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CHROMONE 6--SALICYLHYDRAZONE COMPLEXES OF SOME DIVALENT TRANSITION METAL IONS

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Abstract. Metal complexes of 2-methyl 5-methoxy 7-hydroxy chromone 6-salicylhydrazone with some divalent transition metal ions were investigated by the use of spectrophotometric, electric conductance, pH titration and infrared measurements. Isolation of solid complexes and physical measurements revealed the existence of mono and bisligand complexes. Complex formation has been to take place through a proton displacement from the hydroxy group in 7-position of the chromone residue and also with the azomethine and carbonyl groups of salicylhydrazide residue. Spectrophotometric studies supported the using of this ligand for the microdetermination of small quantities of metal ions in solution.

Interest in the chemistry of hydroxy chromones is based on their ability to function as chelating agent, which can be used in the analytical determination of a large number of transition metal ions.[1] In addition, structural studies[2-5] revealed that chelation of Schiff's bases to transition metal through the azomethine group is stabilised by the presence of an auxochrome group in ortho-position.

In continuation of our investigations on complexes of hydrazine derivatives with transition metals[5-10], the present work deals with complexes formed by the interaction of 2-methyl 5-methoxy 7-hydroxy chromone 6-salicylhydrazone with Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) in alcoholic solution. In order to define these complexes, it is necessary to use more than one of the many methods known for determining the existence and structure of complex compounds. For this reason isolation of pure ,compounds, spectrophotometric, electrical conductance, pH titration and infrared measurements were carried out to elucidate the nature of the complexes under consideration.

Experimental

Materials and Analysis. Analar or Merck grade metal salts were used for preparing molar solutions. The weighed amounts of salts or ligand, were dissolved in the requisite volumes of absolute ethanol. Determinations of chloride and metal contents were performed by standard known procedures. Microanalysis of C, H and N was undertaken by the microanalytical unit, of the University of Cairo. The results of analysis are given in Table 1.

Preparation of Compounds. The ligand was obtained by condensation of *o*-hydroxy benzoylhydrazine[11] with 2-methyl 5-methoxy 6-formyl 7-hydroxy chromone, as prepared by the oxidation of visnagine with pota-

TABLE 1. ELEMENTAL ANALYSIS RESULTS OF COMPLEXES.

Complex	% Calculated					% Found				
	C	H	N	Cl	M	C	H	N	Cl	M
$Cu(C_{19}H_{16}O_6N_2)Cl.2H_2O$	45.7	3.9	5.6	7.0	12.5	46.2	4.3	5.9	6.9	12.2
$Cu(C_{19}H_{15}O_6N_2)_2.3H_2O$	53.3	4.2	6.5	—	7.4	53.5	4.6	6.6	—	7.8
$Co(C_{19}H_{15}O_6N_2)_2.4H_2O$	52.7	4.4	7.0	—	6.9	52.9	4.7	8.0	—	7.3
$Ni(C_{19}H_{15}O_6N_2)_2.3H_2O$	53.4	4.5	6.9	—	7.0	53.8	5.0	7.6	—	7.2
$Mn(C_{19}H_{15}O_6N_2)_2$	58.0	3.9	—	—	7.0	58.4	4.3	—	—	7.4
$Zn(C_{19}H_{15}O_6N_2)_2$	57.0	4.2	7.0	—	8.2	57.3	3.7	7.4	—	7.9

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ssium dichromate[12]. The product was recrystallized from ethanol, m.p. > 280°.

The solid complexes were prepared by mixing equimolecular amounts of the ligand and hydrated metal salts in the solid state followed by the addition of 20 ml absolute ethanol. The mixture was then refluxed on a water bath for 3 hr, on cooling the complexes separated as fine crystals.

Working Procedures: Infrared spectra of solid complexes and the ligands were investigated by KBr disc technique,using a Pye Unicam SP 1000 infrared spectrophotometer.

For the spectrophotometric measurements, volumes of 0.1 M ethanolic solution of the metal chloride were added to the necessary volumes of 0.01 M ethanolic solution of the ligand, then diluted to 10 ml with absolute ethanol and thoroughly mixed. The absorption spectra of the resulting solutions were then recorded using a blank containing the same concentration of the ligand in ethanol.

For the conductometric titration, a known volume of the metal ion solution was placed in a 25 ml closed beaker of tall type. This solution was titrated with the ligand solution delivered from a microburette. The conductance values were measured using a Beckmann conductivity bridge. A volume correction was applied.

For the pH titration, 25 ml of 2x10.4M solution in both ligand and the metal halide were titrated with 0.01 N NaOH solution. The pH values were measured using a Pye Unicam Model 290 pH meter.

Results and Discussion

Isolation of Pure Complexes. The interaction of 2-methyl 5-methoxy 7-hydroxy chromone 6-salicyl hydrazone (Ch.S.H.) with the studied hydrated metal salts gave mono- and bis- ligand complexes. $CuCl_2$ gave a mono-ligand complex having the stoichiometry Cu(L) $Cl.2H_2O$. The water of hydration content of this complex could be determined. The colour changed from green to yellowish brown on heating at 120°. The stoichiometry of the isolated pure bis-ligand complexes was $ML_2.nH_2O$ where M= Cu(II), Co(II), Ni(II), Mn(II) and Zn(II). The colours of aquo complexes change when heated in an electric oven for two hours at 120° but the original colour is regained immediately on exposure to air. Thus it was difficult in most cases to determine the water content for these complexes. These were found to be insoluble in water and organic solvents. Results of elemental analysis of the isolated complexes are given in Table 1.

Spectrophotometric Studies. Ethanolic solutions containing different proportions of Ch. S.H. with Cu^{2+} Co^{2+} and Ni^{2+} ions indicated characteristic absorption maxima at 298, 382; 298, 384; 300, 398 nm respectively which show the formation of complexes in the three. systems. Absorption spectra are represented in Fig.1.

On keeping the metal ion concentration constant while changing that of the ligand, the optical density increases steadily and finally attains a more or less cons-

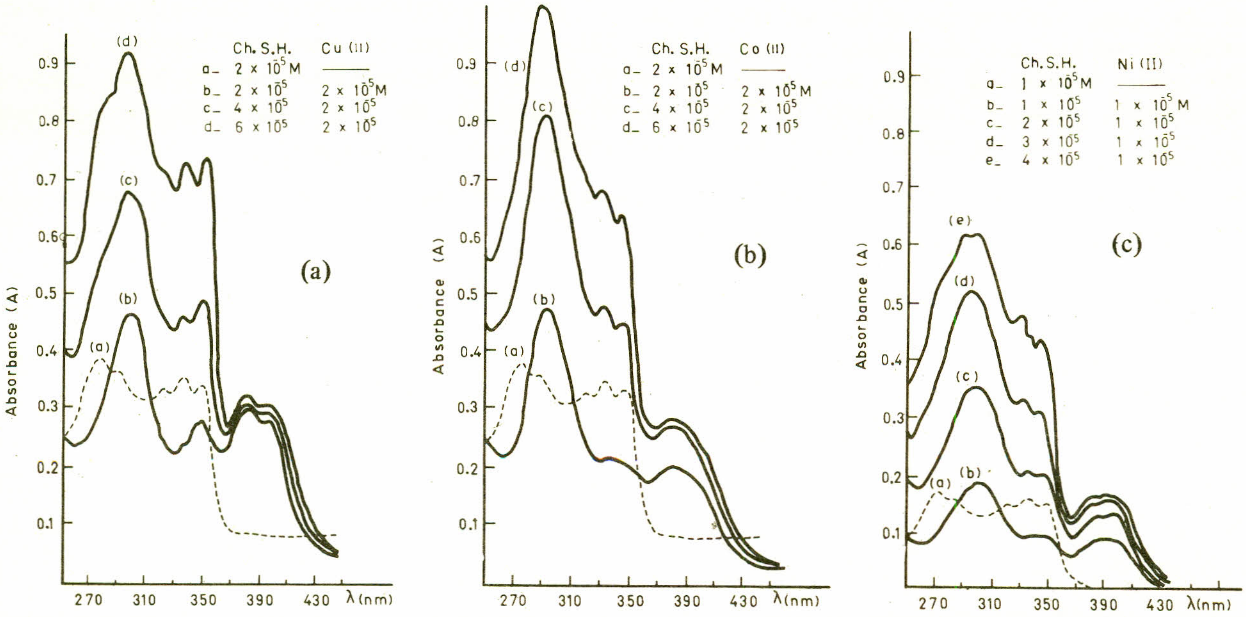


Fig. 1. (a) Absorption spectra of Cu (II) - Ch.S.H. Mixtures.(b) Absorption spectra of Co(II) - Ch.S.H. Mixtures.(c) Absorption spectra of Ni (II) - Ch.S.H. Mixtures.

tant value. When the solution contains a constant concentration of the ligand and variable quantities of the metal ions, the optical density increases regularly with metal ion concentration. The plot of absorbance as a function of the metal ion concentration (Fig.2) gave straight lines in the concentration range up to 1.2×10^{-5}M. Also the high $\in$ Values (2.5×10^4, 2.5×10^4, 2.0×10^4 at λ_{max} for Cu^{2+}, Co^{2+} and Ni^{2+} respectively) suggest the possible application of the method for the determination of small amounts of the pure metal ion.

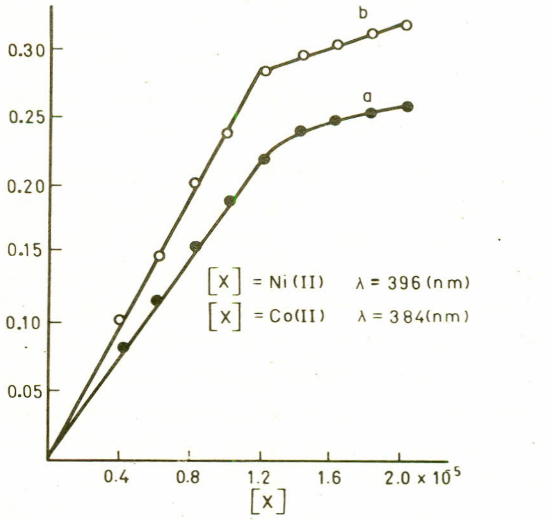


Fig. 2. (a) Validity of Beer's law for Ch.S.H. system.

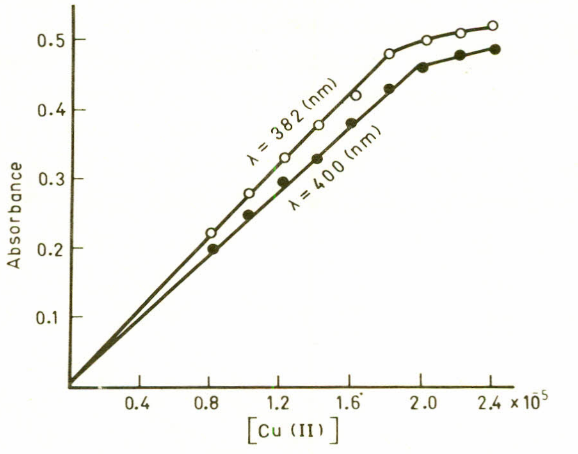


Fig. 2. (b) Validity of Beer's law for Cu (II) - Ch.S.H. system.

The metal-ligand ratio of the complexes formed in solution was traced by applying the well known molar ratio[13], straight line[14], continuous variation[15], slope ratio[16] and limiting logarithmic methods .[17] The results obtained revealed the formation of two types of complexes with the composition (metal:ligand) 1:1 and 1:2 for each metal ion. (Fig. 3).

The apparent formation constants of the complexes

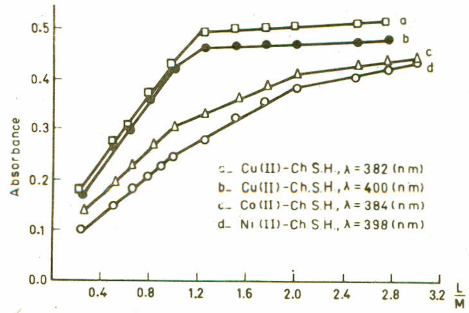


Fig. 3. (a) Molar ratio plots for Ch.S.H. system Ch.S.H. system.

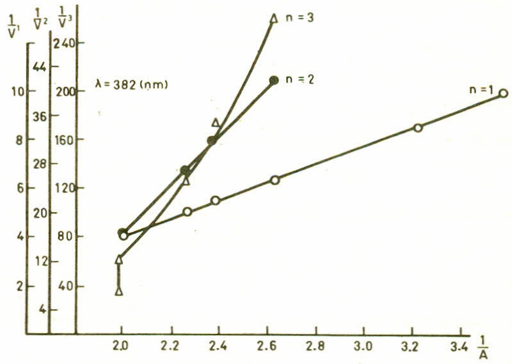


Fig. 3. (b) Straight line method plos for Cu (II) Ch.S.H. system,

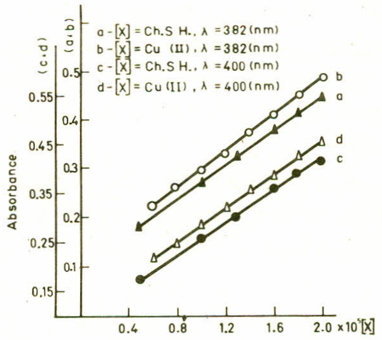


Fig. 3. (d) Slope ratio method plots for Cu (II) - Ch.S.H. system

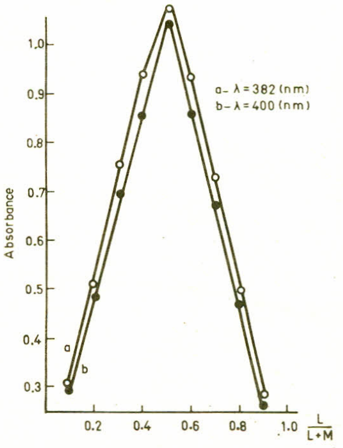


Fig. 3. (c) Continuous variation method plots for Cu (II), Ch.S.H. system

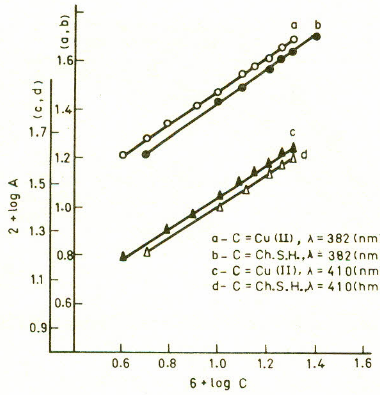


Fig. 3. (e) Limiting logarithmic method plots for Cu (II), Ch.S.H. system.

TABLE 2. STOICHIOMETRY OF Cu^{2+}, Co^{2+}, AND Ni^{2+} COMPLEXES.

Metal ion	λmax	Stoichiometry M.R.	C.V.	S.L.	S.R.	L.L.
Cu^{2+}	382	1:1	1:1	1:1,1:2	1:1	1:1
Co^{2+}	384	1:1,1:2	1:1,1:2	1:1,1:2	1:1	1:1
Ni^{2+}	398	1:1,1:2	1:1,1:2	1:1,1:2	1:1	1:1

were calculated from the results of the molar ratio[13] and continuous variation[15] methods. Results are given in Tables 2 and 3.

Conductometric Titrations. The formation of 1:1 and 1:2 metal: ligand complexes is supported by the results of conductometric titrations. The titration of 10 ml 10^{-3} M of the metal ion solutions with 10^{-2} M of the ligand solution yields curves (Fig. 4) having two breaks at molar ratio of 1:1 and 1:2 for Cu(II), Co(II) and Mn(II) and one break at 1:1 for Cd(II) Zn(II), and Ni(II).

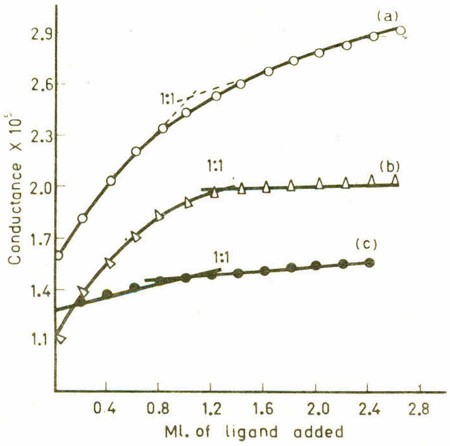


Fig. 4. (a) Conductometeric titration curves for (a) $ZnBr_2$, (b) $ZnCl_2$, and (c) $CdCl_2$ with Ch.S.H. system

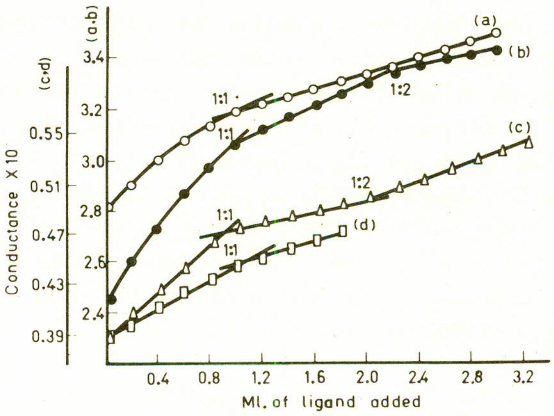


Fig. 4. (b) Conductometeric titration curves for (a) $MnCl_2$, (b) $CoCl_2$, (c) $CuCl_2$ and (b) $NiCl_2$ with Ch.S.H. system.

Generally the titration curves are characterized by an increase in conductance, indicating the displacement of protons from the ligand on complex formation.[18] Fig.5

The effect of dilution on the specific conductance of the complexes formed between Ch.S.H. and different metal ions shows an increase in conductance for the mixtures over that of ligand or metal ion alone. This variation in conductance measurements supports the opinion that the ligand reacts with the metal ions through the liberation of highly mobile H^+

pH-Titration. The interaction of Ch.S.H. with different metal ions under investigation was studied by pH titration in 80% Water-Dioxan, 25 ml solutions were titrated with NaOH in presence of metal ions.

Titration of the ligand along with NaOH shows an inflection point corresponding to the consumption of two equivalents of alkali due to the simultaneous liberation of two H^+ ions. The start of the curve at a pH value slightly higher than 7 was observed in similar ca-

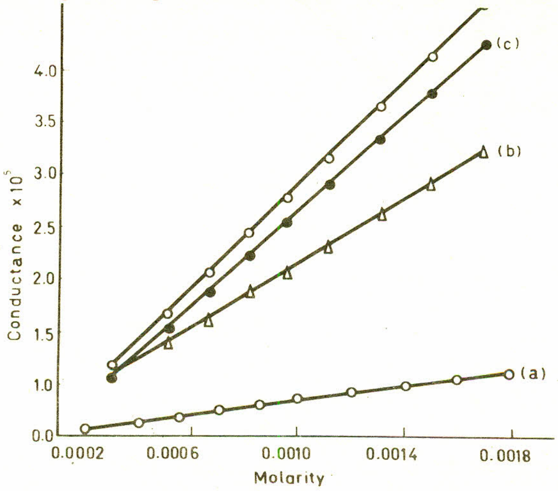


Fig. 5. Increase of conductance on interaction between $MnCl_2$ and Ch.S.H. (a) Ch.S.H., (b) $MnCl_2$ (c) $MnCl_2$ + Ch.S.H. (1:1) and (d) $MnCl_2$ + Ch.S.H. (1:2).

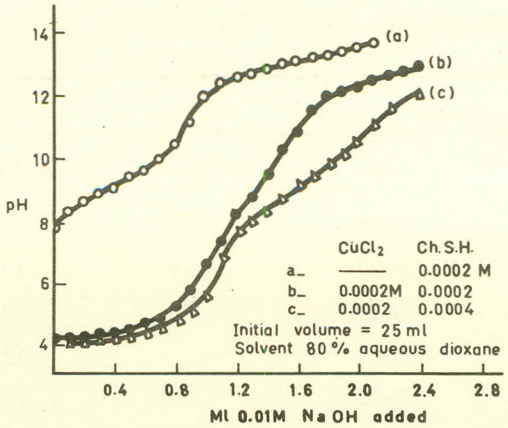


Fig. 6. (a) Titration curves of Ch.S.H. system in absence and in presence of $CuCl_2$ with 0.01 M NaOH.

ses.[19] The titration curves in the presence of Cu(II), Zn(II) and Mn(II) (Fig. 6) exhibit two inflection points corresponding to the successive liberation of two H^+ ions together with an initial drop in pH. In all curves the first inflection point, which indicates the liberation of one proton, suggests the formation of stable monoligand complexes. The second less pronounced inflection points to the presence of higher complexes, or to the dissociation of the first formed aquo monocomplex at higher pH's to a H^+ ion and the corresponding hydroxo complex.

IR Spectra. The mode of bonding between the ligand and metal ions can be readily revealed by comparing the IR spectra of the solid complexes with those of the organic ligand. The comparison in Table 4 show that the band at 1670 cm^{-1} in the spectrum of the ligand due to the stretching frequency of C=O in chromone moiety[20] is not influenced by coordination thus indicating that this group does not take part in complex formation. The band at 1680 cm^{-1} which corresponds to the stretching frequency of the C=O group in salicylhydrazide residue shifts to a lower frequency due to coordination with the metal ion.

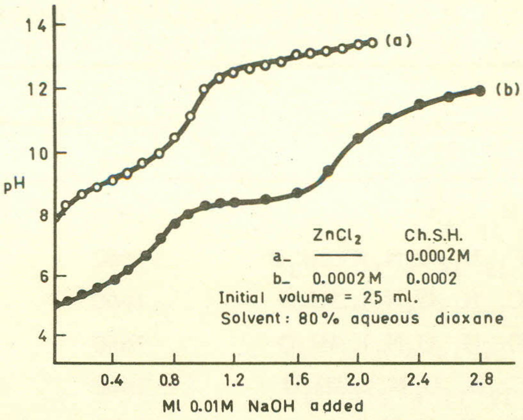


Fig. 6. (a) Titration curves of Ch.S.H. system in absence and presence of $ZnCl_2$ with 0.01 M NaOH

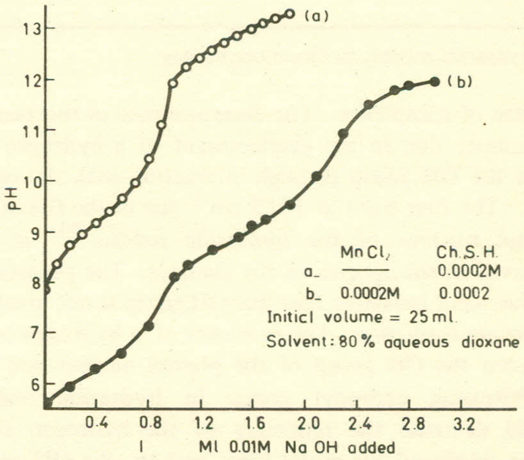


Fig. 6. (c) Titration curves of Ch.S.H. system in absence and in presence of $MnCl_2$ with 0.01 M NaOH

Also, the C=N band at 1635 cm^{-1} [21,22] is shifted to a lower wave number in the spectra of complexes. This shows that the azomethine group is one of the coordination sites of the ligand. Two bands due to δ-OH groups are observed in the ligand spectrum at 1315 and 1350 cm^{-1}. The latter band corresponds to δ-OH in chromone moiety [23] and is absent in the

TABLE 3. APPARENT FORMATION CONSTANTS OF Cu^{2+}, Co^{2+} AND Ni^{2+} COMPLEXES.

Metal ion	λ max	Stoichiometry	Apparent formation constant M.R.	Apparent formation constant C.V.	Mean value
Cu^{2+}	382	1:1	$3.25x10^7$	$9.8x10^6$	$2.12x10^7$
Co^{2+}	384	1:1	$5.4x10^5$	$1.2x10^6$	$8.7x10^5$
		1:2	$1.97x10^{12}$	------	$1.97x10^{12}$
Ni^{2+}	398	1:1	$1.48x10^5$	$4.08x10^6$	$2.16x10^6$
		1:2	$3.77x10^{11}$	$7.35x10^{11}$	$5.56x10^{11}$

M.R. = Molar Ratio, C.V. = Continuous Variation, S.L. = Straight Line, S.R. = Slope Ratio and L.L. = Limiting Logarithmic Methods.

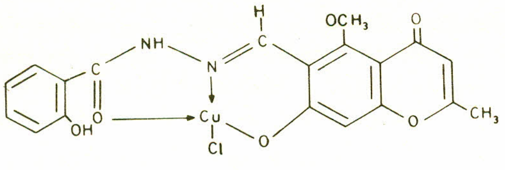
TABLE 4. IMPORTANT IR BANDS FOR LIGAND AND METAL COMPLEXES.

Compound	Frequencies in cm^{-1}				
	C=O	C=O	C=N	δ-OH	δ-OH*
$C_{19}H_{16}O_6N_2$	1680	1670	1635	1350	1315
$Cu(C_{19}H_{16}O_6N_2)Cl.2H_2O$	1662	1670	1622	---	1315
$Cu(C_{19}H_{15}O_6N_2)_2.3H_2O$	1660	1670	1620	---	1315
$Co(C_{19}H_{15}O_6N_2)_2.4H_2O$	1660	1670	1615	---	1310
$Ni(C_{19}H_{15}O_6N_2)_2.3H_2O$	1660	1670	1620	---	1320
$Mn(C_{19}H_{15}O_6N_2)_2$	1660	1670	1620	---	1320
$Zn(C_{19}H_{15}O_6N_2)_2$	1655	1670	1625	---	1310

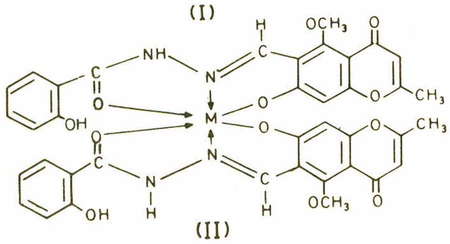
***In hydrazide residue, In Chromone moiety**

spectra of complexes. The disappearance of this band is apparently due to the displacement of a hydrogen ion from the OH group through interaction with the metal ions. The first band at 1315 cm^{-1} due to the OH in the phenyl nucleus of the hydrazide residue [24] is still observed in the spectra of the chelates. The persistance of this band indicates that this OH group is not involved in chelate formation. The existence of a hydrogen bond between the OH group of the phenyl nucleus and the neighbouring carbonyl group in hydrazide residue would decrease the tendency of the hydrogen atom to be displaced by metal ions, and so, the OH group in the hydrazide residue is not involved in chelation.

From the results of all previous physicochemical measurements the structure of 1:1 and 1:2 complexes may thus be represented as follows:



(I)



(II)

M = Cu (II) Co(II) Ni (II) Zn (II) and Mn (II)

X = Cl, Br

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