

## CHROMONE 3-SALICOYLHYDRAZONE COMPLEXES OF SOME TRANSITION METAL IONS

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Complexes of the types:  $MCl(Ch.S.H.)2H_2O$  where  $M=Cu(II)$  or  $Zn(II)$  and  $(Ch.S.H.) =$  chromone 3-salicylhydrazone;  $MCl_2(Ch.S.H.)_nH_2O$  where  $M=Co(II), Ni(II), Mn(II), Pd(II), Cd(II)$  or  $Cr(III)$ , and  $MCl_2(Ch.S.H.)_2nH_2O$  where  $M=Cu(II), Co(II), Ni(II), Mn(II)$  or  $Cd(II)$  have been prepared and characterized on the basis of elemental analysis and spectral measurement. IR spectral data of the first type indicate that the ligand acts as a tridentate chelating agent coordinating through a proton displacement from the hydroxy group, also with the carbonyl and azomethine groups of salicyl hydrazide residue. In case of other types of complexes, it probably chelated as a bidentate coordinating through the carbonyl and azomethine groups of salicylhydrazide residue. Spectrophotometric studies denotes the suitability of this ligand for the microdetermination of small quantities of metal ions in solution. The apparent stability constants of the complexes are also determined. The visible absorption spectra of the solid complexes in dimethyl formamide indicate that all these complexes have an octahedral configuration except for Pd-complex which has a square-planar structure.

### INTRODUCTION

Metal chelates with hydrazide derivatives were the subject for 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].

In continuation of previous investigations on complexes of hydrazine derivatives of chromone with transition metals [8,9], the present work deals with complexes formed through the interaction of chromone 3-salicylhydrazone with some transition elements in view of throwing some light on their stoichiometry, structure and stability.

### EXPERIMENTAL

**Materials and Analysis.** Analar 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. The analysis of the final products are shown in Table 1.†

**Preparation of Compounds.** The ligand was obtained by condensation of *o*-hydroxy benzoyl hydrazine [10] with chromone 3-carboxaldehyde [11]. The product was recrystallized from ethanol, m.p. 237°.

The solid complexes were prepared by mixing equi-

molar amounts of the ligand and hydrated metal chloride in the solid state followed by the addition of 20 ml absolute ethanol. The mixture was then subjected to reflux on a water bath for 2 hr. On cooling, the complexes separated as fine crystals, that were filtered, washed with small quantities of absolute ethanol and dried over silica gel.

The absorption spectra of the solution were recorded on a Pye-Unicam SP 1800 spectrophotometer. The IR spectra of the solid complexes were investigated by KBr disc technique, using a Pye Unicam SP 1000 IR spectrophotometer.

### RESULTS AND DISCUSSION

**Isolation of Pure Compounds.** The analytical results (Table 1) indicate that the complexes with chromone 3-salicylhydrazone (Ch.S.H.) are of three types: (1)  $MCl(Ch.S.H.)2H_2O$  where  $M=Cu$  or  $Zn$ . (b)  $MCl_2(Ch.S.H.)_nH_2O$  where  $M=Co, Ni, Mn, Cr, Pd,$  or  $Cd$ . (c)  $MCl_2(Ch.S.H.)_2nH_2O$  where  $M=Cu, Co, Ni, Mn$  or  $Cd$ .

These were found to be insoluble in water but slightly soluble in organic solvents and dissolve appreciably in DMF. The DMF solutions of complexes are nonconducting indicating a nonionic nature.

**Spectrophotometric Studies.** Ethanolic solutions containing different proportions of Ch.S.H. with  $Cu(II), Co(II), Ni(II), Mn(II), Cr(III)$  and  $UO_2^{2+}$  ions indicated characteristic absorption maxima at 370, 420, 440, 360, 415, 360, 362, 420, 440, 350, 422, 442, 385, 442 nm respectively, which show the formation of complexes with all these

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† Analysis performed at Microanalytical Unit of Cairo University.

Table 1. Elemental analysis of complexes.

Complex	M.p.	Found (calcd %)					
		C	H	N	Cl	M	H <sub>2</sub> O
Cu(C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	247	46.12 (46.06)	3.61 (3.64)	6.52 (6.32)	8.00 (8.00)	14.30 (14.33)	7.90 (8.13)
Zn(C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	277	45.92 (45.81)	3.51 (3.62)	6.52 (6.29)	8.11 (7.96)	14.59 (14.68)	8.00 (8.10)
Co(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·5H <sub>2</sub> O	246	38.93 (38.66)	4.10 (4.20)	5.50 (5.30)	13.60 (13.43)	11.10 (11.16)	17.30 (17.05)
Ni(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·6H <sub>2</sub> O	282*	37.51 (37.40)	4.42 (4.43)	5.23 (5.13)	13.10 (12.99)	10.80 (10.75)	19.60 (19.80)
Mn(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·4H <sub>2</sub> O	305*	40.26 (40.03)	4.12 (3.98)	5.72 (5.53)	14.00 (14.00)	10.90 (10.85)	14.50 (14.24)
Cr(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·4H <sub>2</sub> O	285	40.81 (40.57)	4.11 (4.10)	5.60 (5.57)	14.20 (14.10)	10.40 (10.33)	14.30 (14.32)
Pd(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	293	38.30 (38.14)	3.21 (3.09)	5.42 (5.37)	13.50 (13.59)	20.40 (20.40)	6.90 (6.91)
Cd(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	†	38.70 (38.70)	3.31 (3.06)	5.12 (5.31)	13.30 (13.44)	21.30 (21.30)	6.70 (6.83)
Cu(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	258	51.80 (51.88)	3.62 (3.58)	7.00 (7.12)	9.00 (9.00)	8.00 (8.10)	4.30 (4.57)
Co(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	263	54.90 (54.71)	3.41 (3.24)	7.40 (7.51)	9.32 (9.50)	7.50 (7.89)	----- (-----)
Ni(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	312*	52.11 (52.21)	3.80 (3.61)	7.00 (7.16)	9.20 (9.07)	7.50 (7.51)	4.53 (4.61)
Mn(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·3H <sub>2</sub> O	†	51.51 (51.27)	3.85 (3.80)	7.10 (7.03)	8.90 (8.90)	6.90 (6.90)	6.70 (6.79)
Cd(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	†	51.15 (51.05)	3.11 (3.02)	7.00 (7.00)	8.90 (8.87)	14.00 (14.05)	----- (-----)

\*Decomposes, † More than 350°

metal ions (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 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 gave straight lines in the concentration range up to  $3.0 \times 10^{-5} M$ . Also the high  $\epsilon$  values ( $3.25 \times 10^4$ ,  $1.63 \times 10^4$ ,  $1.13 \times 10^4$ ,  $2.45 \times 10^4$ ,  $1.17 \times 10^4$  and  $1.83 \times 10^4$  at  $\lambda_{\max}$  for Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, and UO<sub>2</sub><sup>2+</sup> respectively) suggest the possible application 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 [12], straight line [13], continuous variation [14], slope ratio [15], and limiting logarithmic methods [16]. 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 except for copper ion that formed 1:1 complex only.

The apparent stability constants of the complexes were calculated from the results of the molar ratio [12], continuous variation [14], straight line [13] and limiting logarithmic [15] methods. Results are given in Table 2.

The visible absorption spectra of the solid complexes in dimethylformamide indicate that Cu(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O and Cu(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O have a single broad absorption band at 13330 and 12200 cm<sup>-1</sup> respectively, corresponding to transition  ${}^2E_g \rightarrow {}^2T_{2g}$  which is typical of octahedral Cu(II) complexes [17].

The bands observed at 8200, 13520 and 25000 cm<sup>-1</sup> in the spectrum of Ni(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O are characteristic of high-spin octahedral Ni(II) complexes and may be assigned to the transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (F),  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) respectively [18]. Further, the shoulder at 21050 cm<sup>-1</sup> may be attributed to the transition  ${}^3A_{2g} \rightarrow {}^1A_{1g}$  (G). These bands are similar to those

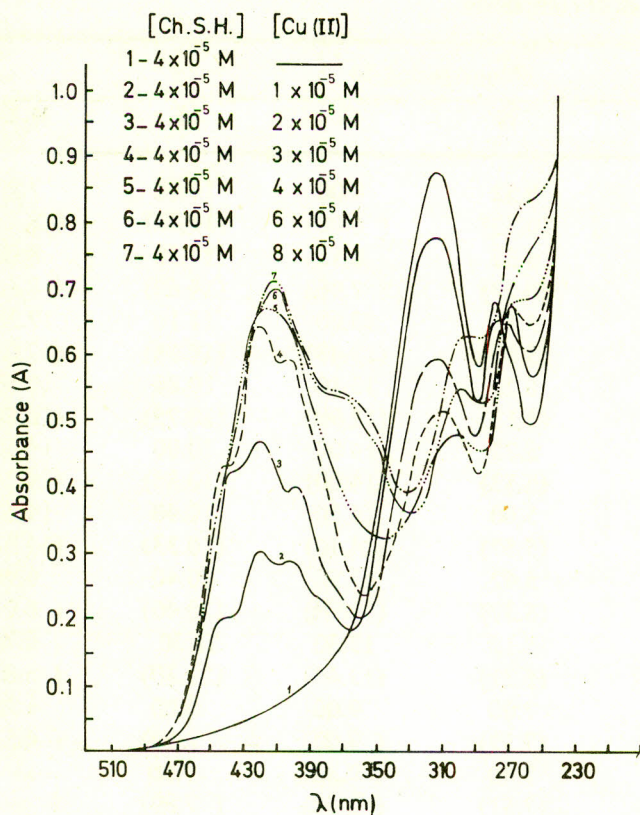


Fig. 1. Absorption spectra of Cu(II)-Ch.S.H. mixtures.

Table 2. Apparent stability constants of metal complexes.

Metal ion	$\lambda_{\max}$	Stoichiometry	Mean value of $\log K$
Cu <sup>2+</sup>	370	1:1	6.44
	440	1:1	6.31
Co <sup>2+</sup>	360	1:1	5.92
	415	1:2	9.94
Ni <sup>2+</sup>	360	1:1	6.12
	360	1:2	10.30
Mn <sup>2+</sup>	362	1:1	5.73
	362	1:2	10.46
UO <sub>2</sub> <sup>2+</sup>	440	1:1	4.52
	385	1:1	9.28
	442	1:2	5.21
Cr <sup>3+</sup>	440	1:1	5.22
	385	1:1	8.43
	442	1:1	5.13
Cr <sup>3+</sup>	442	1:1	5.13
	350	1:1	8.76
	350	1:2	3.61
	442	1:1	7.26
Cr <sup>3+</sup>	442	1:1	3.92
	442	1:2	8.25

observed in case of Ni(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O complex.

The spectra of Pd(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O complex indicate three absorption bands at 22200, 26500 and 30600 cm<sup>-1</sup> which can be assigned to the transition <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub>, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>E<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2u</sub> respectively. Thus the Pd(II) complex have a square-planar configuration [19].

Co(C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> complex gives rise to three bands at 8195, 19040 and 21050 cm<sup>-1</sup> that may be assigned to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> (F), <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> (F) and <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (P) transition respectively in octahedral field [20].

The visible spectrum of Mn(II) complexes exhibit shoulder at 25000 cm<sup>-1</sup> which may be referred to the transition <sup>6</sup>A<sub>1g</sub> → E<sub>g</sub> (G) in the octahedral environment [21].

**Infrared Spectra.** The mode of bonding between the ligand and metal ion can be readily revealed by comparing the IR spectra of the solid complexes with those of the organic ligand. The ligand exhibits a broad band at 3260 cm<sup>-1</sup> which is attributed to ν -OH frequency. It is reasonable to expect hydrogen bonding between phenolic hydrogen atom and hydrazone C=O oxygen atom on the basis of the broadening of this band and magnitude of shift from normal position of the free phenolic ν -OH vibration (3700 - 3500) [22,23]. This band disappears in Cu-(C<sub>17</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O complexes, indicating that phenolic -OH group of the ligand gets deprotonated in complex formation [22,24]. In other complexes, however, the band is still observed in the same position indicating that -OH group does not take part in complex formation.

The IR spectra of all complexes, except Co(C<sub>17</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> and Cd(C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> complexes, exhibit a weak and broad band in the range 3550 - 3300 cm<sup>-1</sup> denoting the presence of associated water molecules in the complexes [25,26].

Comparison of the data in Table 3 shows that the band at 1640 cm<sup>-1</sup> in the spectrum of ligand due to the stretching frequency of C=O in chromone moiety [27] is not influenced by coordination indicating that this group does not participate in complex formation. The band at 1665 cm<sup>-1</sup> which corresponds to the stretching frequency of the C=O group in salicylhydrazone residue shifts to a lower frequency in all complexes due to coordination with the metal ion. Also, the C=N band at 1625 cm<sup>-1</sup> [28] is shifted to a lower wave number in the spectra of complexes. This reveals azomethine group as one of the coordination sites of the ligand. The coordination of nitrogen to the metal atom would be expected to reduce the electron density in the azomethine link and thus causing a reduction in the ν C=N frequency.

A medium band already observed at 1330 cm<sup>-1</sup> in the free ligand, attributed to inplane deformation vibration [29] of OH, disappears in the spectra of Cu(C<sub>17</sub>H<sub>11</sub>O<sub>4</sub>H<sub>2</sub>)-

Table 3. Important IR bands for ligand and metal complexes.

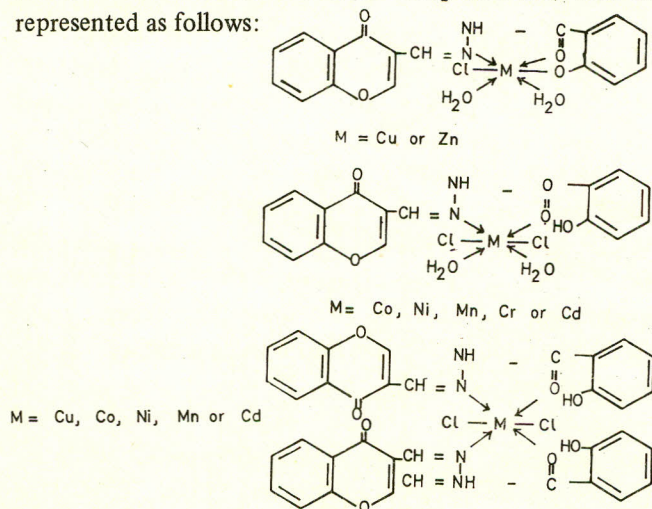
Compound	Frequencies (cm <sup>-1</sup> )				
	$\nu\text{C}=\text{O}^*$	$\nu\text{C}=\text{O}^\dagger$	$\nu\text{C}=\text{N}$	$\delta\text{-OH}$	$\nu\text{M-Cl}$
C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub>	1665	1640	1625	1330	---
Cu(C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	1645	1640	1595	---	360
Zn(C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	1645	1640	1600	---	340
Co(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·5H <sub>2</sub> O	1650	1640	1610	1330	360
Ni(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·6H <sub>2</sub> O	1645	1649	1595	1332	355
Mn(17H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·4H <sub>2</sub> O	1645	1640	1615	1330	360
Cr(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·4H <sub>2</sub> O	1650	1640	1615	1325	355
Pd(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	1650	1640	1610	1330	350
Cu(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	1655	1640	1610	1328	355
Co(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	1650	1640	1610	1330	355
Ni(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	1650	1640	1615	1330	350
Mn(C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ·3H <sub>2</sub> O	1650	1640	1610	1330	350
Cd(17H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> O	1648	1640	1610	1330	355
Cd*C <sub>17</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	1650	1640	1605	1330	345

\*In chromone moiety, †in hydrazide moiety.

Cl<sub>2</sub>·2H<sub>2</sub>O and Zn(C<sub>17</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O complexes. This is apparently due to the displacement of a hydrogen ion from the OH group through interaction with the metal ions. In the other complexes the band is still prominent in the spectra of the chelates near the same position, as in the ligand, indicating that the -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.

The IR spectra of all complexes exhibit a medium band in the region at 360–340 cm<sup>-1</sup> due to the stretching frequency of the M–Cl [25].

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



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