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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF Fe(III), Mn(II) AND Cu(II) COMPLEXES WITH N'-MALEOIL-SALICYLIC-HYDRAZID

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*$[Fe(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot 3(C_3H_7NO)$ (**1**), $[Mn(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot 3(C_3H_7NO)$ (**2**) and $[Cu(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot 3(C_3H_7NO)$ (**3**)complexes have been synthesized and characterized by elemental analysis, FT-IR and EPR spectra, magnetic susceptibility and thermal analysis. All complexes show distorted octahedral geometry. In 1, 2 and 3complexes, metal ions are coordinated by means of two oxygen atoms of salicylic residue and two nitrogen atoms bonded with maleic residue and two water molecules.*

Keywords: *synthesis, Fe(III), Mn (II) and Cu(II) complexes, thermal behavior, magnetic properties*

1. Introduction

Hydrazides of carboxylic and dicarboxylic acids are of theoretical and practical interest. An emphasis laid on these compounds is due, first of all, to their ability to change the dentation depending on reaction conditions and form both mononuclear and polynuclear complexes. N'-acylsalicyl-hydrazides contain two or three nitrogen and oxygen donor atoms which can coordinate with metal atoms and give rise to various structural types such as trinuclear polymer [1], hexanuclear, octanuclear, decanuclear and dodecanuclear metalladiazamacrocycles [2-4].

At present, quite a lot of theoretical and experimental data have been accumulated on the physical-chemical properties, composition and structural features of transition metal complexes. This is due to the fact that many of their coordination compounds have high physiological activity to serve as a basis for creating promising materials. In particular, they are based on characteristic hydrazides complexes TB [5-6], anticancer [7-9], anti-malaria [10] and antimicrobial [11-12] activity and bactericidal, fungicidal, and antiviral [13] effect.

The aim of our work is to search for ligands that form polynuclear complexes. With that end in view, we synthesized a N'-acylsalicylhydrazide ligand [(2-hydroxy-benzoyl) of hydrazinyl]-4-oxobut-2-enoic acid (H_4L) by means of the method [14] based on the following: it is a potential heptadentate ligand with –OH, -COOH and –CONHNHCO- which can construct multinuclear coordination polymers with transition metals. However, as shown in the work, this compound together with Fe(III), Mn(II) and Cu(II) ions behave as a bidentate monoanionic ligand.

2. EXPERIMENTAL

2.1. Measurements

Note that IR spectra were recorded on a NicoletIS10 Spectrometer using KBr discs in the range 4000–400 cm^{-1}. The ^1H and ^{13}CNMR spectra were obtained on a BrukerDPX-400 Spectrometer using MeOD-solvent at 300 K. Magnetic moments at 25°C were determined using the Faraday method with $Hg[Co(SCN)_4]$ as calibrant.

2.2 Synthesis of H_4L (N'-maleoyl-salicylic hydrazide)

Salicylhydrazide was synthesized according to the literature procedure.
Maleic anhydride (0.981 g, 10 mmol) was added to the solution of methanol (40 mL) with salicylhydrazide (1.52 g, 10.0 mmol) at room temperature. The reaction mixture was stirred. The reaction was over in a short time (5~10 min) with higher yields. The white crystalline product was washed with methanol, and dried on air. The purity of the ligand was checked by IR spectra, and melting point. Yield: 95% m.p. 188^0C; Found: C, 52.8; H, 4; N, 11.2 %. Anal. Calcd. for: $C_{11}H_{10}O_5N_2$ C, 53.4; H, 4.2; N, 10.8 %.^{1}H NMR (MeOD), δ ppm: 7.92 (d, 1H, o-PhCH); 7.46-7.43(m,1H;p-PhCH), 6.98-6.96(m, 2H m-PhCH), 6.41-6.39 (m, 2H; -CH=CH-); ^{13}C NMR (MeOD), δ ppm:166.92 (-COOH-), 166.03 (-CO-PA),163.54 (Ph-CO-), 158.53 (PhC-OH), 134.01($_{-NHCO-}$CH=), 131.76 (p-PHC), 129.94 (=CH$_{-COOH}$), 128.82 (o-PhC), 119.25 (m-Ph), 116.77 (PhC$_{-CO-}$), 114.74 (m-PhC$_{-C-OH}$); IR (KBr pellet, cm-1): νN-H, 3029vs; broad;νC=O, 1704s; νC=C, 1659 s; νC=N, 1610 s; νNC=O, 1525vs; δN-H, 1490vs; νC-OH (phenolic), 1228 s, 1160 s.

2.3 Synthesis of complexes

2.3.1 Synthesis of $[Fe(H_3L)_2{\cdot}2H_2O]{\cdot}3DMF$

Solution of H_4L (0.25g, 0.1mmol) in methanol and DMF (2:1), and solution of $FeCl_3$ (0.135 g, 0.05mmol) in methanol were mixed and stirred for 0.5 h. Then the solution obtained was adjusted to pH = 8-9 by NH_4OH.

Further, the solution was stirred for 1 h and filtered. After slow evaporation of the mother solution within a month, a dark brown precipitate of **1** was obtained from the filtrate in 45% yield.

2.3.2 Synthesis of $[Mn(H_3L)_2{\bullet}2H_2O]{\bullet}3DMF$

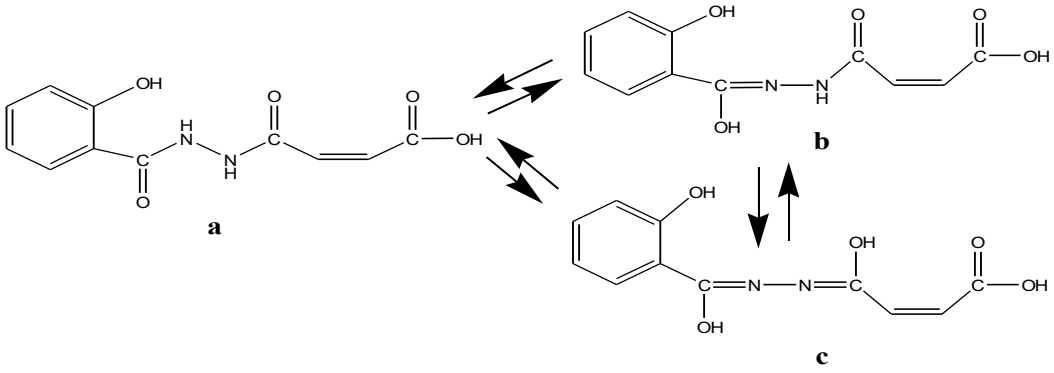
The complex was prepared in a manner similar to that used for **1**; a brown precipitate was obtained in 55% yield.

2.3.3 Synthesis of $[Cu(H_3L)_2{\bullet}2H_2O]{\bullet}3DMF$

The complex was prepared in a manner similar to that used for **1**; a dark green precipitate was obtained in 62% yield.

3. RESULTS AND DISCUSSION

The ligand H_4L was obtained by a method different from the one known in literature [10], under relatively mild conditions by reaction of salicylhydrazide with maleic anhydride in a methanol solution. The structure of the prepared hydrazide ligand was studied by elemental analyses, IR, and ^{1}H and ^{13}C NMR spectral studies. The results obtained are in good agreement with those calculated for the suggested formula, and the melting point is sharp indicating the purity of the prepared ligand (H_4L) (Scheme 1.).



Scheme 1. *H_4L **a**- diketo-form, **b**-mono-enol form, **c**-dienol form*

3.1 Spectral characterization

Note that the IR spectra of thehydrazide ligand contain a strong C=O absorption band at 1704 cm^{-1} and N–H absorption band at 3029 cm^{-1}. Bands at 1228 cm^{-1} is assigned to the stretching vibration of ν(Ph-O). For all complexes, the absence of stretching band N-H and C=O is consistent with deprotonation of CONH groups and coordination with metal ions in enol form. Also, the characteristic absorptions at 1607cm^{-1} indicate the presence of C=N-N=C group (scheme 1-c). The complexing process involves the oxygen of the carbonyl group of the salicylic residue and the nitrogen atom bonded with the maleic residue. Deprotonation and coordination can also be confirmed by band at 524-534 cm^{-1} (M-O bonds) and 406-466 cm^{-1} (M-N bonds) respectively. Note that the absence of carboxyl absorption band is explained by the formation of strong intermolecular hydrogen bonds due between of O (carboxyl group) and H (phenolic), O (carboxyl group) and H (crystallization water).

3.2 Elemental analysis

Elemental analysis data show that $Fe^{2+,}$ Mn^{2+} and Cu^{2+} ions form complexes of the composition $M(LH_3)_2$ (where M is the metal ion and LH_3 is the singly ionized ligand). Fig. 1.

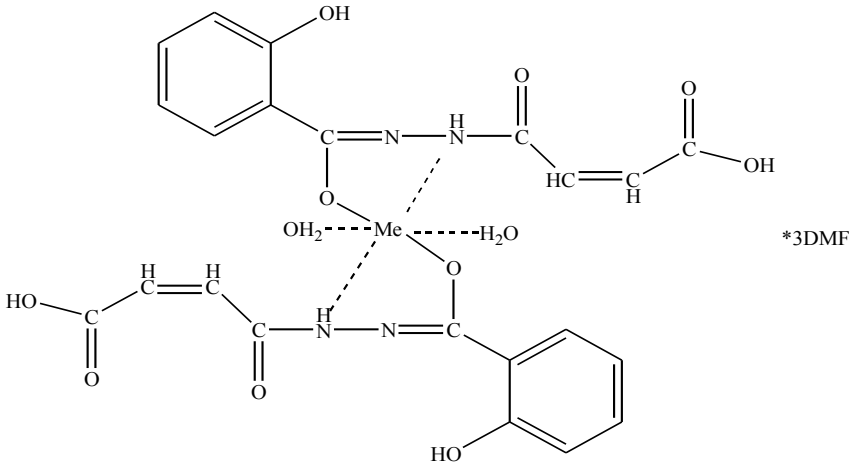


Fig. 1 The structure of complexes

3.3. Thermal Analysis (TG)

Thermogravimetric analysis showed that the decomposition of compounds occurs in two stages. The main weight loss occurs at the first stage within the temperature range 250-350^{0}C (55-75%, depending on the nature of metal ion); at the second stage within the temperature range of 400-600^{0}C; the final decomposition takes place to form appropriate oxides. Note that the amount of oxides remaining after the decomposition corresponds to the content of metals in the complexes (Table 1).

Table 1. Some characteristics of synthesized compounds

Compounds	Brutto-formula	T_m, ^{0}C	Elemental analysis, % Calc./anal.					M_r, q\mol
			C	H	N	O	M	
I	$C_{11}H_{10}O_5N_2$	188	53.4	4.2	10.81	31.59	-	250
			52.8	4	11.2	32	-	
II	$C_{22}H_{18}O_{10}N_4Fe$	>260	47.65	3.25	10.11	28.88	10.11	554
			47.45	3.28	10.02	27.87	11.38	
III	$C_{22}H_{18}O_{10}N_4Mn$	>260	47.75	3.26	10.13	28.93	9.93	552.9
			47.72	3.34	9.49	28.23	11.22	
IV	$C_{22}H_{18}O_{10}N_4Cu$	>260	46.98	3.21	9.96	28.47	11.38	562
			47.01	3.18	9.89	28.28	11.64	

3.4. EPR spectra

The EPR spectra of all complexes in the polycrystalline state are practically symmetrical singlet indicating a high degree of symmetry around the metal ion close to the octahedral one. The intense signals observed in iron and manganese complexes are manifest on high-spin ^{6}S ground state of Fe(III) ions (d^5-configuration) and Mn(II). The values of ΔH and g-factors for complexes **1** and **2** have values of ΔH = 1400 G and ΔH = 800 G and g = 2.02 and g = 2.014 respectively. As for the Cu(II) complex (**3**), the line width peak to peak is ΔH = 350 G, and the g-factor is 2.12.(fig.2).

3.2. Magnetic susceptibility

The iron complex shows the value of the magnetic moment equal to 5.71 B.M. at room temperature, manganese - 5.90 B.M, and copper - 1.9 B.M. It revealed that the complexes have magnetic moments in the normal range typical for octahedral complexes.

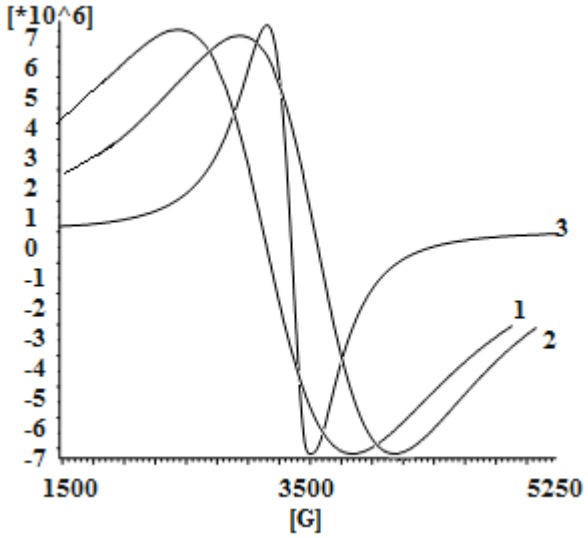


Fig.2 EPR spectra of complexes **1**, **2**, and **3**.

4. CONCLUSION

$[Fe(H_3L)_2•2H_2O]•3DMF$,$[Mn(H_3L)_2•2H_2O]•3$ DMF and $[Cu(H_3L)_2•2H_2O]•3DMF$ have been prepared on the basis of N'-maleoyl-salicylic hydrazide and characterized by elemental analysis, FT-IR,magnetic susceptibility and thermal analysis. It found that the ligand behaves as a monoanionicbidentate where the ligand is in the enol form and coordinates with metal ions through the oxygen atoms of salicylic residue and nitrogen atom bonded with maleic residue.

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N'-MALEOİL-SALİSİLHİDRAZİD İLƏ Fe(III), Mn(II) VƏ Cu(II) KOMPLEKSLƏRİNİN SİNTEZİ VƏ SPEKTROSKOPİK XÜSUSİYYƏTLƏRİ

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*$Fe(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**1**), $[Mn(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**2**) və $[Cu(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**3**) kompleksləri sintez edilmiş və element analizi, İQ- və EPR spektroskopiya, maqnit həssaslığı və termiki analiz vasitələri ilə tədqiq edilmişdir. Bütün komplekslər təhrif edilmiş oktaedrik quruluş əmələ gətirir. **1**, **2** və **3** komplekslərində metal ionları iki liqand molekulunun salisil qalığının oksigen atomu, malein qalığı ilə birləşmiş azot atomu və iki molekul su ilə koordinasiya olunur.*

Açar sözlər: *sintez, Fe(III), Mn (II) və Cu(II) kompleksləri, termiki analiz, maqnit həssaslığı*

СИНТЕЗ И СПЕКТРОСКОПИЧЕСКИЕ ХАРАКТЕРИСТИКИ КОМПЛЕКСОВ Fe(III), Mn(II) И Cu(II) С N'-МАЛЕОИЛ-САЛИЦИЛГИДРАЗИДОМ

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*Были синтезированы комплексы $Fe(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**1**), $[Mn(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**2**) и $[Cu(C_{11}H_9N_2O_5)_2(H_2O)_2]\cdot3(C_3H_7NO)$ (**3**) и охарактеризованы элементным анализом, ИК- и ЭПР спектрами, магнитной восприимчивостью и термическим анализом. Все комплексы показывают искаженную октаэдрическую геометрию. В комплексах **1,2 и 3** ионы металлов координируются с двумя молекулами лиганда посредством двух атомов кислорода салицилового остатка, двух атомов азота, связанных с малеиновым остатком и двумя молекулами воды.*

Ключевые слова: *синтез, комплексы Fe(III), Mn (II) и Cu(II), магнитная восприимчивость, термический анализ.*

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