THE Cu (II), Co (II), Ni (II), Mn (II) AND Zn (II) CHELATES WITH CHROMONE 6-ACETYL HYDRAZONE

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Abstract. The metal chelates formed through the reaction of Cu (II), Co (II), Ni (II), Mn (II) and Zn (II) with 2-methyl 5-methoxy 7-hydroxy chromone 6-acetyl hydrazone are investigated by the use of spectrophotometric, electric conductance and pH titration measurements. Isolation of solid complexes and physical measurements revealed the existence of mono and bis ligand complexes in the keto-form. Complex formation has been shown 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 acetyl hydrazide residue. Spectrophotometric studies supported the using of this ligand for the microdetermination of small quantities of metal ions in solution. The apparent formation constants of the complexes are also determined. The visible absorption spectra of the solid complexes in dimethyl formamide indicate that all these complexes have a distorted octaherdral configuration.

Metal chelates with hydrazide derivatives were the subject several investigations. The interest in such studies arose mainly from structural problems[1,4] and the tendency of hydrazides to function as antituberculous compounds[5,6] through their ability to form metal chelates.[7]

Also the interest in Schiff's base complexes of transition metals arose mainly from structural problems [8-11] It was found that chelation through the azomethine group is stabilised by the presence of an auxochrome group in *ortho*-position.

In continuation of our studies on metal chelates with hydrazine derivatives [3,4,11-14], the present work deals with complexes formed by interaction of 2-methyl 5-methoxy 7-hydroxychromone 6-acetylhydrazone with some transition elements in view of throwing some light on their stoichiometry, structure and stability.

Experimental

The ligand was obtained by the condensation of acetyl hydrazine [15] with 2-methyl 5-methoxy 6-formyl 7-hydroxy chromone, prepared by the oxidation of visnagine with potassium dichromate.[16] The product was recrystallized from ethanol.

The solid complexes were prepared by mixing equimolecular amounts of the ligand and hydrated metal halides in the solid state followed by the addition of 20 ml. absolute ethanol. The mixture was then refluxed on a water bath for about 2 hr. At the beginning, the materials dissolve forming a homogeneous solution, then the solid complexes start to precipitate. To ensure the isolation of pure complexes, the reaction product was filtered immediately while the solution was still hot. The solid complexes were washed several times with hot ethanol. All solid complexes isolated were insoluble in the majority of organic solvents and had melting

points above 280°.

Analar or Merck grade metal salts were used for preparing molar solutions. The weighed amounts of salts or ligand were dissolved in 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, Cairo University. The results of analysis are given in Table 1.

The working procedure is the same as given before[4,14]. The UV - and visible spectra were recorded on a Pye Unicam SP 1800 spectrophotometer. The IR spectra of solid complexes were investigated by KBr disc technique, using a Pye Unicam SP 1000 IR spectrophotometer. The pH values were measured using a Pye Unicam model 290 pH meter. The conductance values were measured using a Beckmann conductivity bridge.

Results and Discussion

Isolation of Pure Compounds. The interaction of 2-methyl 5-methoxy 7-hydroxy chromone 6-acetyl hydrazone (Ch.Ac.H.) with the studied hydrated metal salts gave mono-and bis- ligand complexes. Monoligand complexes have the stoichiometry $MCl.nH_2O$, where M=Cu (II), Ni (II), Co (II), Mn (II) and Zn (II) L = ligand mono basic anion. Bis-ligand complexes have the stoichiometry $Cu (HL)_2X_2$ where X = Cl or Br. The colours of aquo complexes change when heated in an electric oven for two hours at 120°, but the original colour is retained 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.

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TABLE 1. ELEMENTAL ANALYSIS RESULTS OF COMPLEXES.

Complex	% Calculated					% Found				
	C	H	N	Halogen	M	C	H	N	Halogen	M
Cu $(C_{14}H_{14}O_5N_2)$ Cl.2H$_2$O	39.5	4.2	6.6	8.3	14.9	40.2	3.9	6.5	8.2	15.5
Ni $(C_{14}H_{14}O_5N_2)$ Cl.H$_2$O	41.8	4.0	7.0	8.8	14.5	41.6	3.9	7.4	8.5	14.1
Co $(C_{14}H_{14}O_5N_2)$ Cl	43.7	3.6	7.3	9.2	15.3	43.5	4.0	7.2	9.0	15.0
Mn $(C_{14}H_{14}O_5N_2)$Cl.2H$_2$O	40.4	4.4	6.7	8.5	13.2	40.1	4.5	5.9	8.7	12.6
Zn $(C_{14}H_{14}O_5N_2)$ Cl.2H$_2$O.	39.5	4.25	6.5	8.3	15.0	40.0	4.1	6.3	8.4	15.4
Cu $(C_{14}H_{14}O_5N_2)_2$Br$_2$	41.1	3.8	7.0	19.8	7.8	41.5	3.5	6.9	19.3	7.5
Cu $(C_{14}H_{15}O_5N_2)_2$Cl$_2$	46.9	4.2	7.8	9.9	8.9	46.9	4.6	7.9	9.8	8.7

Spectrophotometric Studies. Ethanolic solutions containing different proportions of Ch.Ac.H. with Cu^{2+} Co^{2+} and Ni^{2+} ions indicated characteristic absorption maxima at 296, 376, 294, 396, 296, 380 nm respectively which show the formation of complexes in the three systems. Absorption spectra are represented in Fig. 1.

On keeping the metal ion oncentration constant while changing that of the ligand, the optical density increases steadily and finally attains a more or less constant 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 2 x 10^{-5} M. Also the high $\in$ values (2.1 x 10^4, 1.2 x 10^4; 2.0 x 10^4, 1.1 x 10^4: 1.9 x 10^4, 1.3 x 10^4 for Cu2, Co^{2+} Ni^{2+} respectively) suggest the possible applicat...

of the method for the determination of small amounts of the pure metal ion.

The metal-ligand ratio of the complexes formed in solution was traced by applying the well known molar ratio[17], straight line[18], continuous variation[19], slop ratio[20] and limiting logarithmic methods.[21] 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. Representative curves for the Cu (II) system are indicated in Fig. 3.

The apparent formation constants of the complexes were calculated from the results of the molar ratio[17] and continuous variation[19] methods. Results are given in Tables 2 and 3.

The visible absorption spectra of solid complexes, Cu(L)Cl. 2H$_2$O, Cu(HL)$_2$ Br$_2$ and Cu(HL)$_2$Cl$_2$, in dimethyl formamide show a single absorption band at 14,000, 14,000, 15,000 cm^{-1} respectively with no
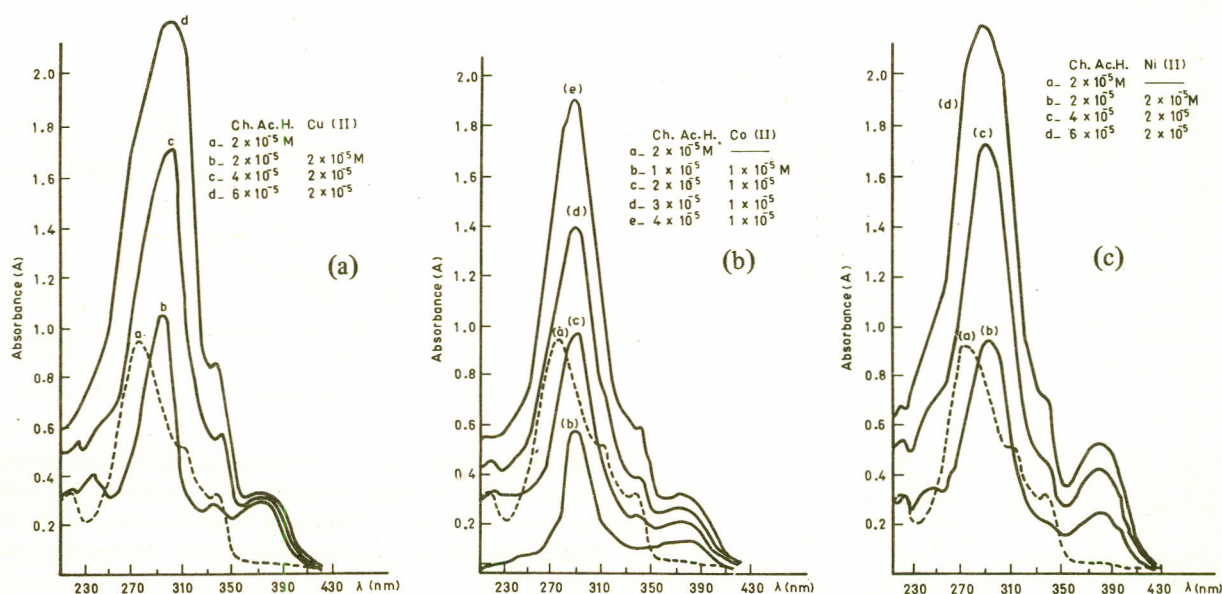

Fig. 1 (a) Absorption spectra of Cu (II) - Ch.Ac.H. Mixtures.   (b) Absorption spectra of Co (II) - Ch.Ac. H. Mixtures.
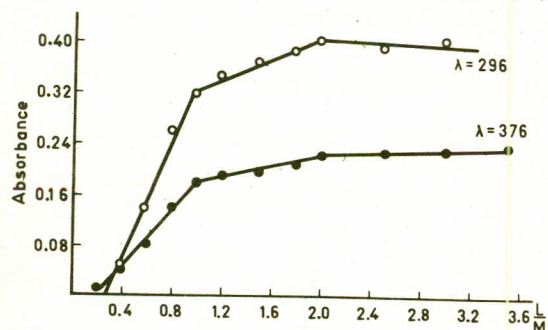(c) Absorption spectra of Ni (II) - Ch.Ac.H. Mixtures.

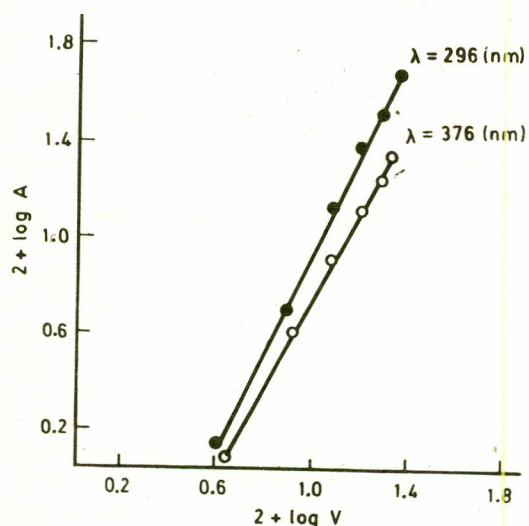Fig. 2. (s) Molar ratio plots for Ch.Ac.H. Cu (II) system.

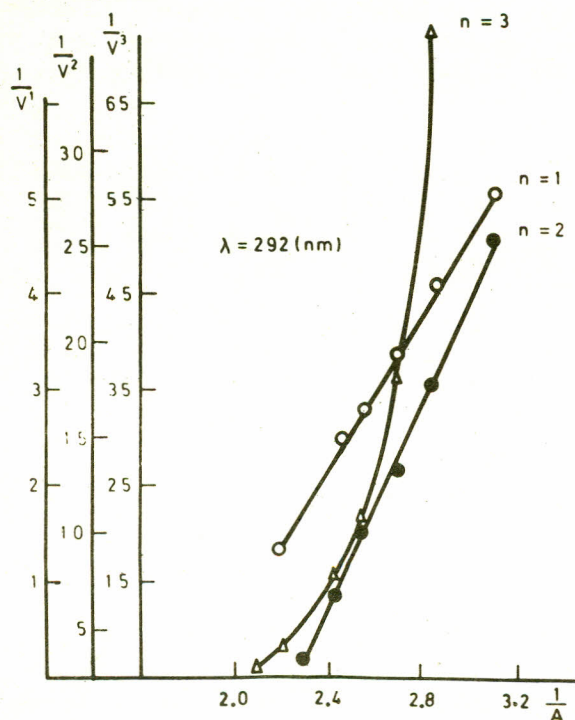Fig. 2. (b) Straight line method logarithemic plots for Cu (II) Ch.Ac.H. system.

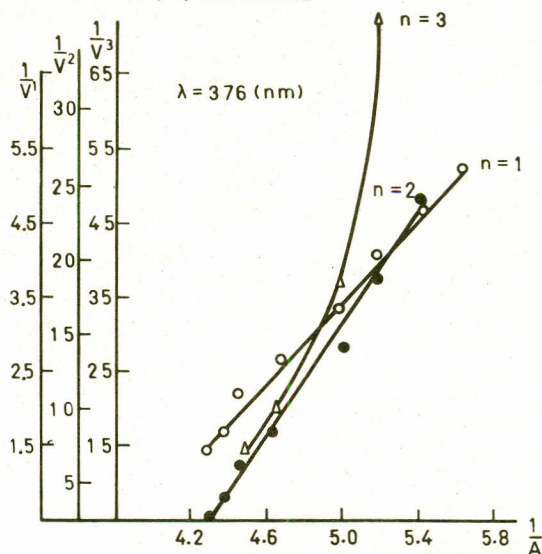Fig. 2. (d) Straight line method of Cu (II) - Ch.Ac.H. system.

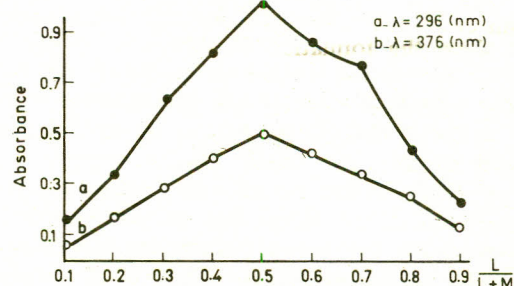Fig. 2 (c) Straight line method plots of Cu (II) - Ch.Ac.H. system

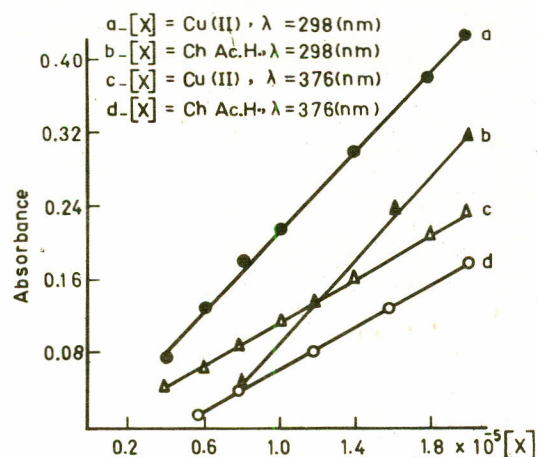Fig. 2. (e) Continuous variation method plots for Cu (II) Ch.Ac.H. system.

Fig. 2. (f) Slope ratio method plots for Cu (II) Ch.Ac.H.

shoulder. The position of the single "d-d" band in these compounds is very close to that found in the other studied cases, [22-24] thus it may be concluded that these complexes possess a distorted octaherdral structure[22,25]..

Conductometric Titrations. The formation of 1:1 and 1:2 metal:ligand complexes is supported by the re-
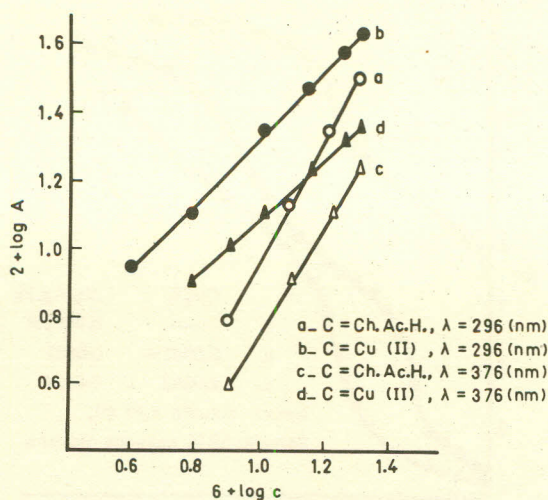
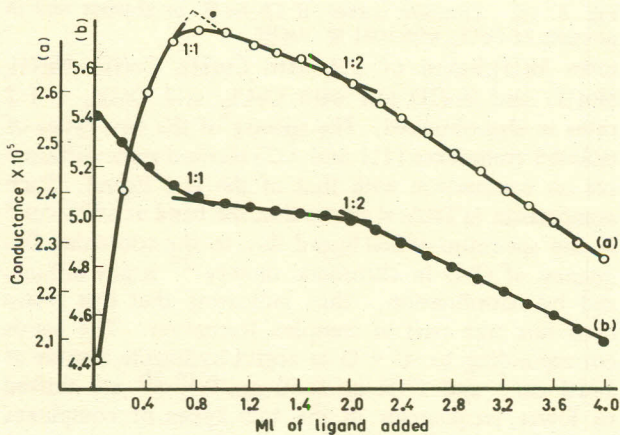Fig. 2. (g) Limiting logarithemic method plots for Cu (II) Ch.Ac.H. system.

Fig. 3. (a)   Conductometeric titration curves for (a) ZnCl$_2$ and (b) MnCl$_2$ with Ch.Ac.H.
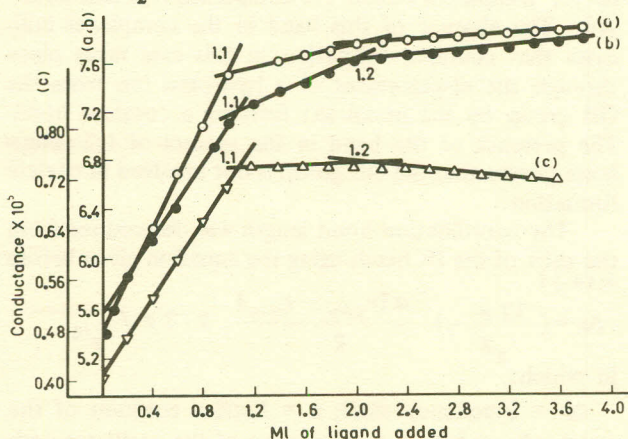

Fig. 3. (b) Conductometric titration curves   for (a) NiCl$_2$ and (b) CoCl$_2$ and (c) CuCl$_2$ with Ch.Ac.H.

sults of conductometric titrations. The titration of 10 ml 10^{-3}M of the metal ion solution with 10^{-2} M of ligand solution yields curves characterised by two inflections corresponding to the stoichiometric ratios 1:1 and 1:2. A common behaviour of these curves is the

### 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+}	296	1:1, 1:2	1:1, 1:2	1:1, 1:2	1:1	1:2
	376	1:1, 1:2	1:1	1:1, 1:2	1:1	1:2
Co^{2+}	294	1:1, 1:2	1:1, 1:2	1:1, 1:2	1:1	1:1
	396	1:1, 1:2	1:1, 1:2	1:1, 1:2	1:1	1:1
Ni^{2+}	296	1:1, 1:2	1:1, 1:2	1:1, 1:2	1:1	1:2
	380	1:1, 1:2	1:1, 1:2	1:1, 1:2	1:1	1:2

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

Metal ion	λmax	Stoichiometry	Apparent formation constant		
			M.R.	C.V.	Mean value
Cu^{2+}	296	1:1	8.1×10^5	8.4×10^6	4.6×10^5
		1:2	-----	-----	
	376	1:1	9.1×10^6	-----	9.1×10^6
		1:2	2.4×10^{12}	-----	2.4×10^{12}
Ni^{2+}	296	1:1	1.0×10^5	4.5×10^6	2.3×10^6
		1:2	7.0×10^{10}	-----	7.0×10^{10}
	380	1:1	1.4×10^5	1.4×10^6	7.7×10^5
		1:2	7.04×10^{10}	-----	7.04×10^{10}
Co^{2+}	294	1:1	5.2×10^5	6.6×10^6	3.56×10^6
		1:2	2.75×10^{10}	-----	2.75×10^{10}
	394	1:1	3.0×10^5	2.2×10^6	1.25×10^6
		1:2	3.0×10^{10}	-----	3.0×10^{10}

continuous increase in the conductance of the solutions except those of Zn (II) and Mn (II). The increase in conductance due to the displacement of H^+ ions from the OH-group of the ligand on complex formation.[26] The decrease in conductance is observed as a result of the decreased charge on the metal ion through covalent bond formation with the ligand, and the increase in size of the metal ion on chelate formation.

The effect of dilution on the specific conductance of the complexes formed between Ch.Ac.H. and different metal ions shows an increase in conductance for mixtures over that of ligand or metal ion alone. The large increase in electrical conductance of the complexes present in solution over that of divalent metal chlorides (MCl_2) and ligand (HL) is typical of strong complex formation. The increased conductance of the medium results from conducting ions, produced in the course of a reaction of the type.

$$HL + MCl_2 \rightarrow ML + H^+ + Cl^-$$
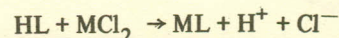
The highly mobile H^+ ions produced in the above reaction greatly increase the conductance of the complex over that of the metal chloride and ligand.

pH-*Titration.* The interaction of Ch.Ac.H. with different metal ions under investigation was studied by pH titrations in 50% Water- Dioxan. 25 ml solutions were titrated with NaOH in presence of Cu(II), Co(II) Ni(II), Zn(II) and Mn(II) ions. Titration of the ligand alone 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 titration curves in presence of Cu(II), Co(II) and Ni(II) (Fig. 4) exhibit two inflection points corresponding to the successive liberation of two H^+ ions together with an initial drop in pH. This indicates the formation of 1:1 and 1:2 metal:ligand complexes in solution.

IR Spectra. The IR spectra of chromone 6-acetyl hydrazone and its metal complexes were compared. The metal complexes were found to have stoichiometric
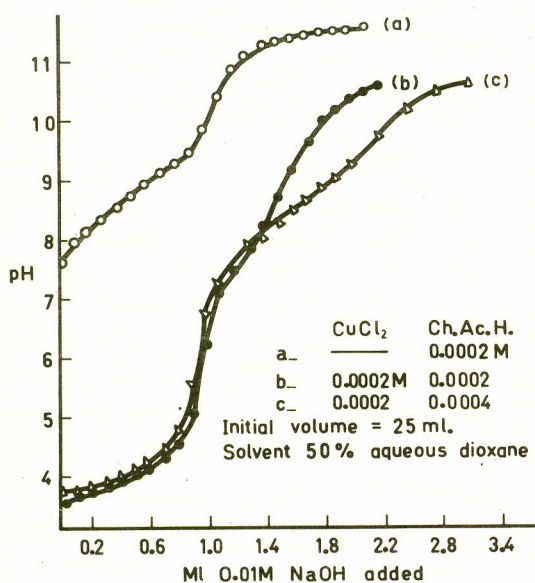

Fig. 4. (a) Titration curves of Ch.Ac.H. in absence and in presence of CuCl$_2$ with 0.01 M NaOH.
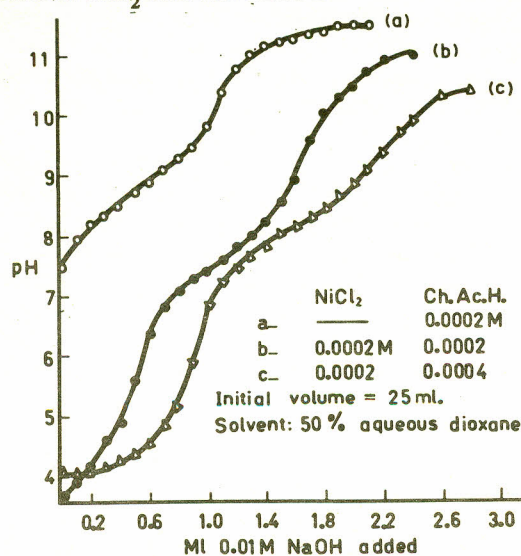

Fig. 4. (b) Titration curves of Ch.Ac.H. in absence and in presence of NiCl$_2$ with 0.01 M NaOH.
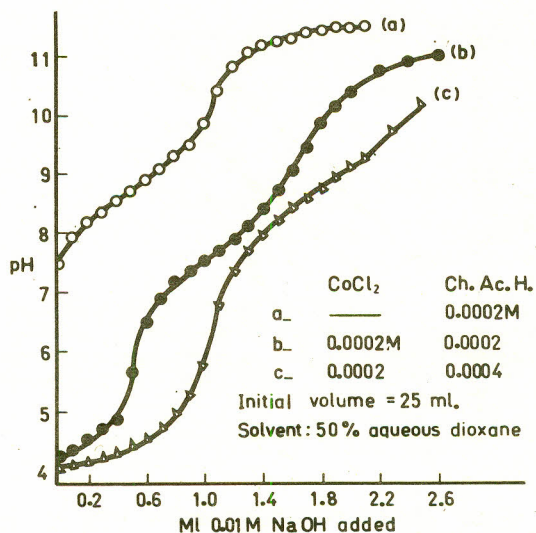

Fig. 4. (c) Titration curves of Ch.Ac.H. in absence and in presence of CoCl$_2$ with 0.01 M NaOH.

ratio M(II):ligand of 1:1 with Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) but with CuCl$_2$ and CuBr$_2$ a 1:2 ratio is also obtained. The spectra of the two types of isolated complexes (1:1 and 1:2) showed some differences on comparison with that of the free ligand. Such comparison in Table 4 shows that the band at 1670 cm^{-1} in the spectrum of the ligand due to the stretching frequency of C=O in chromone moiety [27] is not influenced by coordination, thus indicating that this group does not take part in complex formation. The bands corresponding to -C = O in acetyl hydrazide residue at 1710 cm^{-1} and C=N at 1650 cm^{-1}[28,29] are shifted to lower frequencies in the two types of complexes on chelation with the metal ions. The intense δ-OH band located at 1345 cm^{-1} [30] is absent in the spectra of 1:1 complexes but in 1:2 complexes it is still observed. The absence of this band in the complexes indicates that complex formation in this case takes place through the displacement of a hydrogen ion from the OH group by the metal ion forming a covalent bond. The presence of the band in the spectra of 1:2 complexes proves that the OH group is not involved in chelate formation.

The coordination bond length was determined from the shift of the IR bands using the equation given before [4,14,31]

$$\Delta\nu = \left(\frac{32\pi}{a^2}\right) \frac{\alpha(\nu_{x=y} - \nu_{x-y})}{\ell} \cdot \ell - 2\pi\sqrt{2_r/a}$$

in which:

$\Delta\nu$ = Frequency shift; a = Lattice constant of the metal salt used; $\nu_{x=y}$ = Frequency of the oscillator with double bond e.g. C=O; ν_{x-y} = Frequency of the oscillator with single bond e.g. C-O; ℓ = Length of the oscillator; α = Bond polarisability; r = Distance between oscillator and metal ion, i.e. coordination bond length.

The values of r, determined from the shifts of the C=O and C=N bands are given in Table 4, the results are in good agreement with the values known for the

THE Cu(11), Co(11), Ni(11), Mn(11) AND Zn(11) CHELATES

TABLE 4. IMPORTANT IR BANDS AND COORDINATION BOND-LENGTH
FOR LIGAND AND METAL COMPLEXES.

Compound	Frequencies in cm^{-1} value of r A^o				
	ν C=O	ν C=N	δ -OH	C=O	C=N
$C_{14}H_{15}O_5N_2$	1710	1650	1345	--------	--------
Cu $(C_{14}H_{14}O_5N_2)$ Cl.2H$_2$O	1670	1627	--------	2.53	3.07
Ni $(C_{14}H_{14}O_5N_2)$ Cl.H$_2$O	1680	1630	--------	2.69	3.10
Co $(C_{14}H_{14}O_5N_2)$ Cl	1675	1620	--------	2.61	2.93
Mn $(C_{14}H_{14}O_5N_2)$ Cl.2H$_2$O	1690	1630	--------	2.96	3.12
Zn $(C_{14}H_{14}O_5N_2)$ Cl.2H$_2$O	1690	1630	--------	2.96	3.14
Cu $(C_{14}H_{14}O_5N_2)_2Br_2$	1670	1625	1345	2.53	3.04
Cu$(C_{14}H_{15}O_5N_2)_2Cl_2$	1670	1625	1345	2.53	3.03

coordination bond length determined from X-ray methods.

From the results of all previous physicochemical measurements the structure of 1:1 and 1:2 complexes may thus be represented as follows:
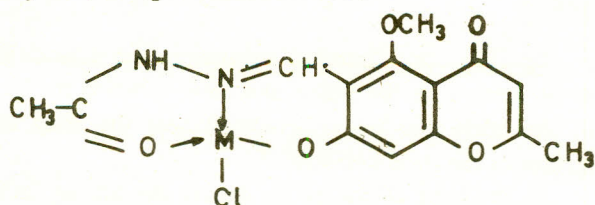
M=Cu(II), Co(II), Ni(II), Zn(II) and Mn(II)
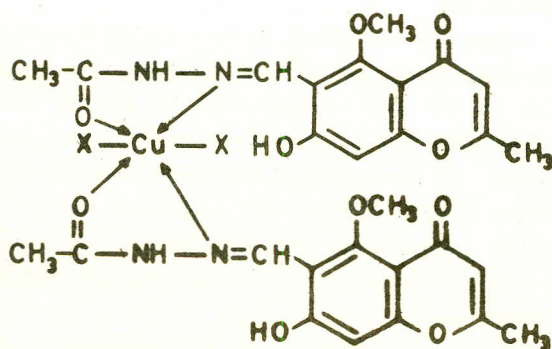
X = Cl, Br

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