This article was downloaded by: [University of Chicago Library] On: 20 November 2014, At: 01:50 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

# Separation and Characterization of New Transition Metal Complexes of Some Chromone Derivatives

Nabil S. Youssef<sup>a</sup>

<sup>a</sup> Inorganic Chemistry Department, National Research Center, Dokki, Giza, Egypt Published online: 23 Apr 2008.

To cite this article: Nabil S. Youssef (2000) Separation and Characterization of New Transition Metal Complexes of Some Chromone Derivatives, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 30:2, 225-238, DOI: 10.1080/00945710009351759

To link to this article: http://dx.doi.org/10.1080/00945710009351759

## PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages,

and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

### SEPARATION AND CHARACTERIZATION OF NEW TRANSITION METAL COMPLEXES OF SOME CHROMONE DERIVATIVES

Nabil S. Youssef

Inorganic Chemistry Department, National Research Center, Dokki, Giza, Egypt

#### ABSTRACT

Transition metal complexes of two new ligands derived from the condensation of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone with barbituric acid  $(H_2L^1)$  and 6-formyl-5,7-dihydroxy-2-methylchromone with thiobarbituric acid  $(H_3L^2)$  have been prepared and characterized by elemental analyses, IR and electronic spectra and thermogravimetric analyses. Square-planar structures are suggested for the Cu(II) and Pd(II) complexes, whereas octahedral structures are proposed for the Cr(III), Ni(II), Co(II), Pt(IV) and Rh(III) complexes.

#### **INTRODUCTION**

There is some interest in the chemistry of chromone derivatives due to their ability to form metal chelates<sup>1-3</sup>. On the other hand, barbiturates and thiobarbiturates, classified as substituted pyrimidines, have been shown to exert pronounced physiological effects<sup>4,5</sup>. Moreover, certain substituted pyrimidines are being studied as antitumor agents<sup>6</sup>. In addition, barbiturates and thiobarbiturates are known to form complexes with transition metals<sup>7-10</sup>. Thus, it was considered to be of interest to study the synthesis and characterization of chromonebarbituric (H<sub>2</sub>L<sup>1</sup>) and thiobarbituric (H<sub>3</sub>L<sup>2</sup>) acids (Fig. 1) and their Cu(II), Pd(II), Co(II), Ni(II), Cr(III), Pt(IV), and Rh(III) complexes for their expected interesting use.



(1) X = O,  $Y = CH_3$ ;  $(H_2L^1)$ (2) X = S, Y = H;  $(H_3L^2)$ 

Fig. 1. Structure of the Ligands.

#### **EXPERIMENTAL**

#### Materials

All materials used were of the highest purity available. The preparation of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone (1) and 6-formyl-5,7-dihydroxy-2-methylchromone (2) followed the procedure described before<sup>11</sup>.

#### Preparation of the Ligands

The ligand  $H_2L^1$  was prepared by mixing 9.36 g (40 mmol) of (1) with 5.12 g (40 mmol) of barbituric acid in 100 mL of hot absolute ethanol. The second ligand,  $H_3L_2$ , was prepared by mixing of 8.8 g (40 mmol) of (2) in 40 mL of hot toluene, with 6.48 g (40 mmol) of thiobarbituric acid in 50 mL of hot absolute ethanol. The mixtures were then refluxed with constant stirring for 2 h, when the solid ligands precipitated. The solids were filtered off, washed with hot ethanol and purified by crystallization from dioxane. The yield was found to be 12.75 g and 12.54 g for the ligands  $H_2L^1$  and  $H_3L_2$ , respectively.

#### Preparation of the Metal Complexes

The metal complexes of these ligands were prepared by mixing a hot aqueous solution of the metal chlorides (CuCl<sub>2</sub>.2H<sub>2</sub>O, PdCl<sub>2</sub>, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O, PtCl<sub>4</sub> and RhCl<sub>3</sub>) with the required amount of a hot dioxane solution of the ligands  $H_2L^1$  or  $H_3L^2$  to form 1:1, 1:2 or 2:1 M:L complexes, as shown in Table I. The RhCl<sub>3</sub> solution was prepared by dissolving Rh<sub>2</sub>O<sub>3</sub> in the least amount of hot conc. HCl. PdCl<sub>2</sub> was first dissolved in the least amount of hot conc. HCl. The reaction mixture

	Me	etal Chlori	de	Ligand			
Complex	Mass (g)	mmol	Water (mL)	Mass (g)	mmol	Dioxane (mL)	
1:1 M:L							
Cu-H <sub>2</sub> L <sup>1</sup>	0.85	5	20	1.72	5	50	
Co-H <sub>2</sub> L <sup>1</sup>	1.19	5	20	1.72	5	50	
Ni-H <sub>2</sub> L <sup>1</sup>	1.19	5	20	1.72	5	50	
Cr-H <sub>2</sub> L <sup>1</sup>	1.33	5	20	1.72	5	50	
Pt-H <sub>2</sub> L <sup>1</sup>	1.35	4	20	1.37	4	40	
Rh-H <sub>2</sub> L <sup>1</sup>	0.84	4	20	1.37	4	40	
Rh-H <sub>3</sub> L <sup>2</sup>	0.84	4	20	1.38	4	40	
<u>1:2 M:L</u>				1			
Pd-H <sub>2</sub> L <sup>1</sup>	0.44	2.5	10	1.72	5	50	
Pd-H <sub>3</sub> L <sup>2</sup>	0.44	2.5	10	1.73	5	50	
Ni-H <sub>3</sub> L <sup>2</sup>	0.59	2.5	10	1.73	5	50	
Pt-H <sub>3</sub> L <sup>2</sup>	0.84	2.5	10	1.73	5	50	
<u>2:1 M:L</u>							
Cu-H <sub>3</sub> L <sup>2</sup>	0.85	5	20	0.87	2.5	25	
Co-H <sub>3</sub> L <sup>2</sup>	1.19	5	20	0.87	2.5	25	
Cr-H <sub>3</sub> L <sup>2</sup>	1.33	5	20	0.87	2.5	25	

Table I. The Amount of the Reactants Used in the Formation of the Complexes.

was then refluxed for a time depending on the transition metal salt used. The complexes did not separate on standing but when a few drops of aqueous ammonia solution (1:10) were slowly added with stirring until the pH reached 5.0-5.5, the solid metal chelates precipitated. These precipitates were filtered, washed with hot dioxane, then with diethyl ether and dried over anhydrous CaCl<sub>2</sub>.

#### Physical Measurements

IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 200-4000 cm<sup>-1</sup>. The electronic spectra of the ligands and their complexes were obtained in Nujol mulls and in saturated DMF solutions using a Shimadzu UV-240 UV-Visible recording spectrophotometer. <sup>1</sup>H NMR spectra of (1), (2), barbituric and thiobarbituric acids and the ligands were recorded in DMSO-d<sub>6</sub> using a Jeol EX-270 MHz NMR spectrophotometer from 0-14 ppm with TMS as an internal standard. Thermogravimetric analyses of the investigated complexes were carried out using a DTA-7 and TGA-7 Perkin Elmer 7 series thermal analysis system. The mass losses were measured from ambient temperature up to 600° C at a heating rate of 10° C min<sup>-1</sup>. In the case of the Pd and Pt complexes the mass losses were measured up to  $1000^{\circ}$  C and the Pd and Pt contents were then determined. The complexes were analyzed for C, H, N, M and Cl content at the Microanalytical Laboratory, Faculty of Science, Cairo The metal ion (M) contents of the complexes were also University, Egypt. determined<sup>12-14</sup> by the previously reported method<sup>15</sup>.

#### RESULTS AND DISCUSSION

The elemental and in some cases the thermogravimetric analyses of the ligands and the solid complexes, listed in Tables II, III and IV, showed that the stoichiometry of the complexes obtained is either 1:1, 1:2 or 2:1 (metal : ligand) for the two ligands  $H_2L^1$ and  $H_3L^2$ . The formation of the complexes can be represented by the following general equations:

 $H_{x}L + MCl_{2.4} + xH_{2}O \rightarrow [M(H_{x-1 \text{ or } x-2}L)(H_{2}O)_{2 \text{ or } 4}]Cl_{1.3}.aH_{2}O + (1 \text{ or } 2)HCl_{2}H_{x}L + MCl_{2 \text{ or } 4} + yH_{2}O \rightarrow [M(H_{x-1 \text{ or } x-2}L)_{2}(H_{2}O)_{0 \text{ or } 2}]Cl_{0 \text{ or } 2}.bH_{2}O + 2HCl_{2}O)$ 

Ligands	F. Wt.	Yield In %	M.p. (°C)	Colour	%C Found (Calc.)	%H Found (Calc.)	%N Found	%S Found (Calc.)
$H_{2}L^{1}$ C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>7</sub>	344	88	>300 (dec.)	Yellow	55.69 (55.81)	3.42 (3.49)	8.20 (8.14)	
H <sub>3</sub> L <sup>2</sup> C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>6</sub> S	346	82	310-312	Orange	52.15 (52.02)	2.82 (2.89)	8.00 (8.09)	9.18 (9.24)

Table II. Elemental Analyses, Colour and Melting Points of the Ligands.

Table III. Elemental Analyses, Colour and Melting Points of Metal Complexes of the Ligands  $H_2L^1$  and  $H_3L^2$ .

Complexes	Colour	F.Wt.	M.p.	Yield	%С	_%H	%N	%Cl _ =	%M
			or	in	Found	Found	Found	Found	Found
			(d.p.)	%	(Calc.)	(Calc.)	(Calc.)	(Calc.)	(Calc.)
							5.60		10.00
$[Cu(HL^{-})(H_2O)_2]CLH_2O$	Brown	496.1	(435)	90	38.69	3.40	5.60	7.06	12.70
CuC <sub>16</sub> H <sub>17</sub> N <sub>2</sub> O <sub>10</sub> CI		l			(38.70)	(3.43)	(5.64)	(7.16)	(12.81)
$[Pd(HL')_2].4H_2O$	Yellow	864.4	(350)	87	44.31	3.36	6.36		12.18
PdC <sub>32</sub> H <sub>30</sub> N <sub>4</sub> O <sub>18</sub>				ļ	(44.42)	(3.47)	(6.48)		(12.31)
$[Co(HL')(H_2O)_4]Cl.H_2O$	Brown	527.4	(342)	88	36.30	4.00	5.30	6.80	11.05
CoC <sub>16</sub> H <sub>21</sub> N <sub>2</sub> O <sub>12</sub> Cl				I	(36.41)	(3.98)	(5.31)	(6.73)	(11.17)
[Ni(HL <sup>1</sup> )(H <sub>2</sub> O)₄]Cl.3H <sub>2</sub> O	Yellow	563.2	(365)	85	34.12	4.40	4.98	6.35	10.52
NiC <sub>16</sub> H <sub>25</sub> N <sub>2</sub> O <sub>14</sub> Cl					(34.09)	(4.44)	(4.97)	(6.30)	(10.46)
$[Cr(HL^{T})(H_{2}O)_{4}]Cl_{2}.3H_{2}O$	Green	592.0	(410)	80	32.40	4.22	4.70	12.10	8.70
CrC16H25N2O14Cl2			1		(32.43)	(4.22)	(4.73)	(11.99)	(8.78)
[Pt(HL <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> .H <sub>2</sub> O	Yellow	734.6	322	62	26.10	2.80	3.80	14.60	26.50
PtC <sub>16</sub> H <sub>21</sub> N <sub>2</sub> O <sub>12</sub> Cl <sub>3</sub>	1		_		(26.14)	(2.86)	(3.81)	(14.50)	(26.56)
$[Rh(L^{1})(H_{2}O)_{4}]Cl.2H_{2}O$	Orange	588.4	(363)	74	32.67	3.70	4.66	6.10	17.40
RhC16H22N2O13Cl	-				(32.63)	(3.74)	(4.76)	(6.03)	(17.49)
[Cu <sub>2</sub> (1. <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> ]Cl.2H <sub>2</sub> O	Brown	613.6	315	75	29.23	3.08	4.50	5.70	20.85
Cu <sub>2</sub> C <sub>15</sub> H <sub>19</sub> N <sub>2</sub> O <sub>12</sub> SCl		1			(29.34)	(3.10)	(4.56)	(5.79)	(20.71)
[Pd(11,2),1.5H2O	Brown	886.4	(395)	82	40.55	3.10	6.28		12.10
PdC30H28N4O17S2					(40.61)	(3.16)	(6.32)		(12.00)
$[Co_{2}(L^{2})(H_{2}O)_{8}]CI.2H_{2}O$	Blue	676.4	(437)	77	26.60	3.90	4.20	5.30	17.30
C05C15H27N2O16SCI			ľ í		(26.61)	(3.99)	(4.14)	(5.25)	(17.42)
$[Ni(H_{2}L^{2})(H_{2}O)_{2}].5H_{2}O$	Pink	874.7	(405)	68	41.08	3.60	6.45		6.78
NiCanHazNAO 19S2			( ···· /		(41.16)	(3.66)	(6.40)		(6.71)
$\left[\left(C_{12}\left(L^{2}\right)\left(H_{10}\right), \left(C_{12}\right), H_{20}\right)\right]$	Green	715.5	315	78	25.08	3.40	3.80	14.95	14.41
Cr <sub>2</sub> C <sub>1</sub> sH <sub>2</sub> sN <sub>2</sub> O <sub>1</sub> sSC <sub>1</sub>	0.000	1.5.5			(25.16)	(3.49)	(3.91)	(14.88)	(14.54)
[Pt(H <sub>2</sub> ] <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> 3H <sub>2</sub> O	Yellow	1046 1	(428)	80	34 48	2.71	5.30	6.85	18 75
PICaoHaeNaOuzSaCla	1.5.10.0		(` <b>_</b> 0)	Ĩ	(34.41)	(2.68)	(5.35)	(6.79)	(18.65)
IRb(Hal <sup>2</sup> )(HaO)dCla SHaO	Orange	680.9	(334)	92	26.40	3.90	4.10	10.30	15 30
DEC H NO.SCI	Shange		(334)	1 ~~	(26 44)	(3.97)	14 11	(10.43)	10510

		Water	No. of	Temp.	Water	No. of	Temp.
	M:L	Of	Hydrated	(°C)	of	coordinated	(°C)
Complex		Hydration	Water	up to	coordination	water	up to
-		Mass loss %	Molecules/	-	Mass loss %	molecules/	-
		Calc.	Chelate		Calc.	chelate	
		(Found)	Molecule		(Found)	molecule	
[Cu(HL <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ]Cl.H <sub>2</sub> O	1:1	3.63	1	155	7.26	2	221
		(3.71)			(7.34)		
[Pd(HL <sup>1</sup> ) <sub>2</sub> ].4H <sub>2</sub> O	1:2	8.33	4	140			
		(8.50)					
$[Co(HL')(H_2O)_4]Cl.H_2O$	1:1	3.41	1	115	13.65	4	303
		(3.30)			(13.49)		
[Ni(HL <sup>1</sup> )(H <sub>2</sub> O) 4]Cl.3H <sub>2</sub> O	1:1	9.59	3	136	12.78	4	278
		(9.71)			(12.65)		
[Cr(HL <sup>1</sup> )(H <sub>2</sub> O) 4]Cl <sub>2</sub> .3H <sub>2</sub> O	1:1	9.12	3	132	12.16	4	350
		(9.24)			(12.10)		
$[Pt(HL^{T})(H_{2}O)_{4}]Cl_{3}.H_{2}O$	1:1	2.45	1	144	9.80	4	290
		(2.50)			(9.71)	1	
[Rh(L1)(H2O)4]Cl.2H2O	1:1	6.12	2	130	12.24	4	336
		(6.00)			(12.10)		
$[Cu_2(L^2)(H_2O)_4]C1.2H_2O$	2:1	5.87	2	128	11.73	4	228
		(5.90)			(11.58)	1	
$[Pd(H_2L^2)_2].5H_2O$	1:2	10.15	5	140			
	1	(10.33)		1			
[Co <sub>2</sub> (L <sup>2</sup> )(H <sub>2</sub> O) <sub>8</sub> ]Cl.2H <sub>2</sub> O	2:1	5.32	2	120	21.29	8	234
-		(5.40)	]		(21.00)		
[Ni(H <sub>2</sub> L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].5H <sub>2</sub> O	1:2	10.29	5	148	4.12	2	272
		(10.42)			(4.05)		i
$[Cr_2(L^2)(H_2O)_8]Cl_3.H_2O$	2:1	2.52	1	117	20.13	8	254
		(2.60)			(20.00)		
[Pt(H <sub>2</sub> L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> .3H <sub>2</sub> O	1:2	5.16	3	126	3.44	2	261
		(5.05)			(3.32)	1	
[Rh(H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> .5H <sub>2</sub> O	1:1	13.22	5	159	10.57	4	222
		(13.00)		1	(10.68)		

Table IV. Thermogravimetric Analysis Results of the Investigated Metal Complexes of the two Ligands.

 $H_xL + 2MCl_{2 \text{ or } 3} + zH_2O \rightarrow [M_2(L)(H_2O)_{4 \text{ or } 8}]Cl_{1 \text{ or } 3}.cH_2O + 3HCl$  $H_xL = H_2L^1(x = 2); H_3L^2(x = 3)$ 

#### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the ligands  $H_2L^1$  and  $H_3L^2$  showed the aromatic proton signal at 6.7-8.0 ppm. The spectra also showed a signal due to the pyrone ring proton at 5.1-6.65 ppm, whereas the sharp signal observed at 11.4-12.4 ppm may be assigned to the phenolic proton. Moreover, the spectra of the two ligands indicated the

disappearance of the singlet due to the aldehydic proton, which was observed at 10.2-10.3 ppm in the chromon.1 and chromon.2 spectra. A new signal appeared in the spectra of the two ligands in the 6.30-6.65 ppm region which may be due to the proton of the =CII- group joining the chromone and the barbituric or thiobarbituric acid moieties.

#### Infrared Spectra

The most important IR bands of the ligands and their metal complexes and their assignments are given in Table V.

The spectra of all of the  $H_2L^1$  and  $H_3L^2$  complexes exhibit a broad band in the range 3300-3520 cm<sup>-1</sup>, assigned to v(OH), suggesting the presence of water molecules<sup>16</sup>.

The v(C=O) bands of the pure ligand  $H_2L^1$  at 1750, 1710 and 1690 cm<sup>-1</sup> either have disappeared, weakened and/or shifted to lower frequencies in its complexes, indicating that at least one of the carbonyl groups of the barbituric acid moiety is strongly bonded to the metal ion or tautomerized with its adjacent NH group to give the enol form. This may be accompanied by bonding of the ligand to the metal ion via the hydroxyl group with the elimination of the corresponding proton in the case of the Rh(III)-H<sub>2</sub>L<sup>1</sup> complex. Moreover, the v(C=N) band at 1600 cm<sup>-1</sup> in the spectra of the free ligand H<sub>2</sub>L<sup>1</sup> remains nearly unchanged. Such finding generally may give additional support to the tautomerism phenomena in this ligand and its complexes. The redshifting of the amide I and II bands in all H<sub>2</sub>L<sup>1</sup> complexes shows also that one of the carbonyl groups of the barbituric acid moiety acts as a center for complexation.

In Table V, the band at 1360 cm<sup>-1</sup>, ascribed to the phenolic C-O stretching vibration<sup>17</sup> in the spectrum of  $H_2L^1$ , in the spectra of its metal complexes is either shifted to lower frequencies or split into weaker bands. This implies that the hydroxylic oxygen anion in position seven in the chromone moiety takes part in formation of these complexes.

A remarkable feature for one of the thiobarbituric acid carbonyl stretching vibrations of the free  $H_3L^2$  ligand at 1620 cm<sup>-1</sup> is that it is slightly affected on complexation in all the  $H_3L^2$  complexes. However, the second v(C=O) band of the free ligand at 1670 cm<sup>-1</sup> is either still existing in the same position in the Pd, Ni, Pt and Rh

Free Ligand	Cu(II) Complex	Pd(II) Complex	Co(II) Complex	Ni(II) Complex	Cr(III) Complex	Pt(IV) Complex	Rh(III) Complex	Assignment			
H <sub>2</sub> L <sup>1</sup>		$H_2L^1$ Complexes									
3380	3400 b	3320 Ь	3400 Ь	3320-	3320-	3340 b	3420 b	v(OH)			
				3480 b	3440 Ь						
3200 m	3220 m	3180 Б	3260 m	3240 m	3200 Ь	3240 Ъ	3180 Б	v(NH)			
1750 s	1720 w	1730 w	1730 w	1720 w	1730 w	1720 w		v(C=O)			
1710 s	1700 w	1710 m	1700 m	1700 m	1690 m	1700 m	1690 m				
1690 m	1670 m	1680 m	1660 s	1680 s	1660 s	1670 s	1670 m				
1660 s	1640 w	1640 m	1650 m	1640 w	1590 s	1610 m	1620 s	Amide I			
1600 s	1590 s	1600 m	1590 m	1590 m	1590 s	1590 s	1580 s	v(C=N)			
1560 m	1530 s	1550 m	1510 m	1530 w	1510 w	1520 m	1400 s	Amide II			
1360 s	1370 w	1350 w	1350 w	1340 w	1270 s	1270 s	1290 s	$v(C-O)^{a}$			
	1340 w										
H <sub>3</sub> L <sup>2</sup>	$H_3L^2$ Complexes										
3410 b	3380-	3380-	3320-	3320-	3320-	3320-	3360-	v(OH)			
	3480 Ь	3480 Ь	3460 b	3460 Ь	3440 Ь	3520 Ъ	3520 Ь	. ,			
3180 m	3180 s	3160 b	3100-	3140-	3080-	3080-	3040-	v(NH)			
			3280 b	3240 b	3280 Ъ	3120 Ь	3260 Ь				
1670 s	1620 s	1670 m	1650 m	1670 s	1650 s	1670 m	1670 m	v(C=O)			
1620 m	1610 m	1640 m	1610 b	1610 s	1610 m	1610 b	1620 m				
1590 s	1570 w	1550 w	1520 b	1520 b	1510 w	1550 w	1520 s	v(C=O) <sup>b</sup>			
1460 s	1460 w	1460 m	1460 w	1460 m	1460 w	1460 w	1460 w	Thioamide I			
1390 s	1390 s	1390 s	1390 m	1390 m	1400 s	1390 s	1400 s	Thioamide II			
1360 s	1330 w	1330 v w	1330 w	1330 m	1330 w	1330 w	1330 w	v(C-O) <sup>a</sup>			
1280 s	1270 m	1280 m	1240 Ь	1290 Ь	1250 s	1280 s	1280 m				
1100 s	1070 w	1100 s	1100 s	1100 s	1100 s	1100 s	1100 s	Thioamide III			
800 s	800 m	800 m	800 s	800 m	800 m	800 s	800 m	Thioamide IV			

Table V. IR Frequencies of the Bands (cm <sup>-1</sup> ) of H <sub>2</sub> L <sup>1</sup> and H <sub>3</sub> L <sup>2</sup> Ligands and the	eir
Complexes and their Assignments.	

<sup>a</sup>Phenolic C-O

<sup>b</sup>Chromone carbonyl

complexes, or red-shifted in the case of the Cu, Co and Cr complexes. This shows that one of the carbonyl groups may be still tautomerized with the adjacent NH groups in all the  $H_3L^2$  complexes, whereas the other carbonyl group may be involved in complexation with the Cu(II), Co(II) and Cr(III) metal ions.

The IR spectra of the free ligand  $H_3L^2$  showed the four bands, assigned as thioamide bands, at 1460, 1390, 1100 and 800 cm<sup>-1</sup>. The weak intensity of the first band, assigned mainly as  $\delta$ (NH), together with the presence of the second thioamide band in nearly the same position as that in the ligand spectra in all the  $H_3L^2$  complexes, may be taken as another evidence for the keto-enol tautomerism. On the other hand, the bands due to the chromone-carbonyl and one or two of the phenolic C-O stretching vibrations of the ligand  $H_3L^2$  are shifted to lower frequencies in its complexes. Such data suggest the view that the complexation takes place via the chromone carbonyl group and oxygen anions of the OH groups in positions 5 or 5 and 7 in the chromone moiety in the  $H_3L^2$  complexes. However, the thioamide III and IV bands at 1100 and 800 cm<sup>-1</sup>, having main contributions from v(C=S) in the spectra of the pure ligand  $H_3L^2$ , are in the same position in all chelates of this ligand, excluding metal-sulphur bonding<sup>18</sup>.

#### Electronic Spectra

The electronic absorption bands of the ligands and their metal complexes are listed in Table VI. The spectra of the ligands  $H_2L^1$  and  $H_3L^2$  are characterized by three absorption bands in the 330-390 nm region. Generally, the longer wave length bands in the spectra of their metal complexes may be considered as evidence for complex formation.

The broad band located at 470-520 nm in the electronic spectra of the Cu(II) –  $H_2L^1$  and  $H_3L^2$  complexes may be due to the  ${}^2B_{1g} \rightarrow {}^2E_g$  transition<sup>2</sup> or a combination of the  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions<sup>1</sup>, expected for a square-planar configuration.

The Pd(II) complexes show two absorption bands, one at 490-500 nm and the other band at 420-430 nm which may be assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}E_{1g}$  transitions<sup>2,19</sup>, respectively, consistent with square-planar Pd(II) complexes.

The electronic spectra of the Co(II)-H<sub>2</sub>L<sup>1</sup> and H<sub>3</sub>L<sup>2</sup> complexes show an absorption band at 530-540 nm due to the  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$  transition, suggesting a

Ligands	$\lambda_{\text{max}}$ , nm( $\epsilon$ , lit. mol. <sup>-1</sup> cm <sup>-1</sup> )					
their Complexes	Nujol	DMF				
H <sub>2</sub> L <sup>1</sup>		330(34500), 350(31000), 390(28500)				
$[Cu(HL^1)(H_2O)_2]Cl.H_2O$	390, 500	380(25000), 470(123)				
[Pd(HL <sup>1</sup> ) <sub>2</sub> ].4H <sub>2</sub> O	320, 380, 430, 490	400(18500), 420(sh)				
[Co(HL <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> ]Cl.H <sub>2</sub> O	330, 360, 380	490(sh), 540(15.5)				
$[Ni(HL^{1})(H_{2}O)_{4}]Cl.3H_{2}O$	350, 440, 510	480(18), 540(10)				
$[Cr(HL^{1})(H_{2}O)_{4}]Cl_{2}.3H_{2}O$	380, 500, 590	550(128), 630(100)				
$[Pt(HL^1)(H_2O)_4]Cl_3. H_2O$	350, 500, 640	390(18200), 490(50), 545(41)				
$[Rh(L^{1})(H_{2}O)_{4}]Cl.2H_{2}O$	350, 400,660	400(17000), 460(340)				
$H_3L^2$		330(36500), 350(32500), 370(26000)				
$[Cu_2(L^2)(H_2O)_4]Cl.2H_2O$	350, 500	370(15500), 520(332)				
$[Pd(H_2L^2)_2].5H_2O$	390, 430,500	430(240)				
$[Co_2(L^2)(H_2O)_8]Cl.2H_2O$	360, 530, 760	370(12500), 530(17), 665(12.5)				
$[Ni(H_2L^2)_2(H_2O)_2].5H_2O$	330, 490, 560	380(16500), 490(19), 525(9)				
$[Cr_2(L^2)(H_2O)_8]Cl_3.H_2O$	380, 500,590	380(14500), 530(95), 590(65)				
$[Pt(H_2L^2)_2(H_2O)_2]Cl_2.3H_2O$	390, 440, 520, 590	430(sh), 480(38)				
$[Rh(H_2L^2)(H_2O)_4]Cl_2.5H_2O$	350, 510	370(12500)				

# Table VI. Electronic Absorption Spectral Bands of the Ligands H<sub>2</sub>L<sup>1</sup> and H<sub>3</sub>L<sup>2</sup> and their Complexes.

high-spin octahedral structure<sup>20</sup>. However, the spectra of the Co(II)–H<sub>3</sub>L<sup>2</sup> complex has an additional absorption band, assigned to the  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$  transition, in the 665-760 nm region, suggesting a distorted-octahedral configuration due to the Jahn-Teller effect<sup>21</sup> in this complex.

The electronic spectra of the Ni(II) complexes of the two ligands show two absorption bands, one at 510-560 and the other at 440-490 nm, due to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ 



Fig. 2. Suggested Structures of the  $H_2L^1$ Complexes (M:L = 1:1 and 1:2).

and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$  transitions, respectively, observed for octahedral Ni(II)-complexes<sup>22,23</sup>.

The spectra of the two Cr(III) complexes exhibit two absorption bands at 590-630 and 500-550 nm, assigned to the  ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$  and  ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$  transitions, respectively, suggesting an octahedral stereochemistry<sup>19</sup>.

The spectra of the two Pt(IV) complexes show two bands at 590-640 and 480-545 nm. The first band may be due to the spin-allowed  ${}^{I}A_{1g} \rightarrow {}^{I}T_{2g}$  transition, whereas the second may be a charge-transfer band, which favours a low-spin octahedral structure<sup>24</sup>.



Fig. 3. Suggested Structures of the  $H_3L^2$  Complexes (M:L = 2:1 and 1:1).

The broad band observed in the 460-660 nm region in the spectra of the Rh(III) complexes may be attributable to the  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  or  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  transition, suggesting a low-spin octahedral structure for these complexes<sup>25</sup>.

#### Thermogravimetric Analyses

The thermogravimetric data for the  $H_2L^1$  and  $H_3L^2$  complexes are listed in Table IV. The results obtained are in fair agreement with the theoretical tentative formulae suggested from the elemental analysis.





#### Suggested Structural Formulae of the Complexes

From the spectral data and the elemental and thermal analyses, the structure of the prepared complexes may be formulated in Figs. 2, 3 and 4.

#### REFERENCES

- 1. K. M. Ibrahim and M. M. Bekheit, Transition Met. Chem., 13, 230 (1988).
- 2. A. M. Khattab and M. S. Soliman, Transition Met. Chem., 8, 285 (1983).
- A. A. Abd El-Gaber, A. M. A. Hassan, M. El-Shabasy and A. M. El-Roudi, Synth.React. Inorg.-Met. Org. Chem., <u>21</u>, 1265 (1991).
- A. T. Tu. and M. J. Heller, "Metal Ions in Biological Systems", Vol. <u>1</u>, p.1, Dekker, New York (1974).
- 5. R. D. Jones, D. A. Summervitte and F. Basolo, Chem. Rev., 79, 139 (1979).
- 6. I. Sassaki and A. Gaudemer, Inorg. Chim. Acta, <u>112</u>, 119 (1986).
- A. Pezeshk, F. T. Greenawav and J. R. J. Sorenson, Inorg. Chim. Acta, <u>80</u>, 191 (1983).

- A. Jimenez, H. Jimenez, J. Borras and R. Otiz, Synth. React. Inorg. Met.-Org. Chem., <u>14</u>, 8, 1099 (1984).
- 9. N. S. Youssef and A. E. Eid, Egypt. J. Chem. 34, 305 (1991).
- 10. N. S. Youssef and K. H. Hegab, J. Mater. Sci. Technol., 15,263 (1999).
- 11. A. Schomberg, N. Badran, N. A. Starkowsky, J. Am. Chem. Soc., 75, 4992 (1953).
- 12. F. J. Welcher, "The Analytical Uses of EDTA", Van Nostrand, USA (1958).
- "Vogel's Text Book of Quantitative Inorganic Analysis", 4<sup>th</sup> Edn., Longman (1978).
- Z. Holzbecher, L. Divis, M. Kral, L. Sucha and F. V. Lacil, "Handbook of Organic Reagents in Inorganic Analysis", John Wiley, New York (1976).
- 15. A. M. G. McDonald and P. Sirichanya, Microchem. J., <u>14</u>, 199 (1969).
- K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York (1970).
- 17. J. E. Kovacic, Spectrochim. Acta, 23A, 183 (1967).
- 18. P. Carlo and T. Giuseppe, J. Inorg, Nucl. Chem., <u>38</u>, 1125 (1976).
- 19. B. B. Kaul and K. B. Pandeya, J. Inorg. Nucl. Chem. 40, 1035 (1978).
- T. M. Dunn, "The Visible and Ultraviolet Spectra of Complex Compounds", in J. Lewis and R. G. Wilkins, Eds., "Modern Coordination Chemistry", Interscience, New York, P. 290 (1960).
- Y. M. Issa, W. F. El- Hawary, H. A. Abdel-Salam and R. M. Issa, Transition Met. Chem., <u>20</u>, 423 (1995).
- W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw Hill, p. 276 (1976).
- 23. I. Y. Isaac and D. H. Kerridge, J. Chem. Soc. Dalton Trans., 2701 (1988).
- 24. D. L. Swihart and W. R. Mason, Inorg. Chem. J., 1749 (1970).
- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", John Wiley, London, pp. 1024 (1972).

Received:	30 March 1999	Referee I:	F. T. Greenaway
Accepted:	1 September 1999	Referee II:	T. B. Karpishin