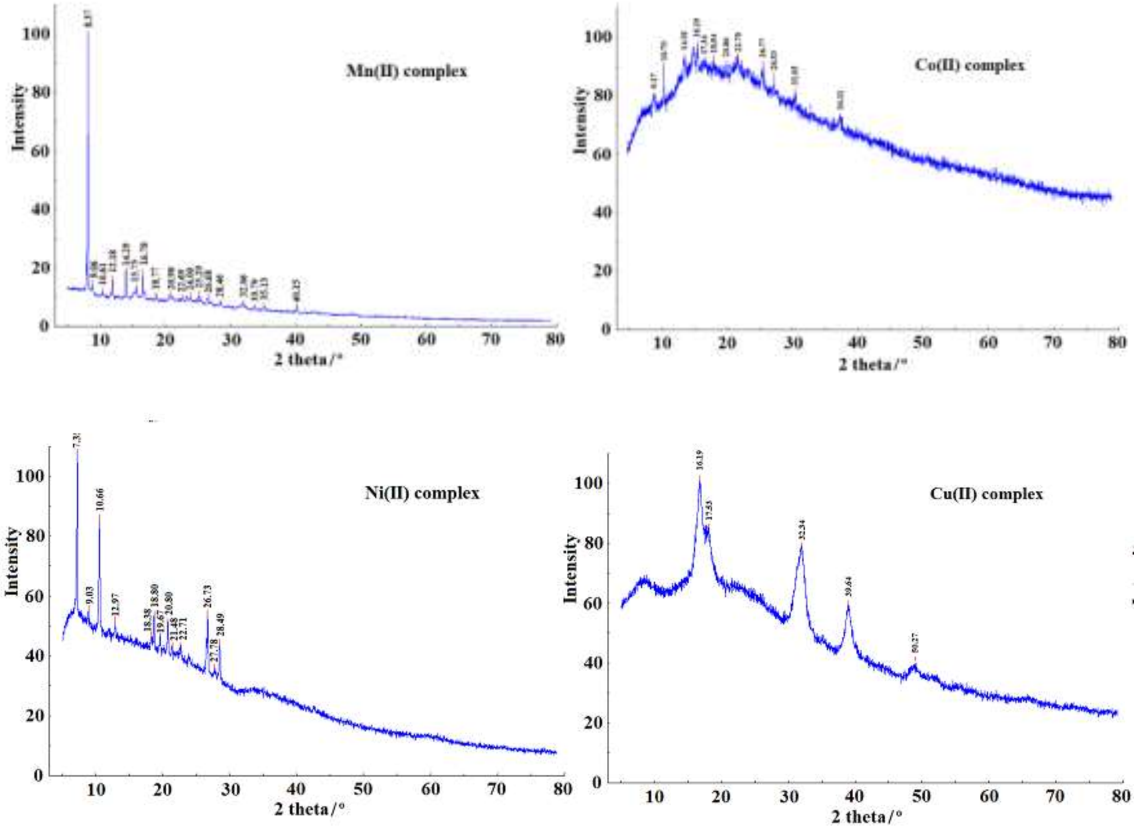


Figure 4. The FTIR spectra of gaseous products for Co(II) complex decomposition in N_2 at 453 and 891 K.

Table 2. The data of unit cell parameters (*α, β, γ, a, b, c* and *V*) obtained for analysed complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the use of Dicvol 06 programme, HL=$C_{13}H_{11}N_2O_5^-$, L=$C_{13}H_{10}N_2O_5^{2-}$.

	$Mn(LH)_2·H_2O$	$CoL·2H_2O$	$Ni(LH)_2·3H_2O$	$CuL·H_2O$	$Zn(LH)_2·H_2O$
a / Å	17.19	8.47	8.26	7.16	12.31
b / Å	5.77	9.57	11.98	12.37	7.66
c / Å	25.27	15.79	15.15	8.85	13.79
α / °	90.00	90.00	94.54	90.00	90.00
β / °	94.77	95.65	91.16	91.12	96.40
γ / °	90.00	90.00	90.19	90.00	90.00
V / Å^3	2499.42	1273.57	1494.81	793.53	1292.42



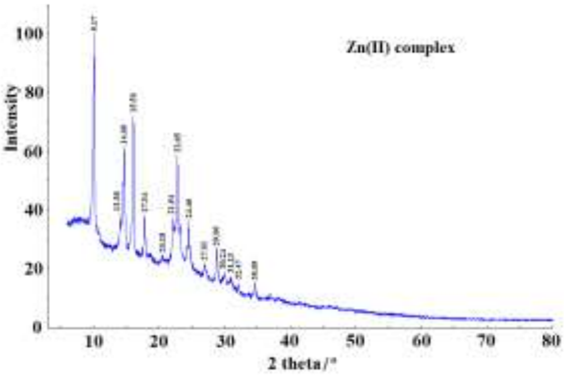


Figure 5. X-ray diffractograms for analysed complexes.

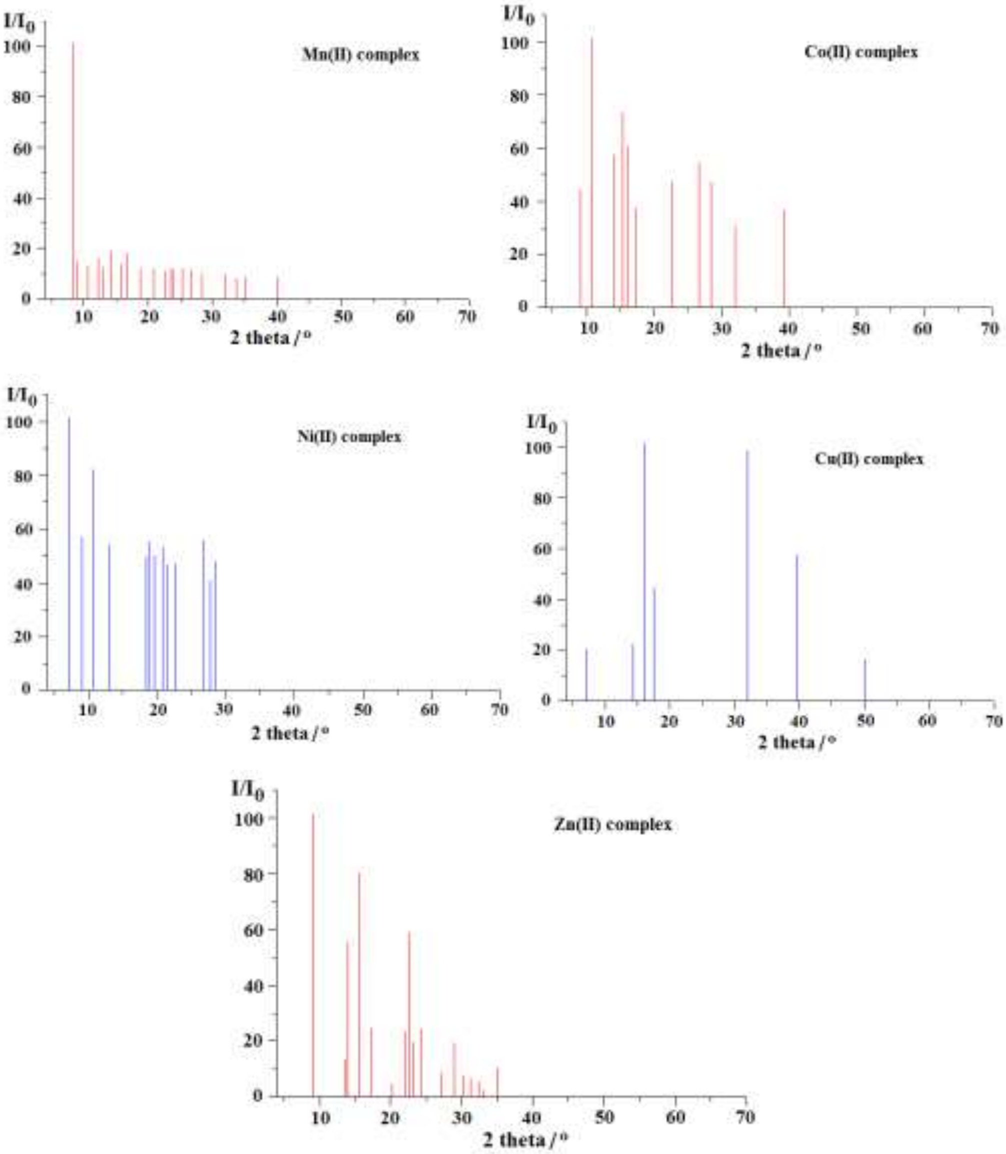


Figure 6. Dependence of I/I_0 vs. 2θ for Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) compounds.

3.4. Infrared spectra

The IR spectrum of ligand exhibits a broad band at 3260 cm^{-1} assigned to the N–H stretching vibration mode, ν(H–N)[34,35]. Also in its spectrum the strong sharp ketonic band of indole group vibration, ν(C=O), appears at 1710 cm^{-1}. A clear band of stretching vibration due to C=N, ν(C=N), appears at 1620 cm^{-1} and band at 1484 cm^{-1} comes from stretching vibration of HC–N group, ν(HC–N). The stretching vibration of C=O from COOH group yields the band at 1712 cm^{-1}, ν(C=O). In the spectrum of ligand, the bands of C=C stretching vibrations, ν(C=C), and C–H scissoring vibrations, δ(C–H), are at 1104 and 752 cm^{-1}, respectively.

In the spectra of analysed complexes, the new wide bands at 3440 – 3332 cm^{-1} appear indicating the presence of water molecules in compounds. It is in good agreement with the results of the elemental analysis and thermogravimetric data. The stretching vibration bands of N–H group, ν(N–H), are present in the region of 3340 – 3200 cm^{-1}. The ketonic bands of indole C=O group vibrations, ν(C=O), occur in their spectra from 1725 to 1704 cm^{-1}. A strong band due to C=N stretching vibrations, ν(C=N), appears at 1620 cm^{-1}. In complex spectra the HC–N vibration band is present at 1468 cm^{-1}. In the spectra of Co(II) and Cu(II) complexes there is not characteristic band of carboxylic acid stretching vibration ν_{COOH} at 1712 cm^{-1} that is splitted into two band peaks of asymmetric and symmetric carboxylate stretching vibrations, ν_{asCOO-} *and* ν_{sCOO}, at 1692 and 1696 cm^{-1} and 1336 and 1328 cm^{-1}, respectively, (Tab. 3). It indicates that two carboxylate anions take part in the metal ion coordination.

Table 3. The frequencies of maximum, cm^{-1}, of absorption bands in FTIR spectra of ligand and its compounds with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), HL=$C_{13}H_{11}N_2O_5^{-}$, L=$C_{13}H_{10}N_2O_5^{2-}$.

Ligand	$Mn(LH)_2{\cdot}H_2O$	$CoL{\cdot}2H_2O$	$Ni(LH)_2{\cdot}3H_2O$	$CuL{\cdot}H_2O$	$Zn(LH)_2{\cdot}H_2O$	
–	3384	3340	3376	3440	3332	ν_{OH}
3260	3216	3230	3200	3340	3248	$\nu_{N\text{-}H}$
1712	1712	–	1692	–	1688	ν_{COOH}
1710	1724	1725	1704	1724	1724	$\nu_{C=O\ ket}$
–	1690	1692	1680	1696	1680	ν_{asCOO-}
1620	1620	1620	1620	1620	1620	$\nu_{C=N}$
1484	1468	1468	1468	1468	1468	$\nu_{HC–N}$
1400	1408	1400	1404	1408	1396	$\delta_{C–H}$
–	1296	1336	1328	1328	1340	ν_{sCOO-}
1220	1196	1196	1196	1216	1220	$\nu_{C\text{-}N}$
1104	1104	1104	1104	1104	1088	ν_{Ar}
752	752	752	752	756	748	$\delta_{C–H}$
–	580	644	580	680	640	$\nu_{M\text{-}O}$
–	416	460	456	488	460	$\nu_{M\text{-}N}$

Bands of CH in plane scissoring vibration, δC–H, bands of C-Car asymmetric ring vibration, νAr, bands of O-H stretching vibration, νOH, bands of C=O stretching vibration, νC=O.

In the case of Mn(II), Ni(II) and Zn(II) complex spectra there are bands of carboxylic acid stretching vibrations, ν_{COOH}, at 1712, 1692 and 1688 cm^{-1} resulting from one carboxylic group that does not coordinate with metal ions. There are also seen the bands of asymmetric and symmetric carboxylate stretching group vibrations, ν_{asCOO-} *and* ν_{sCOO-}, at 1690, 1680 and 1680 cm^{-1} and at 1296, 1328 and 1340 cm^{-1}, respectively (Tab. 3). It suggests that only one carboxylate anion coordinates with central ion. In the spectra of complexes the C=C stretching vibration bands, ν(C=C), and C–H scissoring vibration bands, δ(C–H), are in the ranges of 1104 – 1088 cm^{-1} and 756 – 748 cm^{-1}, respectively.

There are some new bands present in the spectra of compounds not being seen in the ligand IR spectrum. The bands at 680 – 580 cm^{-1} confirmed the presence of the metal ion–oxygen bonds in complexes[38,39]. Their various frequency values may suggest the different stability of M–O bonding. The M–N stretching vibration bands, ν(M–N), in the IR complex spectra appearing at 488 – 416 cm^{-1} indicate the ion metal coordination with nitrogen atom[40,41].

There are the differences between the spectrum of ligand and the spectra of its compounds. In the spectra of complexes are bands at 3440 – 3332 cm^{-1}, characteristic for *ν*(OH) stretching vibrations confirming the presence of water molecules in the compounds. These bands are not in the ligand spectrum. Ketonic bands of indole C=O stretching vibrations, *ν*(C=O), in the spectra of compounds occur in the range of 1725 – 1704 cm^{-1}, while in the H_2L spectrum it appears at 1710 cm^{-1}. The different values of those band frequencies may suggest the C=O group coordination with metal ions in the complex molecules[34,35]. A band due to azomethine nitrogen stretching vibration, *ν*(HC–N), occurs at 1484 cm^{-1}
in the ligand spectrum whereas in all the complex spectra it is observed only at 1468 cm^{-1}. Therefore, azomethine nitrogen was found to coordinate with metal ions.

In the spectrum of ligand and in the spectra of compounds the bands resulting from C=N and C=C, stretching vibrations, *ν*(C=N), *ν*(C=C), and C–H scissoring vibrations *δ*(C–H), occur at 1620, 1104 – 1088 and 756 – 748 cm^{-1}, correspondingly.

3.5. Magnetic measurements

The magnetic susceptibility of Mn(II), Co(II), Ni(II) and Cu(II) compounds was measured in the ranges of 77 – 303 K and 2 – 300 K.

The effective magnetic moment values experimentally determined in the range of 77 – 303 K changed from: 4.24 to 4.34 μ_B for Mn(II), 3.05 – 3.25 μ_B for Co(II), 3.09 – 2.65 μ_B for Ni(II) and 1.21 to 1.47 μ_B for Cu(II) complexes while those at 2 – 300 K varied from: 3.09 to 5.02 μ_B for Mn(II), 2.22 to 3.12 μ_B for Co(II), 3.12 to 3.87 μ_B for Ni(II), 0.79 to 1.31 μ_B for Cu(II) complexes. The molar susceptibility measurements for helium temperatures were carried out in an applied magnetic field of 0.1 T.

All analysed compounds demonstrate paramagnetic properties and obeyed the Curie–Weiss law. Their magnetic susceptibility values decreased with increasing temperature[42-48]. The dependences of magnetic susceptibility, χ_m^{corr}, its reciprocal values and also $\chi_m^{corr}*T$ worths as a function of temperature for Mn(II) and Cu(II) complexes are presented in Figs. 7 and 8.

At a high temperature region, the magnetic moment values approached the theoretical values Tab. 4. They seem close to spin only values which were calculated at room temperature from the equation $\mu_{\text{eff}}=[4s(s + 1)]^{1/2}$ for Mn(II), Co(II), Ni(II) and Cu(II) ions and are equal to 5.92; 3.88; 2.83 and 1.73 μ_B, respectively.

The obtained data indicated that there is no significant orbital contribution to the magnetic moments of the complex, or its contribution may be essential.

Values of μ_{eff} = 3.09 – 5.02 μ_B for Mn(II) compound may suggest that it is high-spin compound with weak ligand field[42–43] and its sp^3d^2 hybridization[44]. The electronic configuration in this case for Mn(II) ion is $t_{2g}{}^3e_g{}^2$. The magnetic moment values changed from 3.09 μ_B (at 2 K) to 5.02 μ_B (at 300 K). At 300 K the $\chi_m{\cdot}T$ value is equal to 3.1416 cm^3 K mol^{-1} (Fig. 7). With a lowering of a temperature its value decreases to 2.6774 cm^3 K mol^{-1} (at 43.35 K) which perhaps results from the antiferromagnetic interaction between the magnetic centres of complex. At the temperature values lower than 43.35 K, the worths of $\chi_m{\cdot}T$ drastically decrease to 1.1914 cm^3 K mol^{-1} (at 2 K). It indicates the antiferromagnetic interaction around magnetic centres as well. The values of magnetic moments are lower than that theoretically calculated. Probably the vectors L and S are aligned by the strong field of the heavy atom in opposite directions which diminishes the resultant magnetic moment. The analysed Mn(II) complex seems high – spin with octahedral symmetry of Mn(II) ion. In the coordination sphere of Mn(II) ion may be four oxygen atoms, two of them coming from monodentate carboxylate groups, two others from indole groups and there are also two nitrogen atoms of azomethine groups. However due to the lack of crystallographic data this interpretation seems rather speculative based only on magnetic moment values and IR spectra data interpretations.

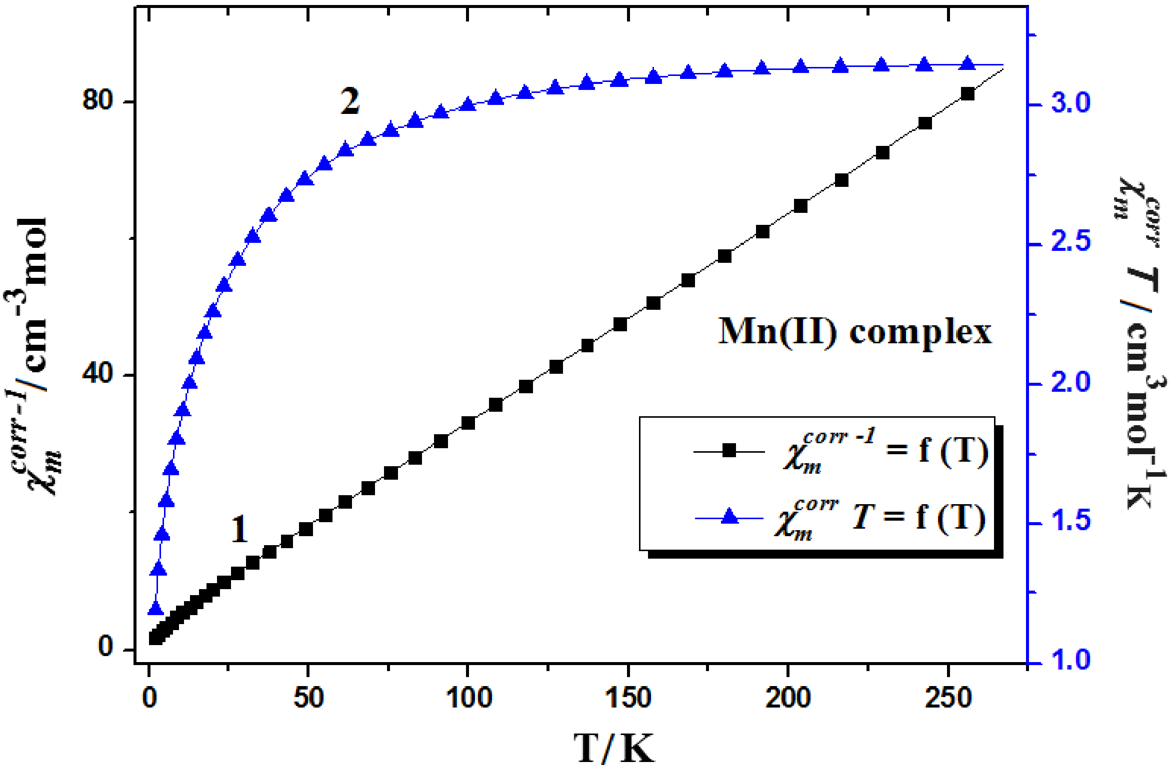


Figure 7. Dependence of (1) χ_m^{corr-1} and (2) $\chi_m^{corr}\cdot T$ values *vs*. *T* for Mn(II) complex.

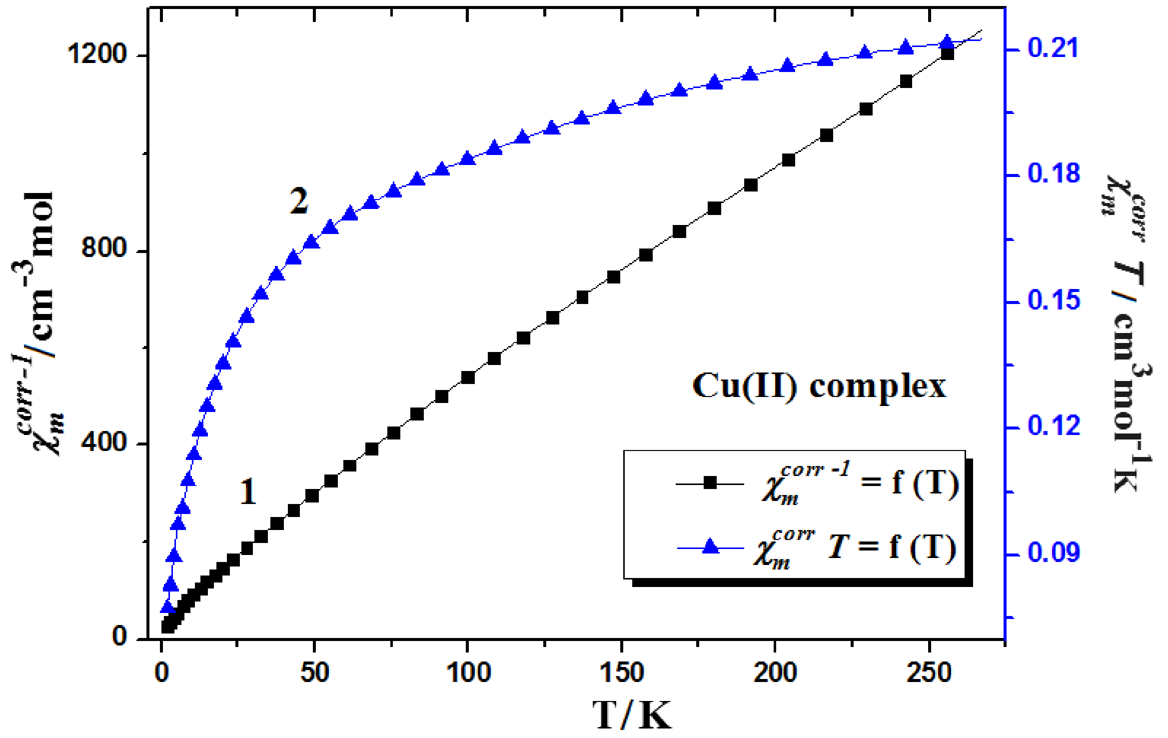


Figure 8. Dependence of (1) χ_m^{corr-1} and (2) $\chi_m^{corr}\cdot T$ values *vs*. *T* for Cu(II) compound.

Table 4. The comparison of spin only values of magnetic moments (μ_B) for ions of Mn(II), Co(II), Ni(II), Cu(II) with those experimentally found for their complexes in literature[42-46] and measured in our experiments

	Central atom			
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Number of *d* electrons	5	7	8	9
High–spin complex				
Number of unpaired electrons	5	3	2	1
Spin-only moment (μ_B)	5.92	3.88	2.83	1.73
Magnetic moment (μ_B) literature data	5.32–6.10	4.30–5.20	2.80–3.50	1.70–2.20
Low–spin complex				
Number of unpaired electrons	1	1	0	
Magnetic moment (μ_B) literature data	1.80–2.10	1.80		
Gouy's method experimental data (76-303 K)	4.24–4.34	3.05–3.25	3.09–2.65	1.21–1.47
SQUID–VSM experimental data (2-300 K)	3.09–5.02	2.22–3.12	3.12–3.87	0.79–1.31

For Co(II) complex the values of magnetic moment values changed from 2.22 (at 2 K) to 3.71 μ_B (at 7.88 K) showing magnetic saturation and then with the increasing temperature it changed to 3.12 μ_B (at 300 K). At 300 K the $\chi_m^{corr}\cdot T$ value was equal to 1.2117 cm^3 K mol^{-1} (μ_{eff} = 3.12 μ_B). Upon temperature lowering the $\chi_m^{corr}\cdot T$ and the magnetic moment values at first gradually increase and next evenly decrease to 0.9215 cm^3 K mol^{-1} at 20.8982 K. Next with the cooling of the sample the $\chi_m^{corr}\cdot T$ values increase rapidly, changing their values from 0.9215 to 1.7149 cm^3 K mol^{-1} (at 7.8803 K) reaching the saturation paramagnetic state and gain the magnetic moment value 3.71 μ_B, (Neel temperature). At 7.8803 K the complex shows the paramagnetic properties, while next changing temperature from 7.8803 to 2 K, the $\chi_m^{corr}\cdot T$ values again rapidly decrease to 0.6159 $cm^3\cdot mol^{-1}$. It results from the antiferromagnetic order between Co(II) centres or from the possible intermolecular hydrogen bonds in the compound crystal lattice[49]. This drastic decrease of $\chi_m^{corr}\cdot T$ indicates a negative θ value which may confirm the antiferromagnetic intermolecular interaction. The magnetic moment values are lower compared to that theoretically calculated. The electronic configuration in Co(II) ion under ligand field influence is $t_{2g}^5e_g^2$.

For Ni(II) ion complex the magnetic moments change from 3.12 μ_B (at 2 K) to 3.87 μ_B (at 300 K). At 300 K the χ_mT value is equal to 1.8659 cm^3 K mol^{-1}. With a lowering of a temperature its value increases to 18.4818 cm^3 K mol^{-1} at 8.9516 K and then drastically decrease to 1.7149 cm^3 K mol^{-1} at 2 K. It is connected with antiferromagnetic interactions that occur in Ni(II) centre, (θ has negative sign). At 8.9516 K (Neel temperature) the complex shows the paramagnetic properties. The magnetic moment values are higher than that calculated theoretically which may indicate the ferromagnetic interaction around the Ni(II) ion. These values may suggest the octahedral environment of Ni(II) ion[49]. The electronic distribution in Ni^{2+} cation in the ligand field may be $t_{2g}^6e_g^2$.

For Cu(II) compound the magnetic susceptibility values decrease with rising temperature. The magnetic moment values change from 0.79 μ_B (at 2 K) to 1.31 μ_B (at 300 K). At 300 K the $\chi_m^{corr}\cdot T$ value was equal to 0.2145 cm^3 K mol^{-1} (μ_{eff} = 1.31 μ_B). Upon temperature lowering the $\chi_m^{corr}\cdot T$ and the magnetic moment values decrease very slowly to 0.1622 cm^3 K mol^{-1} (μ_{eff} = 1.14 μ_B) at 45.15 K (Fig. 8). Next their values drastically decrease from 0.1622 cm^3 K mol^{-1} at 45.15 K to 0.0773 cm^3 K mol^{-1} (0.79 μ_B) at 2 K. This sudden decrease could be caused by crystal field effect, as well as the antiferromagnetic interactions between neighbouring 3d metal ions (interaction between magnetic centres of complex) or intermolecular hydrogen bonds in molecular crystal structure[48]. The study of magnetostructural data may indicate that ferromagnetic and antiferromagnetic coupling between adjacent orbitals (d orbitals of the metal ions and the symmetry adapted linear contribution of the ligand orbitals) on Cu neighbouring ions[48]. The magnetic moment values experimentally determined for Cu(II) compound are lower than that theoretically calculated (μ_{eff} = 1.73 μ_B). This may suggest a bidentate character of carboxylate group. However, this formulation seems rather uncertain because of the lack of crystal data. The coordination sphere may have the shape of a trigonal pyramid with one nitrogen and three oxygen atoms in its corners. Two oxygen atoms derived from carboxylate groups from glutamic acid part and third one from indole group of isatin ring. The apex of the pyramid forms a nitrogen atom from the azomethine group. The complex may have a tetragonal geometry around Cu(II) ion[49].

4. Conclusions

The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions form hydrates with 2-(2-oxoindolin-3-ylideneamino)pentanedioic acid anion containing from 1 to 3 water molecules. The compounds are crystalline. The compounds of Mn(II), Co(II), Cu(II) and Zn(II) crystallize in monoclinic while that of Ni(II) in triclinic systems.

Their thermal stability was studied in air at 293 – 1173 K. The complexes are decomposed in three steps. First, they dehydrate in one step releasing all water molecules and form anhydrous compounds to be next decomposed to the oxides of appropriate metals. The enthalpy values of dehydration processes were determined as well. With the rise of temperature, the hydrates release the water molecules the presence of which in the gaseous mixture was confirmed by the bands in the range of 4000–3600 and 1700–1400 cm^{-1}. During heating the complexes being decomposed release the CO_2, CO, hydrocarbons gaseous molecules, the presence of which in the gaseous mixture was identified by FTIR spectra. The magnetic susceptibility of complexes was investigated in the ranges of 77 – 303 K and 2 – 300 K. All of them obey Curie-Weiss law showing the paramagnetic properties. In the molecular central ion, the ferromagnetic or antiferromagnetic interactions occur.

From the obtained results it appears that in Co(II) and Cu(II) complexes two carboxylate groups take part in the metal ion coordination while in those of Mn(II), Ni(II) and Zn(II) only one carboxylate anion coordinates to central metal. The second carboxylic group does not coordinate with central ions.

5. References

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