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

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Some transition metal complexes of 5-[7-hydroxy-5-methoxy-2-methyl chromonelidene] barbituric acid (H_2L^1) and 5-[5,7-dihydroxy-2-methyl chromonelidene] thiobarbituric acid (H_3L^2) have been separated 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.

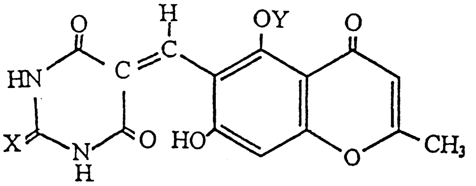
INTRODUCTION

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

EXPERIMENTAL

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

Preparation of the ligands: The two ligands $H_2L^1$and H_3L^2 were prepared by heating two different mixtures of ethanolic solutions of chromon-1 with barbituric acid and chromon-2 with thiobarbituric acid, respectively. The gentle heating was then continued under reflux with constant stirring for *ca.* 2 h, where the solid ligands were precipitated and further purified by re-crystallization from dioxane. Their elemental analyses and some of their physical properties are given in Table-1. The structures of these ligands are shown in Fig. 1.



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

Fig. 1. Structure of the Ligands

Preparation of the metal complexes

The metal complexes of these ligands were prepared by mixing a hot saturated solution (0.0025–0.05 mole) of the metal chlorides: $CuCl_2 \cdot 2H_2O$, $PdCl_2$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $PtCl_4$ and $RhCl_3$ in aqueous medium with the required amount of a hot saturated dioxane solution of the ligands H_2L^1 or H_3L^2 to form 1 : 1, 1 : 2 or 2 : 1 M : L complexes. $RhCl_3$ solution was prepared by dissolving Rh_2O_3 in the least amount of hot conc. HCl. $PdCl_2$ was also at first dissolved in the least amount of hot conc. HCl. The reaction mixture was then refluxed for a time depending on the transition metal salt used. The complexes did not separate on standing but when few drops of ammonia solution (1 : 10) were slowly added with stirring until the pH = 5.0–5.5, the solid metal chelates precipitated. These precipitates were filtered, washed with hot dioxane, then with diethyl ether and desiccated over anhydrous $CaCl_2$. Table-2 represents the physical and analytical data of the prepared complexes.

TABLE-1
ELEMENTAL ANALYSES, COLOUR AND MELTING POINTS OF THE LIGANDS

Ligands (colour)	Yield %	m.p. (°C)	% Analyses, found (calcd.) C	H	N	S
Chromon-1-BA* (ligand H_2L^1) $C_{16}H_{12}N_2O_7$ (yellow)	88	>300 (dec.)	55.69 (55.81)	3.42 (3.49)	8.20 (8.14)	—
Chromon-2-TBA† (ligand H_3L^2) $C_{15}H_{10}N_2O_6S$ (orange)	82	310–312	52.15 (52.02)	2.82 (2.89)	8.00 (8.09)	9.18 (9.24)

*BA = Barbituric acid.
†TBA = Thiobarbituric acid.

IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300 E Fourier transform infrared spectrophotometer covering the range 4000–200 cm^{-1}. The electronic spectra of the ligands and their complexes were obtained in the Nujol mull and in saturated DMF solution using a Shimadzu UV-240 UV-visible recording spectrophotometer. ^1H-NMR spectra of the chromon-1, chromon-2, barbituric and thiobarbituric acids and the ligands were recorded in DMSO using a Jeol EX-270 MH_3NMR spectrophotometer from 0–14 ppm utilizing TMS as an internal standard. Thermogravimetric analyses of the 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^{-1}. In the case of Pd and Pt complexes the mass losses were measured up to 1000°C and the Pd and Pt contents were then determined. The complexes were analyzed for C, H, N, metal and Cl content at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. The metal ion contents of the complexes were also determined according to the previously reported method[12–15].

RESULTS AND DISCUSSION

The elemental and thermogravimetric analyses of the solid complexes are listed in Tables 2 and 5, showed that the stoichiometry of the complexes obtained in either 1 : 1, 1 : 2 or 2 : 1 (metal : ligand) ratio for the two ligands H_2L^1 and

TABLE-2
ELEMENTAL ANALYSES, COLOUR AND MELTING POINTS OF METAL COMPLEXES OF H_2L^1 AND H_3L^2

Complexes	Colour	f.w.	m.p. or (d.p.) (°C)	Yield (%)	% Analyses, found (calcd.) C	H	N	Cl	M
$[Cu(HL^1)(H_2O)_2]Cl{\cdot}H_2O$	Brown	496.1	(435)	90	38.69	3.40	5.60	7.06	12.70
$CuC_{16}H_{17}N_2O_{10}Cl$					(38.70)	(3.43)	(5.64)	(7.16)	(12.81)
$[Pd(HL^1)_2.]4H_2O$	Yellow	864.4	(350)	87	44.31	3.36	6.36	—	12.18
$PdC_{32}H_{30}N_4O_{18}$					(44.42)	(3.47)	(6.48)	—	(12.31)
$[Co(HL^1)(H_2O)_4]Cl{\cdot}H_2O$	Brown	527.4	(342)	88	36.30	4.00	5.30	6.80	11.05
$CoC_{16}H_{21}N_2O_{12}Cl$					(36.41)	(3.98)	(5.31)	(6.73)	(11.17)
$[Ni(HL^1)(H_2O)_4]Cl{\cdot}3H_2O$	Yellow	563.2	(365)	85	34.12	4.40	4.98	6.35	10.52
$NiC_{16}H_{25}N_2O_{14}Cl$					(34.09)	(4.44)	(4.97)	(6.30)	(10.46)
$[Cr(HL^1)(H_2O)_4]Cl_2{\cdot}3H_2O$	Green	592.0	(410)	80	32.40	4.22	4.70	12.10	8.70
$CrC_{16}H_{25}N_2O_{14}Cl_2$					(32.43)	(4.22)	(4.73)	(11.99)	(8.78)
$[Pt(HL^1)(H_2O)_4]Cl_3{\cdot}H_2O$	Yellow	734.6	322	62	26.10	2.80	3.80	14.60	26.50
$PtC_{16}H_{21}N_2O_{12}Cl_3$					(26.14)	(2.86)	(3.81)	(14.50)	(26.56)
$[Rh(L^1)(H_2O)_4]Cl{\cdot}2H_2O$	Orange	588.4	(363)	74	32.67	3.70	4.66	6.10	17.40
$RhC_{16}H_{22}N_2O_{13}Cl$					(32.63)	(3.74)	(4.76)	(6.03)	(17.49)
$[Cu_2(L^2)(H_2O)_4]Cl{\cdot}2H_2O$	Brown	613.6	315	75	29.23	3.08	4.50	5.70	20.85
$Cu_2C_{15}H_{19}N_2O_{12}SCl$					(29.34)	(3.10)	(4.56)	(5.79)	(20.71)
$[Pd(H_2L^2)_2]{\cdot}5H_2O$	Brown	886.4	(395)	82	40.55	3.10	6.28	—	12.10
$PdC_{30}H_{28}N_4O_{17}S_2$					(40.61)	(3.16)	(6.32)	—	(12.00)
$[Co_2(L^2)(H_2O)_8]Cl{\cdot}2H_2O$	Blue	676.4	(437)	77	26.60	3.90	4.20	5.30	17.30
$Co_2C_{15}H_{27}N_2O_{16}SCl$					(26.61)	(3.99)	(4.14)	(5.25)	(17.42)
$[Ni(H_2L^2)_2(H_2O)_2]{\cdot}5H_2O$	Pink	874.7	(405)	68	41.08	3.60	6.45	—	6.78
$NiC_{30}H_{32}N_4O_{19}S_2$					(41.16)	(3.66)	(6.40)	—	(6.71)
$[Cr_2(L^2)(H_2O)_8]Cl_3{\cdot}H_2O$	Green	715.5	315	78	25.08	3.40	3.80	14.95	14.41
$Cr_2C_{15}H_{25}N_2O_{15}SCl_3$					(25.16)	(3.49)	(3.91)	(14.88)	(14.54)
$[Pt(H_2L^2)_2(H_2O)_2]Cl_2{\cdot}3H_2O$	Yellow	1046.1	(428)	80	34.48	2.71	5.30	6.85	18.75
$PtC_{30}H_{28}N_4O_{17}S_2Cl_2$					(34.41)	(2.68)	(5.35)	(6.79)	(18.65)
$[Rh(H_2L^2)(H_2O)_4]Cl_2{\cdot}5H_2O$	Orange	680.9	(334)	92	26.40	3.90	4.10	10.30	15.30
$RhC_{15}H_{27}N_2O_{15}SCl_2$					(26.44)	(3.97)	(4.11)	(10.43)	(15.11)

H_3L^2. The formation of the complexes can be represented by the following general equations:

$$H_{2\text{ or }3}L^{1,2} + MCl_{2,\,3\text{ or }4} + xH_2O \longrightarrow [M(H_{1\text{ or }2}L^{1,2}\text{ or }L^1)(H_2O)_{2\text{ or }4}]Cl_{1,\,2\text{ or }3}\cdot(1\text{–}5)H_2O + (1\text{ or }2)HCl$$

$$2H_{2\text{ or }3}L^{1,2} + MCl_{2\text{ or }4} + yH_2O \longrightarrow [M(H_{1\text{ or }2}L^{1,2})_2(H_2O)_{0\text{ or }2}]Cl_{0\text{ or }2}\cdot(3\text{–}5)H_2O + 2HCl$$

$$H_3L^2 + 2MCl_{2\text{ or }3} + zH_2O \longrightarrow [M_2(L^2)(H_2O)_{4\text{ or }8}]Cl_{1\text{ or }3}\cdot(0\text{–}2)H_2O + 3HCl$$

^{1}H-NMR spectra

The ^{1}H-NMR spectra of the ligands H_2L^1 and H_3L^2 showed the aromatic proton signal at 6.7–8.0 ppm. Their spectra showed also a signal due to the pyrone ring proton appeared 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 prepared 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 =CH— group joining the chromone and the barbituric acid or thio barbituric acid moieties.

Infra-red spectra

The most important IR bands of the ligands and their metal complexes and their assignments are given in Table-3.

All the H_2L^1 and H_3L^2 complexes spectra exhibit a broad band in the range 3520–3300 cm^{-1}, assigned to the ν(OH), suggesting the presence of water molecules[16].

The ν(C=O) bands of the pure ligand H_2L^1 at 1750, 1710 and 1690 cm^{-1} are either 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, which may be accompanied by the bonding of the ligand to the metal ion *via* the hydroxyl group with the elimination of the corresponding proton in the case of Rh(III)-H_2L^1 complex. Moreover, the ν(C=N) band at 1600 cm^{-1} in the spectra of the free ligand H_2L^1 remains nearly unchanged. Such finding may generally give an extra support to the tautomerism phenomena in this ligand and its complexes. The red-shifting of the amide I and II bands in all H_2L^1-complexes shows also that one of the carbonyl groups of the barbituric acid moiety acts as a centre for complexation.

In Table-3, the band at 1360 cm^{-1}, ascribed to the phenolic C—O stretching vibration[17] in the H_2L^1 spectra, is either shifted to lower frequencies or split into weaker bands in the spectra of its metal complexes. This implies that the hydroxylic oxygen anion in position seven in the chromone moiety takes part in formation of these complexes.

TABLE-3

IR FREQUENCIES OF THE BANDS (cm^{-1}) of H_2L^1 AND H_3L^2 LIGANDS AND THEIR COMPLEXESS

Free Ligand	Cu(II) complex	Pd(II) complex	Co(II) complex	Ni(II) complex	Cr(III) complex	Pt(IV) complex	Rh(III) complex	Assignments
H_2L^1	H_2L^1 complexes							
3380 (b)	3400 (b)	3320 (b)	3400 (b)	3320–3480 (b)	3320–3440 (b)	3340 (b)	3420 (b)	ν(OH)
3200 (m)	3220 (m)	3180 (b)	3260 (m)	3240 (m)	3200 (b)	3240 (b)	3180 (b)	ν(NH)
1750 (s)	1720 (w)	1730 (w)	1730 (w)	1720 (w)	1730 (w)	1720 (w)	—	ν(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)	ν(C=N)
1560 (m)	1530 (s)	1550 (m)	1510 (m)	1530 (w)	1510 (w)	1520 (m)	1400 (s)	Amide II
1360 (s)	1370 (w) 1340 (w)	1350 (w)	1350 (w)	1340 (w)	1270 (s)	1270 (s)	1290 (s)	ν(C—O)[a]
H_3L^2	H_3L^2 complexes							
3410 (b)	3380–3480 (b)	3380–3480 (b)	3320–3460 (b)	3320–3460 (b)	3320–3440 (b)	3320–3520 (b)	3360–3520 (b)	ν(OH)
3180 (m)	3180 (s)	3160 (b)	3100–3280 (b)	3140–3240 (b)	3080–3280 (b)	3080–3120 (b)	3040–3260 (b)	ν(NH)
1670 (s)	1620 (s)	1670 (m)	1650 (m)	1670 (s)	1650 (s)	1670 (m)	1670 (m)	ν(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)	ν(C=O)[b]
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 (vw)	1330 (w)	1330 (m)	1330 (w)	1330 (w)	1330 (w)	ν(C—O)[a]
1280 (s)	1270 (m)	1280 (m)	1240 (b)	1290 (b)	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

[a] Phenolic-(C—O).

[b] Chromone-(C—O).

TABLE-4
ELECTRONIC ABSORPTION SPECTRAL BANDS OF THE LIGANDS H_2L^1 AND H_3L^2 AND THEIR METAL-COMPLEXES

Ligands and their complexes	λ_{max} (nm)	
	Nujol	DMF
H_2L^1	—	330, 350, 390
H_2L^1-Cu(II)	390, 500	380, 470
H_2L^1-Pd(II)	320, 280, 430, 490	400, 420
H_2L^1-Co(II)	330, 360, 380	490, 540
H_2L^1-Ni(II)	350, 440, 510	480, 540
H_2L^1-Cr(III)	380, 500, 590	550, 630
H_2L^1-Pt(IV)	350, 500, 640	390, 490, 545
H_2L^1-Rh(III)	350, 400, 660	400, 460
H_3L^2	—	330, 350, 370
H_3L^2-Cu(II)	350, 500	370, 520
H_3L^2-Pd(II)	390, 430, 500	430
H_3L^2-Co(II)	360, 530, 760	370, 530, 665
H_3L^2-Ni(II)	330, 490, 560	380, 490, 525
H_3L^2-Cr(III)	380, 500, 590	380, 530, 590
H_3L^2-Pt(IV)	390, 440, 520, 590	430, 480
H_3L^2-Rh(III)	350, 510	370

A remarkable feature for one of the thiobarbituric acid-carbonyl stretching vibrations of the free H_3L^2 ligand at 1620 cm^{-1} is that it is slightly affected on complexation in all the H_3L^2 complexes. However, the second ν(C=O) band of the free ligand at 1670 cm^{-1} is either still existing in the same position in the Pd, Ni, Pt and Rh complexes, or red-shifted in the case of 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^{-1}. The weak appearance of the first band, assigned mainly as δ(NH), together with the presence of the second thioamide band nearly in 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 are in favour to suggest the view that the complexation takes place *via* the chromone-carbonyl group and oxygen anions of the OH groups in position 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^{-1}, having main contributions from $\nu(C{=}S)$, in the pure ligand H_3L^2 spectra, are in the same position in all chelates of this ligand, to exclude the metal-sulphur bonding[18].

Electronic spectra

The electronic absorption bands of the ligands and their metal complexes are listed in Table-4. 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 wavelength bands in the spectra of their metal complexes can be considered as an 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[2] or a combination of the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions[1], 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 can be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions[2, 19], respectively, consistent with the square-planar Pd(II) complexes.

The electronic spectra of the Co(II)-H_2L^1 and -H_3L^2 complexes show an absorption band at 530–540 nm due to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition, suggesting a high-spin octahedral structure[20]. However, the spectrum of Co(II)-H_3L^2 complex has an additional absorption band, assigned to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition, in the 665–760 nm region, suggesting a distorted-octahedral configuration due to the Jahn-Teller effect[21] in this complex.

The electronic spectra of the Ni(II) complexes of the two ligands show two absorption bands, one at 510–560 nm and the other at 440–490 nm due to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, observed for octahedral Ni(II)-complexes[22, 23].

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

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

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

TABLE-5
THERMOGRAVIMETRIC ANALYSIS DATA OF THE METAL COMPLEXES

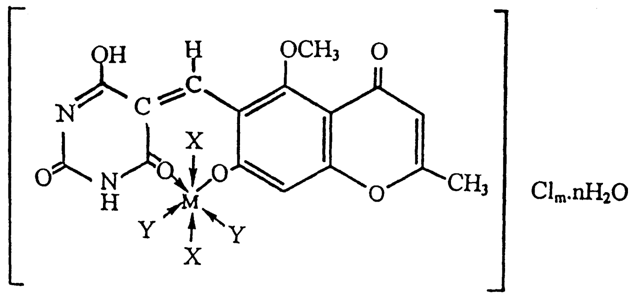
Complex	M : L	Water of hydration mass loss % calcd. (found)	No. of hydrated water molecules/ chelate molecule	Temp. (°C) upto	Water of coordination mass loss % calcd. (found)	No. of coordinated water molecules/ chelate molecule	Temp. (°C) upt
$[Cu(HL^1)(H_2O)_2]Cl\cdot H_2O$	1 : 1	3.63 (3.71)	1	155	7.26 (7.34)	2	221
$[Pd(HL^1)_2]\cdot 4H_2O$	1 : 2	8.33 (8.50)	4	140	—	—	—
$[Co(HL^1)(H_2O)_4]Cl\cdot H_2O$	1 : 1	3.41 (3.30)	1	115	13.65 (13.49)	4	303
$[Ni(HL^1)(H_2O)_4]Cl\cdot 3H_2O$	1 : 1	9.59 (9.71)	3	136	12.78 (12.65)	4	278
$[Cr(HL^1)(H_2O)_4]Cl_2\cdot 3H_2O$	1 : 1	9.12 (9.24)	3	132	12.16 (12.10)	4	350
$[Pt(HL^1)(H_2O)_4]Cl_3\cdot H_2O$	1 : 1	2.45 (2.50)	1	144	9.80 (9.71)	4	290
$[Rh(L^1)(H_2O)_4]Cl\cdot 2H_2O$	1 : 1	6.12 (6.00)	2	130	12.24 (12.10)	4	336
$[Cu_2(L^2)(H_2O)_4]Cl_2\cdot 2H_2O$	2 : 1	5.87 (5.90)	2	128	11.73 (11.58)	4	228
$[Pd(H_2L^2)_2]\cdot 5H_2O$	1 : 2	10.15 (10.33)	5	140	— —	—	—
$[Co_2(L^2)(H_2O)_8]Cl\cdot 2H_2O$	2 : 1	5.32 (5.40)	2	120	21.29 (21.00)	8	234
$[Ni(H_2L^2)_2(H_2O)_2]\cdot 5H_2O$	1 : 2	10.29 (10.42)	5	148	4.12 (4.05)	2	272
$[Cr_2(L^2)(H_2O)_8]Cl_3\cdot H_2O$	2 : 1	2.52 (2.60)	1	117	20.13 (20.00)	8	254
$[Pt(H_2L^2)_2(H_2O)_2]Cl_2\cdot 3H_2O$	1 : 2	5.16 (5.05)	3	126	3.44 (3.32)	2	261
$[Rh(H_2L^2)(H_2O)_4]Cl_2\cdot 5H_2O$	1 : 1	13.22 (13.00)	5	159	10.57 (10.68)	4	222

Thermogravimetric analysis

The thermogravimetric data for the H_2L^1 and H_3L^2 complexes are listed in Table-5. The results obtained are in fair agreement with the theoretical tentative formulae suggested from the elemental analysis. The mass loss of 3.71, 3.30, 9.71, 9.24, 2.50, 6.00 and 13.00%; 8.50, 10.33, 10.42 and 5.05%; 5.9, 5.4 and 2.6% for the 1 : 1, 1 : 2, 2 : 1 M : L complexes with the ligands H_2L^1 and H_3L^2, respectively, indicates the loss of 1–5 hydrated water molecules. The mass loss of 7.34, 13.49, 12.65, 12.10, 9.71 and 12.10%, 10.68% for the 1 : 1 complexes with the ligands H_2L^1 and H_3L^2, respectively, within the temperature range of 221 to 350°C indicates the loss of 2–4 coordinated water molecules and the mass loss of 4.05 and 3.32% at 261–272°C for the H_3L^2-Ni and Pt complexes corresponds to two coordinated water molecules. The mass loss of 11.58, 21.00 and 20.00% at 228–254°C indicates the elimination of 4–8 coordinated water molecules from the 2 : 1 M : L complexes. Above 315°C, all the complexes begin to decompose, at first slowly and then increasingly rapidly.

Suggested structural formulae of the complexes

From the spectra data, gathered with the elemental and thermal analyses, the structure of the prepared complexes may be formulated, in Figs. 2 and 3, as follows:



X (Absent), $Y = H_2O$, $m = 1, n = 1$ for the H_2L^1-Cu Complex.
X (Absent), $2Y = HL^1$, Cl (Absent), $n = 4$ for the H_2L^1-Pd Complex.
$X = Y = H_2O$, $m = 1, n = 1$ for the H_2L^1-Co Complex.
$X = Y = H_2O$, $m = 1, n = 3$ for the H_2L^1-Ni Complex.
$X = Y = H_2O$, $m = 2, n = 3$ for the H_2L^1-Cr Complex.
$X = Y = H_2O$, $m = 3, n = 1$ for the H_2L^1-Pt Complex.

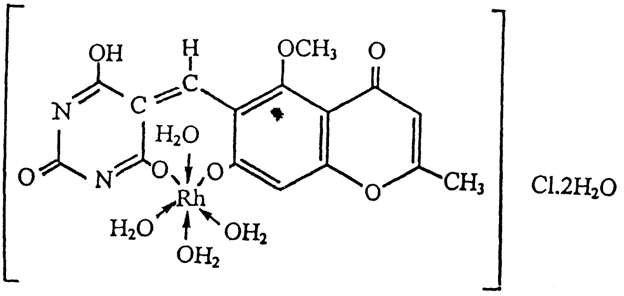
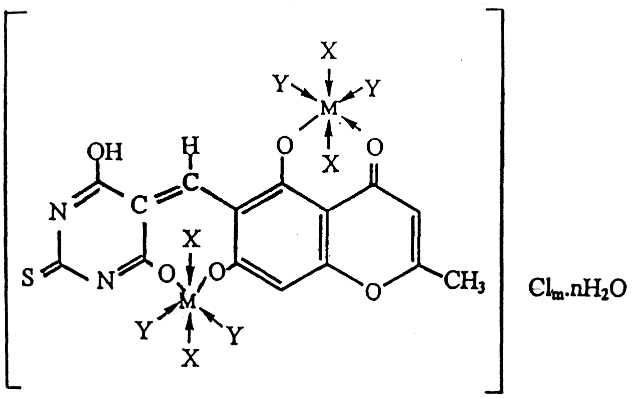
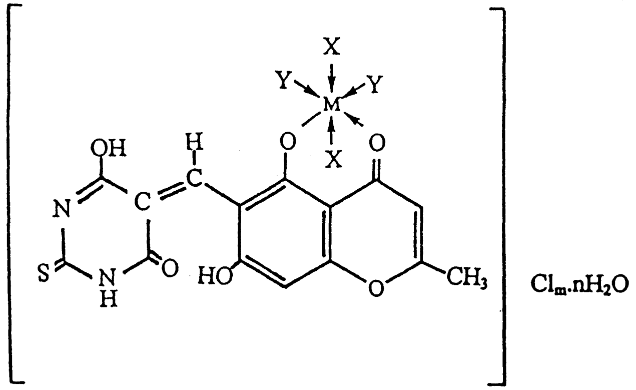


Fig. 2. Suggested structures of the H_2L^1 complexes



X (Absent), Y = H_2O, m = 1, n = 2 for the H_3L^2-Cu Complex.
X = Y = H_2O, m = 1, n = 2 for the H_3L^2-Co Complex.
X = Y = H_2O, m = 3, n = 1 for the H_3L^2-Cr Complex.



X = Y = H_2O, m = 3, n = 5 for the H_3L^2-Rh Complex.
X (Absent), 2Y = H_2L^2, m = 0, n = 5 for the H_3L^2-Pd Complex.
X = H_2O, 2Y = H_2L^2, m = 0, n = 5 for the H_3L^2-Ni Complex.
X = H_2O, 2Y = H_2L^2, m = 2, n = 3 for the H_3L^2-Pt Complex.

Fig. 3. Suggested structure of the H_3L^2 complexes

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