

SYNTHESIS, SPECTROSCOPIC AND THERMAL STUDIES OF SOME SULFA DRUGS SCHIFF BASES AND THEIR METAL COMPLEXES

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ABSTRACT

New Co(II), Ni (II), Cu (II), Zn(II), Mn (II) and Fe (III) complexes of Schiff bases have been prepared and characterized by elemental analysis, IR, Uv - vis. atomic absorption spectra, conductometric measurements and thermogravimetric analysis. The thermal decomposition of the complexes follows first order, kinetics and thermodynamic parameters of the decomposition were calculated.

Key words:- Spectroscopy, Thermal analysis, Thermodynamic parameters.

INTRODUCTION

Schiff bases are widely use for synthesis of many complexes as ligands such as in the synthesis of complexes of transition metals. Schiff bases derived from sulfa drugs have acquired wide interest for their useful applications in biological systems. It is known that the metal complexes are mach more active than the ligands¹.

New Co (II), Cu (II) and Zn (II) complexes of the chelates of 3-methoxy salicylidene-2-aminothiophenol Schiff bases have been prepared and characterized by elemental analysis, IR and ¹H-NMR spectroscopy, thermogravmetric analysis, conductometric and magnetic measurement². Abo Aly and Khalil also assigned the modes of the ligand salicylidene -2-ammothiophenol (SATP)³.

Complexes of nickel (II) of N,N'- disalicylidene -1,2-phenylenediamine (H₂ dsp), N, N' - disalicylidene -3,4- diaminotoluene (H₂ dst), 4-nitro- N, N'-disalicylidene-1,2-phenylene-

diamine (H₂ ndsp) and N,N'-disalicylidene ethylenediamine (H₂ salen) have been prepared and characterized by elemental analysis, electronic spectra, IR, magnetic susceptibility measurement, ¹H NMR and thermal studies⁴.

A number of Ni (II) complexes with tridentate Schiff bases ligands with a N₂O donor set and coordinating NNN⁻ and SCN⁻ anions have been synthesized and characterized by analytical spectroscopic and electrochemical techniques⁵.

A new polydentate Schiff base (H₃L) was synthesized from the condensation of 2,6-diformyl-4-methylphenol and S-methyl-hadrazine carbodithionate. The complexes were characterized by elemental analysis and IR spectroscopy,detailed studies of the thermal properties of the complexes were investigated by thermogravimetry techniques⁶.

The present article is devolved to characterization spectroscopic and thermal studies of some Schiff bases derived from sulfa

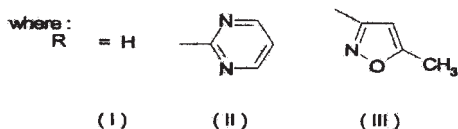
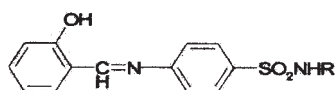
drugs and their complexes.

EXPERIMENTAL CHEMICAL

Reagent grade salicylaldehyde (Merck), sulphonamide, sulphadiazine (Tiba), sulphmethoxazole (Luna Co.), nickel chloride, copper (II) chloride 2-hydrate, ferric chloride, potassium dihydrogen orthophosphate and manganous chloride (BDH) were used as received. Cobalt (II) chloride hexahydrate, zincacetate (Meric).

Preparation of sulphonamide Schiff bases compounds:

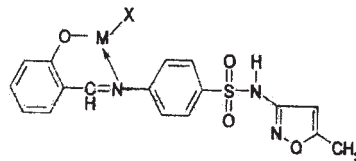
The preparation of Schiff base compounds depends on the condensation of the sulphonamide, sulphadiazine and sulphmethoxazole under reflux in ethanol^{7,8}. The structures of presented compounds were conformed by IR spectra ¹H-NMR and elemental analysis [I C₁₃H₁₂N₂O₃S- C%56.521(55.670), H%4.347(3.94), N% 10.144(9.69) and S%11.630(11.30)], [II C₁₇H₁₄N₄O₃S- C%57.562(56.87), H% 3.950 (3.68), N% 15.801(14.75) and S%9.057 (8.962)] and [III C₁₇H₁₅N₃O₄S- C%57.074 (56.86), H%4.196(3.76), N%11.750(10.70) and S%8.980 (8.75)]. Schiff bases under investigation have the general structural formula:



Preparation of solid complexes :

The solid complexes of stoichiometric ratios (1:1) (metal:ligand) of ligands I, II and III with metal ions Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺, Fe³⁺ and Cu²⁺ ions were prepared. A hot ethanolic solution containing 10⁻³ or 2 x 10⁻³ mole of the organic ligand was mixed with another solution metal chloride (containing 10⁻³ mole). The mixture was then refluxed on a water

bath for at least 10 hrs, and allowed to cool whereby the solid complex separated. The complexes were filtered, recrystallized and dried.



A known weight of the solid complex (~ 0.05 gm) was dissolved in enough hot dilute nitric acid (1:1) and then evaporated to a small volume till all the heavy fumes of nitric acid evolved. After cooling the solution which contains the metal cation, it was transferred quantitatively to a 25 ml measuring flask. The metal ion content was then determined using Perkin-Elmer atomic absorption control A. Analyst -800 Lap Faculty of Science, King Abdul Aziz University. In case of copper ions, the solution was first neutralized with sodium hydroxide solution. Ammonium hydroxide was then added to the solution to be determined until the formed precipitate was just dissolved. The concentration of ammonium hydroxide in the dilute solution of copper must not exceed 0.01 M. Then few milligrams of meruxide was added as indicator for each 100 ml of copper solution⁹. Finally the solution was titrated immediately with a previously standardized 0.01 M, EDTA solution the end point was indicated by a colour change from orange-yellow to purple.

Measurement of water of hydration by dehydration method :

An accurate weight of the solid complex was dried in an air oven at 110-120 °C to constant weight with aid sutourions balance. The difference in weight from the original one was utilized to determine the number of hydrated water molecules.

Electronic spectra of the solid complex :

The Uv-visible spectra of the solid complexes were recorded using a Shimadzu Uv-visible 240 Spectrophotometer. The electronic spectra of the solid complexes were

also studied in DMF using the appropriate concentration of metal complexes.

Apparatus and working procedure

Elemental analysis

Carbon, hydrogen and nitrogen of the metal complexes of compounds I, II and III were determined in the micro analytical unit of the Faculty of Science King Abdul Aziz University. The metal ion concentrations were determined by atomic absorption spectra.

Thermal analysis :

The percent of water molecules and metal ions were confirmed by thermogravimetric analysis (TGA and DTA) of the solid complexes. The material was subjected to thermal analysis using the TG 50-Thermogravimetric Analyzer (Shimadzu) in which the temperature was recorded as a function of percent weight losses from room temperature up to 700 °C, with a heating rate of 10 °C/minute and 20 °C/minute using N₂ as atmospheric gas.

The IR-Spectra :

The IR-spectra of the solid complexes were recorded as KBr discs using a Perkin Elmer 1430 double beam spectrophotometer within the range 4000-200 cm⁻¹.

¹H- NMR Spectra

¹H-NMR spectra of the compounds were carried out using E M-390-90 Mhz spectrometer with tetramethylsilane (TMS) as internal standard at Micro analytical unit of Tanta University.

RESULTS AND DISCUSSION

¹H-NMR spectra:

¹H- NMR spectra of compounds (I, II and III) showed a doublet signal within the range 7.4-8.5 ppm which corresponds to proton of the hydroxyl group in o-position of the azomethine group. The protons of the aromatic ring (two protons) show multiple signals at 6.5-7.5 ppm (I), while that of compound (II) (three protons) give rise to a multiple signals within the range

6.3- 7.8 ppm. Finally the four protons of the aromatic ring of compound III show signals at $\delta = 7.2-7.6$ ppm. The protons of the substituent groups have signals interference with aromatic moiety.

Infrared spectra :

The broad bands appearing in the IR-spectra of these compounds (I, II and III) within the range 3435-3325 cm⁻¹ corresponding to the stretching vibration of these OH-hydroxyl groups, the low frequency value of this band is ascribed to the intramolecular hydrogen bond formation. In the IR spectra of the compounds under investigation the medium to strong bands appearing within the range 1630 -1580 cm⁻¹ can be assigned to the stretching vibrations of the C = C ring absorption bands. It is worthy to mention that the symmetric stretching vibration of the C = N group related to the azomethine which should be observed in this region is masked by the intense bands due to C = C ring vibrations. The C-H in-plane deformation vibration and various skeletal vibrations such as OH stretching modes gives rise to a broad intense band in the range 1280-1230 cm⁻¹. The IR spectra of the free ligands with those of their metal chelates showed the absence of the weak broad band at ~2910 cm⁻¹ due to the intramolecular hydrogen bonded OH group¹⁰. The absence of this weak broad band in the IR spectra of the complexes indicates the participation of the o-OH group in complex formation through the proton displacement of the hydrogen atom of this hydroxyl group Fig. (1). The metal ions are chelated covalently with the hydroxyl group of the substituent on the phenyl moiety and coordinately with the nitrogen atom of the azomethine group to form the complex compound whose bonding mode, Table(1). This is supported by the displacement of the stretching vibration of the -CH = N- band to lower frequency side along, with the appearance of new bands within the ranges 510- 460 and 410-375 cm⁻¹ due to the stretching vibrations of M - O and M- N bonds respectively¹¹⁻¹³.

Table (3-7). Important IR data for the ligand (III) and its complexes

Compound	color	IR data Cm^{-1}					
		$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{CH-N})$	$\gamma(\text{C-H})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
$\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$	Yellow	3081,2993,2848	1923	1615,1574,1478	908,847	–	–
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{MnCl}$	Orange	3376,3296,3144	1914,1809	1616,1474	928,837	570	452
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{ZnCl}$	Lime	3435,3088	1904	1607,1466	947,825	596	–
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{NiCl}$	Orange	3145	1918,1807	1611,1476	908,840	566	445,411
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{CuCl}$	Yellow	3444,3345	1949	1586,1443	935,849	518	459
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{CoCl}$	Orange	3288,3147	1920	1611,1472	923,838	567	454
$\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})\text{FeCl}_2$	Brown	3081,2989	1921,1803	1611,1476	909,843	568	454

Table 2. Elemental analysis of Co^{2+} , Ni^{2+} , Cu^{2+} , and Fe^{3+} complexes with compound I.

Compound	Tentative formula	C%	Calc. (found)			M%	$A_M(\text{ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1})$
			H%	N%	S%		
I-Co^{2+}	$[\text{L}_1\text{Co}(\text{H}_2\text{O})_3]$	40.113	3.085	7.199	8.254	15.145	27.80
		(39.02)	(2.650)	(6.54)	(7.900)	(14.20)	
I-Ni^{2+}	$[\text{L}_1\text{Ni}(\text{H}_2\text{O})_3]$	40.133	3.087	7.203	8.258	15.101	8.32
		(39.860)	(3.020)	(6.80)	(7.820)	(14.40)	
I-Cu^{2+}	$[\text{L}_1\text{Cu}(\text{H}_1\text{O})_4]$	37.910	2.916	6.804	7.800	15.431	10.24
		(36.200)	(2.840)	(6.40)	(7.200)	(14.55)	
I-Fe^{3+}	$[\text{L}_1\text{Fe}(\text{H}_2\text{O})_4]$	38.632	2.971	6.934	7.949	13.818	9.44
		(38.400)	(2.80)	(6.640)	(7.300)	(12.600)	

Elemental analysis:

Carbon, hydrogen and nitrogen (C, H, N) analysis was done, and the results of analysis along with the proposed chemical formula of the prepared complexes are given in Table (2).

Electronic spectra:

Indeed studies of the absorption spectra of these compounds reveal that they absorb energy in the infrared (IR) and ultraviolet (Uv) regions as well as the visible. Electronic transitions occur, when electrons within the molecule or ion move from one energy level to another that may be observed with element complexes and must consider that concerning the expected probabilities or

intensities of the various types of transition. The results of electronic absorption spectral data for Co^{2+} , Ni^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} and Cu^{2+} complexes with the Schiff bases compounds (I, II and III) are shown in Fig.(2).

Thermogravimetric and Differential Thermal Analysis of Solid Compounds :

The DT curves of these complexes show endothermic peaks within the temperature range 60-130 °C which are due to the removal of humidity or physically combined water molecules from the crystal lattice. On the other hand the removal of all coordinated water molecules is represented by the endothermic peak, within the range 130-160 °C. The strong exothermic peaks at 380-500 °C are

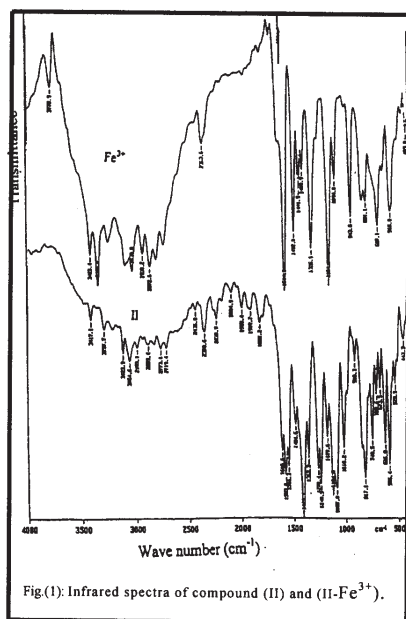
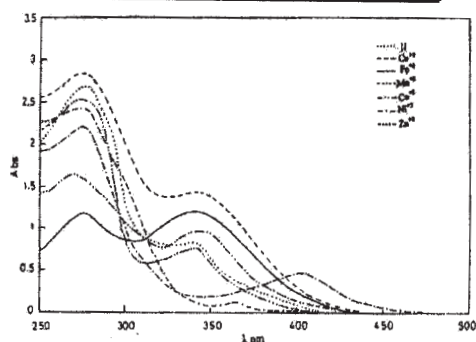
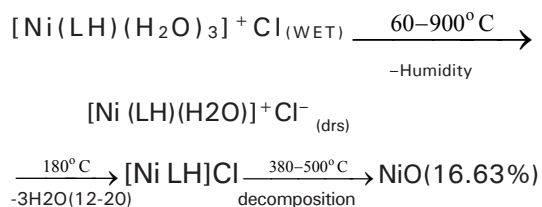
Fig.(1): Infrared spectra of compound (II) and (II-Fe³⁺).

Fig. 2. Electronic absorption spectra of complexes with compound (II) in DMF.

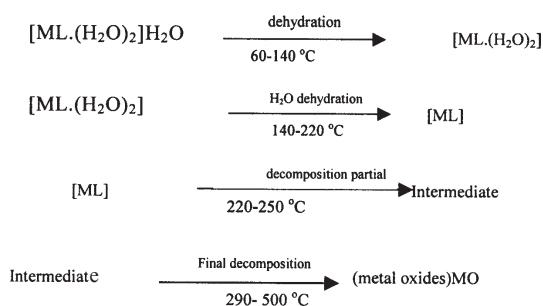
due to the phase of transformation taking place during the decomposition of the anhydrous complex, leading to the formation of NiO, CoO and CuO as final products.

As an example, the thermal decomposition of mono-nuclear Ni²⁺ complex with ligand I (LH) can be represented as follows :



The complexes decompose in two steps via the formation of unstable intermediates, the decomposition starts at 200-290°C (oxides formation). The metal percentages of the complexes are calculated from the residual metal oxide % formed in the final step and are in good agreement with data obtained by the we combustions method¹⁴.

The following general suggestion mechanisms for thermal decomposition may be proposed for the Schiff base (II) metal complexes :



Determination of reaction order of decomposition :

The reaction order of decomposition can be determined from equation¹⁵ :

$$C_s = (n)^{1/1-n}$$

Where C_s is the weight fraction of substance present at the DTG peak temperature T_s , and given by

$$C_s = \frac{(W_s - W_f)}{(W_o - W_f)}$$

Here W_s stands for the weight remaining at a given temperature T_s , the DTG peak temperature, W_o and W_f are the initial and final weight, of the substance, respectively. The values of C_s for the thermal decomposition of the complexes are in the range 0.64 - 0.75 which indicates that the decomposition follows first order kinetics. For a first order process the Coats-Redfen equation^{16,17} may be modified and written in the form :

$$\log(1) \left[\frac{W_f}{W_f - W} \right] \frac{1}{T^2} = \log \left[\frac{A R}{E^*} \frac{2.303 R T}{E^*} \right] - \frac{E^*}{2.303 R T} \quad (1)$$

Where, W_f is the weight loss at the completion of the reaction. W is the weight loss up to temperature T , ($W_f = W_f - W$), R is the gas constant, E^* is the activation energy in J mol^{-1} and β is the heating rate.

Since $1 - \frac{2.303 R T}{E^*} \cong 1$, a plot of the left hand side of equation (1) against $1/T$ was drawn and E^*

was calculated from the slope and then A (Arrhenius constant) was found from the intercept. The activation entropy ΔS^* , the activation enthalpy H^* and the free energy of activation ΔG^* were calculated using the following thermodynamically equations:

$$\Delta S^* = 2.303 (\log(Ah/RT))R$$

$$\Delta H^* = E^* - RT$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Where (K) and (h) are the Boltzman and Plank constants respectively, the calculated values of E^* , A , ΔS^* , ΔH^* and ΔG^* for the decomposition steps are given in Table (3).

Table 3. Kinetic data of the thermal decomposition of the complexes (I)

complex	E^* kJ mol^{-1}	A Sec^{-1}	ΔS^* J K mol^{-1}	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	c_s
Ni^{+2}	7.751	39.64×10^{-2}	-252.65	5.273	80.563	0.868
Mn^{+2}	60.631	30.883×10^3	-158.98	58.153	105.52	
Fe^{+3}	15.341	87.37×10^{-2}	-246.07	12.894	86.222	0.903
Co^{+2}	44.815	11.98×10^2	-186.00	42.367	97.796	
Cu^{+2}	8.320	22.01×10^{-2}	-257.54	5.872	82.619	0.94

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