Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 181–200

CHARACTERIZATION OF TRANSITION METAL ION CHELATES WITH 8-(ARYLAZO) CHROMONES USING THERMAL AND SPECTRAL TECHNIQUES

*Omyma E. Sherif**, *Hussein M. Abd El-Fattah and Marie M. El-Ajily*

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

(Received October 27, 2002; in revised form March 15, 2003)

Abstract

Transition metal chelates of TiO^{IV}, VO^{IV}, Cr^{III}, Fe^{III}, Co^{III} and Pd^{II} ions with 8-(arylazo)chromones have been isolated and investigated by elemental analysis, IR, electronic spectra, thermogravimetric analysis, conductance and magnetic moment measurements. Chelates of general formula $[ML \text{ or } M_2LX_m{\cdot}nH_2O]{\cdot}yH_2O$, where, X=OH^- or Cl^- or SO_4^{2-} ion, m=1, 2 or 4, n=1, 2, 4 or 5, y=1–6, M=TiO^{IV}, VO^{IV}, Cr^{III}, Fe^{III}, Co^{III} and Pd^{II} ions and L=8-(arylazo) chromones have been synthesized. IR spectra indicate that the chromone carbonyl in position four and oxygen anion in position five participate in chelation in the 1:1 (M:L) chelates, whereas, for 2:1 (M:L) chelates the interaction of the metal ion takes place via the chromone carbonyl in position four and oxygen anion in position five as first chelation site, for the second metal ion chelation takes place through the formyl carbonyl in position six and oxygen anion in position seven for some chelates or through the azo group and any acidic substituent in ortho position to it. Octahedral or square planar structures were proposed for the prepared chelates based on their electronic spectra and magnetic moments. Thermogravimetric analysis suggests the presence of hydrated and coordinated water molecules. Non electrolytic nature was assigned based on molar conductance values.

Keywords: 8-(arylazo)chromones, chelates, Co(III), Cr(III), Fe(III), Pd(II), TiO(IV), VO(IV)

Introduction

Chromones are those compounds which contain γ-pyrone nucleus fused to benzene ring at the 5- and 6-positions. Chromones are important compounds having pharmacological activity. Some chromones have marked analgesic anti-inflammatory and antipyretic activities [1]. The interest in the chemistry of hydroxychromones is based on their ability to function as determination of a large number of transition metals [2–7].

The metal chelates of vanadium(IV), chromium(III), manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) ions of 8-(arylazo)-6-formyl-7-hydroxy-5-methoxy-2-methylchromones were prepared and investigated using several techniques [8]. Divalent metal ion chelates of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone; 5,7-dihydroxy-6-formyl-2-methylchromone and 5,7-dihydroxy-2,6-dimethylchromone have been prepared and studied [9].

---

* Author for correspondence: E-mail: salatif_1@yahoo.com

1388–3150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

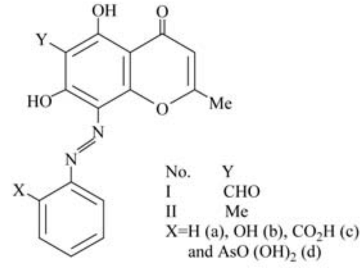
Several 8-(arylazo)chromones were prepared and investigated by using elemental analysis, IR, ^{1}H NMR and mass spectra by Issa *et al.* [10].

Metal chelates of the divalent metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) with 8-(arylazo) derivatives of 5,7-dihydroxy-2,6-dimethylchromones and 5,7-dihydroxy-6-formyl-2-methylchromones were synthesized and characterized by elemental analyses, IR and electronic spectra, thermogravimetric analyses, magnetic and conductance measurements [11].

The preparation and structure elucidation of the metal chelates of Ce(III), Th(IV) and U(VI) with some Schiff bases derived from 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one have been reported [12].

The thermal decomposition of the complexes of N,N-dialkyl-N'-benzoylthiourea with Pd(II) and Fe(III) were studied by TG and DTA techniques. These metal complexes decompose in two stages. The influence of the alkyl substituents in these benzoylthiourea chelates on the thermal behaviour of the metal complexes was investigated [13]. New complexes of $CuL_2\cdot 2H_2O$, $CoL_2\cdot 3H_2O$, $MnL_2\cdot 2H_2O$ and $FeL_3\cdot 2H_2O$, *L*=γ-*L*-glutamyl-5-(*p*-nitroanilide) were synthesized [14] and characterized via investigating their spectral, magnetic and thermal properties. The thermal stabilities of the synthesized complexes were examined in the temperature range 20–500°C. The ligand acted as a bidentate one and its coordination involving the carbonyl oxygen and the nitrogen atom of the second amino group. The metal ion is in the high-spin form with octahedral stereochemistry. Fe(III) complexes of *o*-vanilin oxime have been synthesized and characterized via elemental analysis, NMR, IR and thermal analyses [15]. Investigation of the influence of the Fe(III) and other metal ions on thermal decomposition of humic acids were carried out by using TG and DTA [16].

The aim of the present study is to prepare the metal chelates formed between titanium(IV), vanadium(IV), chromium(III), iron(III), cobalt(III) and palladium(II) with 8-(arylazo)-5,7-dihydroxy-6-formyl-2-methylchromone (Ia–d) and 8-(arylazo)-5,7-dihydroxy-2,6-dimethylchromone (IIa–d). Also, to elucidate the geometrical structures of the obtained chelates.



Scheme 1 Structure of the ligands used

Experimental

Preparation and analysis of the chelates

The chromone derivative, 6-formyl-7-hydroxy-5-methoxy-2-methylchromone was prepared by oxidation of visnagin with chromic acid while 5,7-dihydroxy-6-formyl-

2-methylchromone(I) was prepared by hydrolysis of the previously prepared chromone with HCl and 5,7-dihydroxy-2,6-dimethylchromone(II) was prepared by reduction of compound (I) with Zn [10].

The 8-(arylazo)chromones (Ia–d and IIa–d) were prepared by coupling equimolar amounts of the diazotized corresponding amines (aniline, 2-aminophenol, 2-anthranilic- and 2-arsanilic acids) with the chromones I and II in presence of NaOH [10]. The metal chelates of 8-(arylazo)chromones were synthesized by mixing a hot saturated EtOH solution of the metal salt [$Ti_2(SO_4)_3$, $VOSO_4{\cdot}H_2O$, $CrCl_3{\cdot}2H_2O$, $FeSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$ and $PdCl_2$] (0.01 mole) with the requisite amount of a saturated ethanol solution of the azo dye to form 1:1 or 2:1 (M:L) chelates [8]. The metal ion content of the chelates was determined, after wet decomposition of the chelates [17], as previously described [18].

IR spectra of the chelates were obtained by applying the KBr disc technique using Perkin Elmer 1430 infrared spectrometer. The electronic spectra of the 8-(arylazo)chromones and their chelates were measured by applying the Nujol mull technique using a Perkin Elmer lambda 4B spectrometer with 1 cm matched silica cells. TG for some chelates containing water molecules were achieved using Schimadzu-50 thermal analyzer (Japan). The mass loss was measured from ambient temperature up to 1000°C at a rate of 10°C $\min^{-1}$. The conductivity measurements were carried out in DMF solution by using conductivity bridge model CM-IK, TOA Company (Japan). Magnetic moments were measured using a Johnson–Mathey susceptometer devised by D. F. Evans.

The chemicals used were reagent grade (BDH or Aldrich). All organic solvents used in this work were either obtained as pure materials from BDH or purified by recommended methods [19]. Double distilled water was always used.

Results and discussion

Table 1 comprises the elemental analysis and thermogravimetric data of the transition metal ion chelates of 8-(arylazo)chromones (Ia–d and IIa–d). The obtained data are in good agreement with those calculated for the proposed tentative formulae of the chelates. The suggested formula is [ML] – or $[M_2LX_m{\cdot}nH_2O]{\cdot}yH_2O$ where, X=OH^- or Cl^- or SO_4^{2-} ion, m=1, 2 or 4, n=1, 2, 4 or 5, y=1–6, M=TiO^{IV}, VO^{IV}, Cr^{III}, Fe^{III}, Co^{III} and Pd^{II}) ions, L is the 8-(arylazo)chromones (Ia–d and IIa–d) molecule.

Thermogravimetric analysis

Thermal studies have been carried out using a thermogravimetric TG and a derivative thermogravimetric DTG techniques. TG and DTG curves are given in Figs 1, 2 and 3.

From TG curves (Figs 1, 2 and 3), the mass loss of the metal chelate was calculated using the change produced as a result of the removal of water molecules. Table 2 shows the calculated and the found mass losses of the chelates. The found mass losses were calculated from the TG curves and the calculated ones were obtained from the suggested tentative molecular formulae based on the obtained data of the elemental analyses.

Table 1 Elemental analyses of metal chelates of 8-(arylazo) chromones

Chelates	C/%		H/%		N/%		*M*/%	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$[(VO)_2(Ia)(OH)_2\ \ 4H_2O]\ \ H_2O$	36.4	36.30	4.0	3.56	6.0	4.98	17.90	18.13
$[Cr(Ia)(OH)_2\ \ 2H_2O]\ \ H_2O$	44.0	44.06	4.7	4.10	6.2	6.04	11.47	11.23
$[Fe_2(Ia)(OH)_4\ \ 4H_2O]\ \ H_2O$	34.6	34.46	4.2	4.05	4.5	4.73	18.70	18.92
$[Pd(Ia)(OH)\ \ H_2O]$	43.8	43.92	3.4	3.01	6.0	6.03	22.50	22.92
$[(VO)_2(Ib)(OH)_2\ \ 4H_2O]\ \ H_2O$	34.4	34.23	4.5	3.69	5.0	4.70	17.33	17.10
$[Cr(Ib)(OH)_2\ \ 2H_2O]$	44.8	44.25	4.3	3.68	5.6	6.37	10.96	11.28
$[Pd(Ib)(OH)\ \ H_2O]$	42.2	42.46	3.2	2.91	5.4	5.83	22.33	22.15
$[(TiO)_2(Ic)(OH)_2\ \ 4H_2O]\ \ 6H_2O$	29.7	30.51	4.7	4.52	3.3	3.95	13.65	13.53
$[(VO)_2(Ic)(OH)_2\ \ 4H_2O]\ \ H_2O$	36.5	35.65	4.3	3.30	4.2	4.64	16.96	16.81
$[Cr(Ic)(OH)_2\ \ 2H_2O]\ \ H_2O$	42.2	42.60	4.1	3.75	5.2	5.52	10.70	10.75
$[Pd(Ic)(OH)\ \ H_2O]\ \ H_2O$	41.0	41.03	3.5	3.04	4.7	5.32	20.06	20.22
$[(TiO)_2(Id)(OH)_2\ \ 4H_2O]\ \ 6H_2O$	26.5	26.90	4.0	4.19	3.2	3.55	12.33	12.15
$[(VO)_2(Id)(OH)_2\ \ 4H_2O]\ \ 6H_2O$	25.1	25.70	4.4	4.15	3.8	3.52	12.95	12.83
$[Cr_2(Id)Cl_4\ \ 4H_2O]\ \ \ H_2O$	24.3	24.94	3.3	3.05	4.4	3.42	12.85	12.71
$Fe_2(Id)(OH)_4\ \ 4H_2O]\ \ {}_2O$	28.1	28.49	4.4	3.49	3.5	3.91	15.38	15.64
$[Pd_2(Id)Cl_2\ \ H_2O]\ \ 2H_2O$	25.7	25.44	3.1	2.37	3.5	3.49	26.40	26.55

Table 1 Continued

Chelates	C/%		H/%		N/%		*M*/%	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$[(VO)_2(IIa)(OH)_2\ \ 4H_2O]\ \ 4H_2O$	32.2	32.91	5.1	4.84	3.7	4.52	16.23	16.43
$[Cr(IIa)(OH)_2\ \ 2H_2O]\ \ 2H_2O$	43.3	43.68	4.2	4.92	6.6	5.99	11.28	11.13
$Co(IIa)(OH)_2\ \ 2H_2O]$	47.0	46.57	4.3	4.34	6.0	6.39	13.25	13.47
$[Pd_2(IIa)(OH)_2\ \ 2H_2O]$	34.6	34.55	2.9	3.05	5.5	4.74	35.96	36.03
$[(TiO)_2(IIb)(OH)_2\ \ 4H_2O]\ \ 5H_2O$	31.0	31.49	5.2	4.94	3.5	4.32	14.85	14.78
$[(VO)_2(IIb)(OH)_2\ \ 4H_2O]$	36.2	36.18	4.3	3.90	4.7	4.96	18.18	18.07
$[Cr(IIb)Cl_2\ \ 2H_2O]$	42.5	42.15	4.2	3.51	5.8	5.78	10.05	10.64
$[Fe_2(IIb)(OH)_4\ \ 4H_2O]\ \ 6H_2O$	29.4	29.82	4.8	5.29	3.6	4.09	16.25	16.37
$[Pd_2(IIb)Cl_2\ \ 2H_2O]\ \ 6H_2O$	27.3	27.13	4.2	3.72	4.5	3.72	27.85	28.31
$[(TiO)_2(IIc)(OH)_2\ \ 4H_2O]\ \ H_2O$	31.6	31.96	4.4	4.73	3.5	4.14	14.35	14.17
$[(VO)_2(IIc)(OH)_2\ \ 4H_2O]\ \ 4H_2O$	32.0	32.54	4.7	4.51	4.5	4.22	15.80	15.34
$[Cr(IIc)(OH)_2\ \ 2H_2O]$	45.4	45.47	5.0	4.00	6.5	5.89	11.25	10.95
$[Fe_2(IIc)(OH)_4\ \ 4H_2O]\ \ 2H_2O$	33.6	33.75	4.4	4.38	5.1	4.38	17.74	17.50
$[Pd_2(IIc)Cl_2\ \ 2H_2O]\ \ 2H_2O$	30.3	30.51	3.1	2.83	3.5	3.95	29.85	30.10
$[(TiO)_2(IId)(OH)_2\ \ 4H_2O]\ \ 5H_2O$	26.4	26.99	4.9	4.36	3.7	3.70	12.87	12.67
$[(VO)_2(IId)(OH)_2\ \ 4H_2O]\ \ 5H_2O$	26.1	26.78	4.8	4.33	3.2	3.67	13.49	13.37
$[Cr_2(IId)Cl_4\ \ 4H_2O]\ \ 2H_2O$	25.5	25.95	4.2	3.18	3.3	3.56	12.90	13.23
$[Fe_2(IId)(SO_4)(OH)_2\ \ 4H_2O]\ \ 5H_2O$	24.0	24.40	3.4	3.95	2.8	3.35	13.60	13.40
$[Pd_2(IId)(OH)_2\ \ 2H_2O]$	28.7	28.53	3.3	2.66	3.4	3.92	30.05	29.79

Table 1 Continued

Chelates	Cl/%		Chelate	S/%	
	found	calcd.		found	calcd.
Cr_2–Id	17.4	17.36	Fe_2–IId	4.1	3.83
Pd_2–Id	8.4	8.85			
Cr–IIb	14.4	14.74			
Pd_2–IIb	8.8	9.44			
Pd_2–IIc	10.5	10.03			
Cr_2–IId	18.7	18.07			

The initial mass loss occurring within the 55–160°C range is interpreted as being due to a loss of moisture and hydrated water molecules during the chelate drying process, whereas the second mass loss within the 160–310°C range is due to coordinated water molecules.

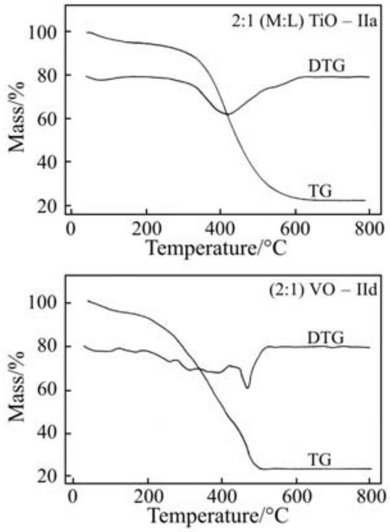


Fig. 1 Thermogravimetric and derivative thermogravimetric analysis curves of Ti chelate of 8-(phenylazo)-5,7-dihydroxy-2,6-dimethylchromone (IIa) and V chelate of 8-(2-arsonophenylazo)-5,7-dihydroxy-2,6-dimethylchromone (IId)

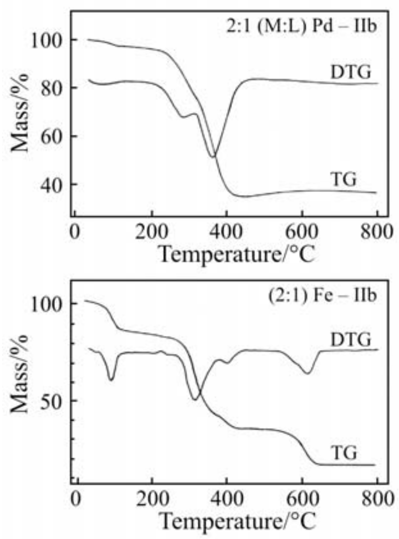


Fig. 2 Thermogravimetric and derivative thermogravimetric analysis curves of Pd and Fe chelates of 8-(2-hydroxyphenylazo)-5,7-dihydroxy-2,6-dimethylchromone (IIb)

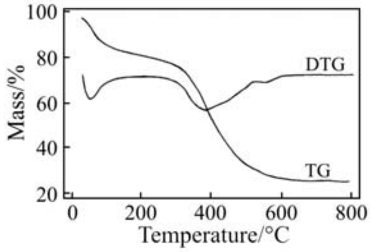


Fig. 3 Thermogravimetric and derivative thermogravimetric analysis curve of Ti chelate of 8-(carboxyphenylazo)-5,7-dihydroxy-6-formyl 2-methylchromone (Ic)

For 2:1 (*M*:*L*) TiO–IIa and VO–IId chelates, the mass losses occurring at 15.20 and 11.20%, respectively, correspond to the loss of five water molecules of hydration in the 66–160°C range. For the TiO–Ic and Fe–IIb chelates, the percentages of mass losses (up to 140°C) are 14.50 and 16.00%, respectively suggesting the presence of six hydrated water molecules. On the other hand, the mass losses are 10.50, 8.5, 12.80 and 9.80% for TiO–Ic, TiO–IIa, Fe–IIb and VO–IId chelates within the 140–310°C range may be due to the existence of four coordinated water molecules. The 2:1 Pd–IIb chelate exhibits mass loss of 5.00% showing the existence of two coordinated water molecules. The results of the TG analyses suggest the formation of the metal oxide as the final product in the temperature range from 500 to 1000°C. The percentages of the metal oxide found experimentally for TiO–Ic, TiO–IIa, Fe–IIb,VO–IId and Pd–IIb chelates amounted to 22.00, 25.71, 23.00, 24.60 and 33.40%, respectively which are in good agreement with the calculated ones for the suggested formulae (Table 1).

The organic part of the complexes (the ligand moiety attached to the metal atom) may decompose in one or more steps with the possibility of the formation of one or more intermediates. These intermediates finally decompose to the stable metal oxides. The 2:1 (*M*:*L*) complexes of TiO–IIa and Pd–IIb were found to decompose in one step (Table 2). The decomposition of (2:1) TiO–Ic, Fe–IIb and VO–IId was completed through more than one decomposition step (Table 2).

In case of 2:1 (*M*:*L*) TiO–Ic, TiO–IIa, VO–IId, Pd–IIb and Fe–IIb chelates, their thermal decomposition may be illustrated using the following scheme:

$$[M_2LX_m \cdot nH_2O] \cdot yH_2O \xrightarrow{55-160^\circ C} [M_2LX_m \cdot nH_2O]$$

$$[M_2LX_m \cdot nH_2O] \xrightarrow{160-310^\circ C} [M_2LX_m]$$

$$[M_2LX_m] \xrightarrow{300-466^\circ C} \text{Intermediate (unstable)}$$

$$\text{Intermediate} \xrightarrow{>500^\circ C} \text{Metal oxide. } (TiO_2,\ V_2O_5,\ PdO \text{ and } Fe_2O_3).$$

$$(X{=}OH^- \text{ or } Cl^-,\ m{=}2,\ 4\ n{=}2\text{–}4 \text{ and } y{=}5 \text{ or } 6).$$

The molar conductance of the 1:1 and 2:1 (*M*:*L*) chelates lie in the 3.50–22.60 ohm^{-1} cm^2 mol^1 range, suggesting their non-electrolytic nature [20].

Table 2 Thermogravimetric and derivative thermogravimetic analysis data of metal chelates of chromone azo dyes (Ic) and (II a,b,d)

Chelate	Temp./ °C	Water of hydration			Temp./ °C	Water of coordination			DTG peak temperature/ °C	Metal oxide residue%	
		Mass loss%		y*		Mass loss%		n*			
		calc.	found			calc.	found			calc.	found
$[(TiO)_2(Ic)(OH)_2\ \ 4H_2O]\ \ 6H_2O$	53–140	15.26	14.50	6	140–260	10.17	10.50	4	379,547	22.57	22.00
$[(TiO)_2(IIa)(OH)_2\ \ 4H_2O]\ \ 5H_2O$	66–160	14.25	15.20	5	160–310	8.87	8.50	4	409	25.29	25.71
$[Fe_2(IIb)(OH)_4\ \ 4H_2O]\ \ 6H_2O$	90–140	16.66	16.00	6	140–286	13.15	12.80	4	309,396,611	23.39	23.00
$[Pd_2(IIb)Cl_2\ \ 2H_2O\ \ \ 6H_2O$	60–150	14.40	13.60	6	150–300	4.87	5.00	2	360	32.57	33.40

IR spectra of ligands and metal chelates

The chelation between the ligands and metal ions can be inferred by comparing the IR spectra of the metal chelates with those of the organic ligands. IR-band assignments of the chelates are depicted in Tables 3 and 4. The presence of water molecules in the solid complex may lead to confusion in assignment of the νOH group. The participation of the hydroxyl groups in the chelation is confirmed by the shift of δOH and γOH bands of the free ligands on chelation. Meanwhile, bands due to different modes of water vibration and M–O are observed (Tables 3 and 4).

In 1:1 (*M*:*L*) chelates of Cr(III) with the ligands Ia–c, the band due to the chromone carbonyl in position four (1662–1680 cm^{-1}) disappeared while in case of 1:1 chelates of Cr(III)–IIa–c and Co(III)–IIa, this band is shifted to lower frequency (1651–1658 cm^{-1}). This suggests the participation of this group in coordination.

The 1409–1440 cm^{-1} band due to –N=N–, 1636–1650 cm^{-1} band attributed to the formyl carbonyl in position six and 1700 cm^{-1} band of the carboxylic carbonyl of free azo dyes are slightly affected on chelation in case of 1:1 chelates.

In the IR spectra of 2:1 (*M*:*L*) chelates, the band due to chromone carbonyl in position four (1662–1680 cm^{-1}) disappeared for the chelates of titanium(IV), vanadium(IV), chromium(III), iron(III) ions and palladium(II) with ligands Ia–d. On the other hand, this band is shifted to lower frequency for chelates of the above mentioned ions with ligands IIa–d. This indicates the participation of the chromone carbonyl group in coordination with the metal ion.

The 1636–1650 cm^{-1} band due to stretching vibration of the formyl carbonyl in position six for 8-(arylazo)-5,7-dihydroxy-6-formyl-2-methylchromones, (Ia–d) is shifted to lower frequency in the 2:1 (*M*:*L*) chelates of titanium(IV), vanadium(IV), chromium(III) and iron(III) ions with ligands Ia, Ib, Id and Pd(II)–Id chelates suggesting for this stoichiometric ratio, that the aldehydic group is involved in chelation. On the other hand, the band due to aldehydic group is not affected by chelation in case of 2:1 VO–Ic chelate, meanwhile, the bands assigned to the carboxylic carbonyl in ortho position to the azo group and that due to the azo group disappeared.

For ligands IIa–d in which the position six is substituted by methyl group rather than formyl group. The IR spectra of 1:1 and 2:1 (*M*:*L*) chelates display a shift in C=O of the chromone moiety (1651–1658 cm^{-1}) to lower frequency (1630–1648 cm^{-1}). The band due to N=N is shifted to lower frequency in case of 2:1 (*M*:*L*) chelates. In the IR spectra of 2:1 (*M*:*L*) chelates of ligand IIc with metal ions, titanium(IV), vanadium(IV), iron III) and palladium(II), the band due to the carboxylic carbonyl at 1700 cm^{-1} disappeared. This indicates the participation of these groups in chelation. The IR spectra of 1:1 chelates of Cr(III)–IIb and 2:1 Cr(III) with the azo dyes Id and IId and Pd(II) chelates with Id and IIb–c exhibit a band at 340–360 cm^{-1} which may be attributed to the M–Cl stretching [21]. The IR spectra of the chelates show a single band at 420–565 cm^{-1} which is assigned to M–O [22].

In case of the 2:1 chelates of VO(IV)–Ic and TiO(IV), VO(IV), Cr(III), Fe(III) and Pd(II) with 8-(arylazo)-5,7-dihyroxy-2,6-dimethylchromones (IIa–d) the IR spectra display a band at 270–390 cm^{-1} due to the M–N vibration [23]. The new band

Table 3 IR band assignments of 2:1 (*M*:*L*) chelates with 8-(arylazo)-5,7-dihydroxy-6-formyl-2-methylchromone

	Free ligand	TiO^{IV}	VO^{IV}	Cr^{III}	Fe^{III}	Pd^{II}	Band assignment
Ia	3577	–	3324	3400*	3410	3460*	OH
	1114		1108	1078	1120	1115	OH
	1647		1636	1641	1633	1650	C=O(CHO)
	1662		–	–	–	–	C=O(chromone)
	1432		1401	1489	1410	1440	N=N
	841		763	761	760	820	OH
	–		517	534	470	511	M–O
Ib	3577	–	3289	3410*	–	3437*	OH
	1114		1110	1119		1120	OH
	1636		1630	1641		1650	C=O(CHO)
	1662		–	–		–	C=O(chromone)
	1434		1405	1463		1459	N=N
	853		755	762		757	OH
	–		518	443		545	M–O
Ic	3577	3418	3415	338*	–	3420*	OH
	1115	1129	1116	1090		1110	OH
	1647	1638	1648	1650		1650	C=O(CHO)
	1662	–	–	–		–	C=O(chromone)
	1700	1702	–	1700		1700	C=O(COOH)
	1434	1459	–	1445		1450	N=N
	848	755	820	780		835	OH
	–	459	457	460		486	M–O,
	–	–	390	–		–	M–N
Id	3500	3440	3380	3420	3480	3290	OH
	1115	1110	1115	1095	1110	1110	OH
	1650	1645	1635	1640	1640	1645	C=O(CHO)
	1680	–	–	–	–	–	C=O(chromone)
	1440	1420	1430	1420	1440	1420	N=N
	855	840	840	755	785	825	OH
	–	462	545	485	515	460	M–O

350 cm^{-1} M–Cl for Cr_2–Id and Pd_2–Id
* For 1:1 (*M*:*L*) chelates

Table 4 IR band assignments of 2:1 (*M*:*L*) chelates with 8-(arylazo)-5,7-dihydroxy-2,6-dimethylchromone

	Free ligand	TiO^{IV}	VO^{IV}	Cr^{III}	Fe^{III}	Co^{III}	Pd^{II}	Band assignment
IIa	3421	3420	3440	3410*	–	3450*	3450	OH
	1120	1095	1110	1110		1110	1115	OH
	1658	1640	1630	1645		1648	1648	C=O(chromone)
	1419	1395	1395	1410		1440	1390	N=N
	847	753	840	770		765	765	OH
	–	485 (370)	510 (385)	430		440	550 (385)	M–O (M–N)
IIb	3418	3440	3420	3440*	3420	–	3330	OH
	1114	1130	1120	1140	1085		1120	OH
	1637	1630	1640	1640	1640		1645	C=O(chromone)
	1426	1395	1390	1400	1395		1390	N=N
	849	760	755	845	840		820	OH
	–	460 (380)	515 (380)	495	420 (370)		490 (385)	M–O (M–N)
IIc	3431	3410	3480	3380*	3410	–	3460	OH
	1157	1115	1110	1090	1130		1110	OH
	1651	1640	1645	1640	1640		–	C=O(chromone)
	1700	–	–	1720	–		–	C=O(COOH)
	1409	1394	1390	1400	1395		1390	N=N
	800	755	780	820	780		765	OH
	–	510 (390)	490 (390)	420	455 (370)		420	M–O (M–N)
IId	3400	3420	3420	3440	3430	–	3410	OH
	1118	1115	1110	1130	1095		1140	OH
	1658	1640	1640	1640	1638		1645	C=O(chromone)
	1415	1390	1400	1405	1400		1398	N=N
	840	820	765	780	820		765	OH
	–	425 (370)	460 (370)	490 (370)	480 (385)		430 (380)	M–O (M–N)

350 cm^{-1} M–Cl for Cr–IIb, Pd_2–IIb, Pd_2–IIc and Cr_2–IId

* For 1:1 (*M*:*L*) chelates

occurring at 1114 cm^{-1} in the IR spectrum of Fe(III) chelate with the ligand IId can be assigned to the normal mode of vibration of the SO_4^{2-} [24].

Electronic spectra and magnetic moments

The electronic spectra of the organic ligands and their metal chelates are depicted in Table 5. The 8-(arylazo)chromones (Ia–d and IIa–d) display a shoulder in the 320–330 nm (31250–30303 cm^{-1}) and 300–314 nm (33333–31847 cm^{-1}) range, respectively. This band is attributed to electronic transition within the chromone ring. On the other hand, the bands in the 352–450 nm (28392–22222 cm^{-1}) range may be due to the π–π transition of the azo moiety influenced by the intramolecular charge transfer within the ligand molecules.

The electronic spectra of the 1:1 Cr(III) chelates with ligands Ia, Ib and IIa–c show a band in the 20665–22794 cm^{-1}, which can be assigned to the $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ transition. The magnetic moment values for these chelates, given in Table 4, indicate the presence of three unpaired electrons in each chelate molecule. The electronic spectrum of 1:1 Co(III)–IIa chelate exhibits a band at 22237 cm^{-1} corresponding to the $^1A_{1g}\rightarrow{}^1T_{2g}$ transition, and it is diamagnetic indicating the presence of Co ion in the trivalent state. It is to be mentioned that in the other cobalt chelates with the ligands Ia–d and IIb–d the cobalt is formed in oxidation state II [11].

The 2:1 (*M*:*L*) TiO(IV) chelates with the 8-(arylazo)chromones (IIa–d) display a band in the 22016–22614 cm^{-1} range and they are diamagnetic. Whereas, the VO(IV) chelates with the ligands (Ia–d and IIa–d) exhibit bands in the 19747–22675 and 20312–23866 cm^{-1} ranges, respectively which may be due to the $^2T_{2g}\rightarrow{}^2E_g$ transition. The magnetic moment values per VO(IV) ion (Table 4) indicate the presence of one unpaired electron confirming the quadrivalent state of vanadium ion (VO^{2+}). The electronic spectra of Cr(III) chelates with the ligands Id and IId reveal an absorption band at 21958 and 22060 cm^{-1}, respectively, corresponding to the $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ transition. The magnetic moments per Cr(III) ion are 3.04 and 3.44 B.M, indicating the presence of high spin octahedral structure [19]. The Fe(III) chelates with the chromone azo dyes Ia, Id and IIb–d display a band in the 21834–24509 cm^{-1} range, which can be attributed to the $^2A_{2g}\rightarrow{}^2T_{1g}$ transition. The obtained magnetic moment values per Fe(III) ion are given in Table 4 suggesting the presence of Fe(III) ion in each chelate. From the foregoing observations, the octahedral geometry was suggested for all chelates [25, 26].

The electronic spectra of the 1:1 (*M*:*L*) Pd(II) chelates with the ligands (Ia–c) show bands in the 19230–22629 and 19948–22472 cm^{-1} ranges, respectively which can be assigned to $^1A_{1g}\rightarrow{}^1B_{1g}$ transition. Whereas, the electronic spectrum of the 2:1 (*M*:*L*) Pd–Id chelate exhibits a band at 22614 cm^{-1}, corresponding to the same transition. The electronic spectra of the Pd–IIa–d chelates display a band in the 19853–22614 cm^{-1} range, due to the $^1A_{1g}\rightarrow{}^1B_{1g}$ transition. A square planar geometry was thus suggested for all chelates [27].

Table 5 Electronic absorption bands and magnetic moments of the metal chelates of 8-(arylazo) chromones

M	*M*:*L*	Ia		Ib		Ic		Id	
		/cm^{-1}	B.M*.	/cm^{-1}	B.M.	/cm^{-1}	B.M.	/cm^{-1}	B.M.
Free ligand		31250 23256	–	30303 22727	–	30769 23809	–	31250 24390	–
TiO^{IV}		–		–		–		–	
VO^{IV}	2:1	22583	1.65	19747		22675	1.60	21786	1.64
Cr^{III}	1:1	22060	3.36	18518	3.56			21958	3.04
Fe^{III}	2:1	22614	5.84	–				22492	5.13
Co^{III}		–		–		–		–	
Pd^{II}	1:1	22472	–	19948		22076		22614*	–

* For 2:1 chelates

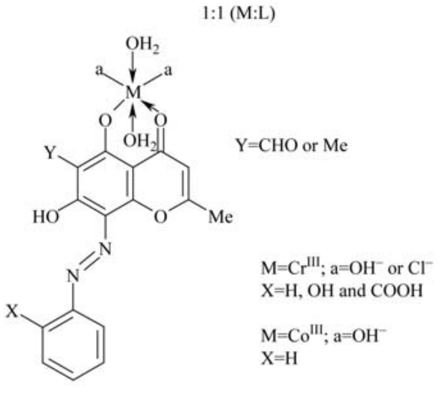
Table 5 Continued

M	*M*:*L*	IIa		IIb		IIc		IId	
		/cm^{-1}	B.M.	/cm^{-1}	B.M.	/cm^{-1}	B.M.	/cm^{-1}	B.M.
Free ligand		32786 26315	–	33333 28368	–	32258 28392	–	31847 22222	–
TiO^{IV}	2:1	22416	0.00	22614	0.00	22016	0.00	22341	0.00
VO^{IV}	2:1	23310	1.67	20312	1.64	20764	1.60	23866	1.66
Cr^{III}	1:1	22794	3.65	20665	3.53	22163	3.64	22060*	3.44
Fe^{III}	2:1	–	–	21834	5.28	22509	5.25	22753	5.10
Co^{III}	1:1	22237	0.00	–	–	–	–	–	–
Pd^{II}	2:1	22614	–	19843	–	22002	–	22614	–

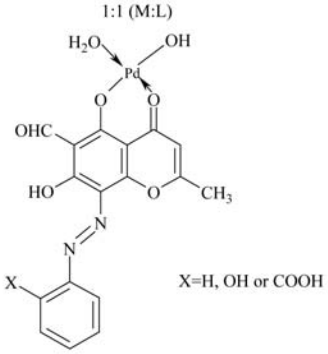
* For 2:1 chelates

Conclusions

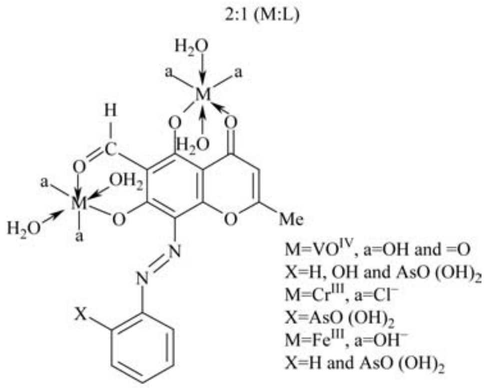
From the previous investigation [elemental analysis, thermal analysis, spectral and magnetic properties of metal chelates], the following conclusions can be drawn concerning the chromone azo dyes as well as the stereochemistry of the corresponding chelates. The infrared spectral data reveal two different modes of chelation. In the 1:1 (*M*:*L*) chelates of Cr(III) with ligands (Ia–c and IIa–c), Co(III)–IIa and Pd(II)–Ia–c the ligands behave as monobasic bidentate and the coordination sites are via the chromone carbonyl in position four and hydroxyl oxygen anion in position five. The electronic spectral data are in agreement with an octahedral geometry, formula [1] in case of Cr(III) and Co(III) chelates whereas in case of Pd(II) chelates a square planar geometry was proposed, formula [2]. In the binuclear chelates, the first metal ion bound via the same positions of the 1:1 (*M*:*L*) chelates, whereas, the second metal ion chelation takes place through the formyl carbonyl in position six and oxygen anion in position seven for the chelates of VO(IV) with ligands Ia, Ib, Id, Cr(III) and Pd(II) with Id and Fe(III) with Ia, d, formulae [3 and 4]. On the other hand, the chelates of



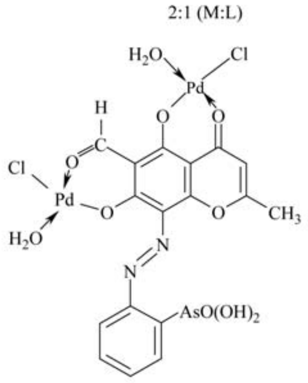
Formula [1]



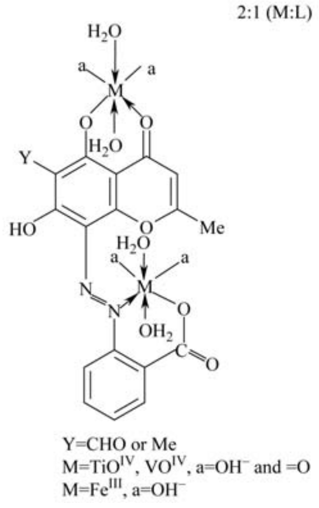
Formula [2]



Formula [3]

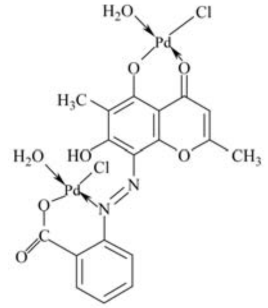


Formula [4]

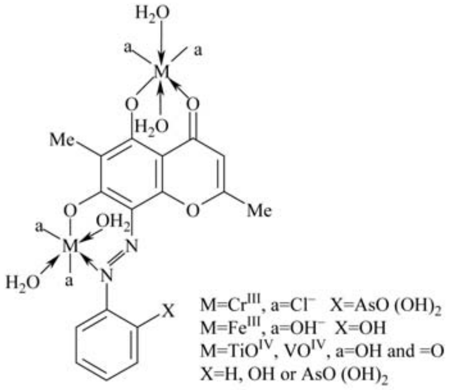


Formula [5]

VO(IV) with ligand Ic and TiO(IV), VO(IV), Fe(III) and Pd(II) with IIc, the second metal ion combines through the nitrogen azo and the carboxylic carbonyl in ortho position to it, formulae [5 and 6]. In the 2:1 chelates of Cr(III) with IId, Fe(III) with IIb, and Pd(II) chelates with IIa,b,d the first chelation is through the same position of 1:1 chelates, while the second chelation is via the azo group and oxygen anion (chromone) in position seven, formulae [7 and 8].

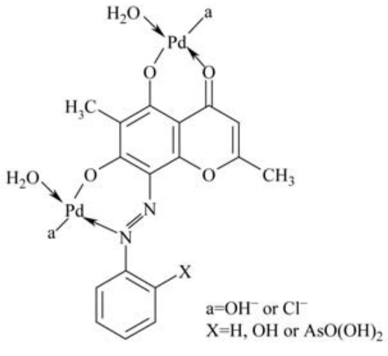


Formula [6]



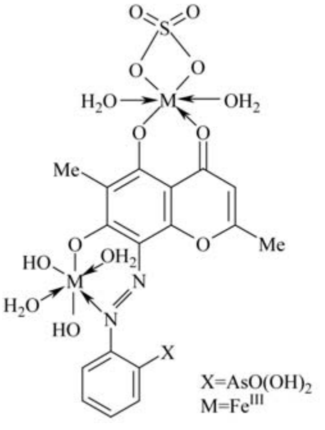
$M=Cr^{III}$, $a=Cl^-$ $X=AsO(OH)_2$
$M=Fe^{III}$, $a=OH^-$ $X=OH$
$M=TiO^{IV}$, VO^{IV}, $a=OH$ and $=O$
$X=H$, OH or $AsO(OH)_2$

Formula [7]



$a=OH^-$ or Cl^-
$X=H$, OH or $AsO(OH)_2$

Formula [8]



Formula [9]

It is to be mentioned that in most 2:1 (*M*:*L*) chelates the coordination sphere is completed with chloride or hydroxyl ion except Fe(III)-chelate with ligand IId the sulphate ion takes place in chelation as shown from the IR spectrum, formula [9].

References

1 F. A. Ragab, E. K. El-Said and S. A. K. Kenawy, Egypt. J. Pharm. Sci., 33 (1992) 83.
2 A. Murata, T. Ito, K. Fujiyasu and T. Suzuki, Bunseki Kagaku, 15 (1966) 143 [C.A.: 65, 6275h (1966)].
3 A. Murata, T. Ito and T. Suzuki, Bunseki Kagaku, 17 (1968) 1284 [C.A.: 70, 63913r (1969)].
4 T. Ito and A. Murata, Bunseki Kagaku, 20 (1971) 335 [C.A.: 76, 94209u (1972)].
5 A. Murata and T. Ito, Bunseki Kagaku, 18 (1969) 1131 [C.A.: 72, 50591a (1970)].
6 A. Murata, T. Ito and T. Suzuki, Nippon Kagaku Zasshi, 89 (1968) 54 [C.A.: 69, 5695q (1968)].
7 A. Murata and K. Mizoguchi, Bunseki Kagaku, 18 (1969) 1471 [C.A.: 72, 96371g (1970)].
8 Y. M. Issa, A. L. El-Ansary, O. E. Sherif and M. M. El-Ajily, Trans. Met. Chem., 22 (1997) 441.
9 A. M. El-Roudi, Bull. Fac. Sci., Assiut University, 18 (1989) 77–78; [C.A.:114, 113926x (1991)].
10 Y. M. Issa, A. L. El-Ansary, O. E. Sherif and M. M. El-Ajily, Asian J. Chem., 9 (1997) 301.
11 A. L. El-Ansary, O. E. Sherif and M. M. Ajily, Synth. React. Inorg. Met-Org. Chem., 29 (1999) 1501.
12 Y. M. Issa, O. E. Sherif and S. M. Abbas, Synth. React. Inorg. Met-Org. Chem., 29 (1999) 897.
13 M. Merdivan, F. Karipcin, N. Kulcu and R. S. Aygun, J. Therm. Anal. Cal., 58 (1999) 551.
14 L. Ghizdavu, C. Bãlan, L. David, C. Bâtiu, O. Cozar and D. Ristoiu, J. Therm. Anal. Cal., 62 (2000) 729.
15 M. R. P. Kurup, E. Lukose and K. Muraleedharan, J. Therm. Anal. Cal., 59 (2000) 815.
16 H. Martyniuk, J. Wiekowska and J. Lipman, J. Therm. Anal. Cal., 65 (2000) 711.
17 F. J. Welcher, The analytical uses of ethylenediaminetetraacetic acid, Van Nostrand, New York 1958.
18 A. M. G. Macdonald and P. Sirichanya, Microchem. J., 14 (1969) 199.
19 Vogel's, Textbook of Practical Organic Chemistry, 5th Edn., Longman, London 1989.

20 M. M. Shallaby, M. M. Mostafa and M. M. Bekheit, J. Inorg. Nucl. Chem., 41 (1978) 267.
21 J. R. Ferrano and W. R. Walker, Inorg. Chem., 4 (1985) 1382.
22 J. A. Faniran, K. S. Patel and L. O. Nelson, J. Inorg. Nucl. Chem., 38 (1976) 77, 81.
23 J. R. Ferrano, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York 1971.
24 A. A. Salah, F. M. El-Zawawy and S. M. Abu El-Wafa, Egypt. J. Chem., 36 (1993) 373.
25 A. D. Liehr, J. Phys. Chem., 67 (1963) 1314.
26 W. L. Jolly, Principles of Inorganic Chemistry. MacGraw-Hill, New York 1976, p. 272.
27 S. Yamada, Coord. Chem. Rev., 1 (1966) 415.