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A. L. El-Ansary , O. E. Sherif & M. M. El-Ajily

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PREPARATION AND SPECTROSCOPIC INVESTIGATION OF CHELATES OF DIVALENT TRANSITION METAL IONS WITH 8-(ARYLAZO)-CHROMONES

A. L. EL-Ansary*, O. E. Sherif, and M. M. EL-Ajily

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

ABSTRACT

Metal chelates of the divalent transition metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) with 8-(arylażo)chromones have been prepared and characterized by elemental analyses, IR and electronic spectra, thermogravimetric analyses, magnetic and conductance measurements. The obtained data suggest the formation of 1:1 and 2:1 (M:Ligand) chelates with the general formula $[MH_{k-1}LX_{10}(H_2O)_n].yH_2O$ or $[M_2H_{k-2}LX_{10}(H_2O)_n].yH_2O$ where X = OH or Cl, m = 1 or 2, n = 1-3 or 6, y = 1-3 or 5, k = 2-4. M is a divalent transition metal ion and H_kL represents the 8-(arylazo)-chromones. The study revealed that the ligands behave as monobasic bidentates in the case of 1:1 (M:Ligand) chelates. Electronic spectra and magnetic measurements indicate that the metal chelates have square-planar, tetrahedral or octahedral geometries. The TG analyses indicate the presence of hydrated and coordinated water molecules. A nonelectrolytic nature was assigned based on molar conductance measurements.

INTRODUCTION

Hydroxychromones are used as analytical reagents for the microdetermination of metal ions¹, as they are capable of forming metal chelates with transition metal ions.

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The composition and stability constants of 3-hydroxychromone iron(III) chelates were studied spectrophotometrically². The preparation and characterization of new metal chelates derived from chromone-3-carboxaldehyde-4-phenylthiosemicarbazone were reported³. Divalent metal ion chelates of 6-formyl-7-hydroxy-5-methoxy-2-methyl-chromone, 5,7-dihydroxy-6-formyl-2-methylchromone and 5,7-dihydroxy-2,6-dimethyl- chromone have been prepared and studied⁴. The chelates of chromone Schiff bases derived from *o*-substituted anilines with divalent Co, Ni and Cu ions have been investigated by Abd El-Gaber *et al*⁵. Recently, 8-(arylazo)chromones were synthesized⁶, yet their metal chelates have not been prepared or studied.

The aim of the present investigation is to prepare and elucidate the geometrical structures of the metal chelates formed between the divalent transition metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) with 8-(arylazo)chromones. The structures of the 8-(arylazo)chromones are represented in Fig.1.

EXPERIMENTAL

Materials

All chemicals used were of pure grade (BDH or Aldrich). All organic solvents used in this work were either purified by the recommended methods⁷ or obtained as spectroscopic grade solvents from BDH. Double-distilled water from glass equipment was used in all experiments. The preparation of 5,7-dihydroxy-2,6-dimethylchromone and 5,7-dihydroxy-6-formyl-2-methylchromone followed the procedure described earlier⁸.

Preparation of Chromone Azo Dyes

8-(Arylazo) derivatives of 5,7-dihydroxy-2,6-dimethylchromones $[H_k L^{1-4}]$ and 5,7-dihydroxy-6-formyl-2-methylchromones $[H_k L^{5-8}]$ were prepared by a literature procedure⁶.

Synthesis of Metal Chelates

The metal chelates of 8-(arylazo)chromones were synthesized by mixing 20 mL of hot ethanolic solutions of the dye (0.01 mol) and 20 mL of an ethanol solution of

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Н	CH3	H_2L^1	Н	СНО	H_2L^5
OH	CH3	$H_{3}L^{2}$	OH	СНО	H3L6
COOH	СН3	H_3L^3	COOH	СНО	$H_{3}L^{7}$
AsO(OH) ₂	CH3	H_4L^4	AsO(OH) ₂	CHO	H₄L ⁸

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Fig. 1. Structure of the 8-(Arylazo)chromones

the metal salt (0.01 mol) [MnCl₂.4H₂O, FeSO₄.7H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, Zn(CH₃COO)₂.2H₂O and PdCl₂]. The mixtures were left to stand on a steam bath for 30 min. In some cases, the metal chelates did not separate on standing and a few drops of ammonia solution were added slowly with stirring to adjust the pH to 6-8 which resulted in precipitation. The formed metal chelates were then filtered and washed several times with distilled water and hot ethanol until the filtrate became colourless. Then the chelates were dried over anhydrous CaCl₂.

Physical Measurements

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Elemental analyses were performed in the Microanalytical Center of Cairo University. The metal contents of these chelates were determined after wet decomposition of the chelates as previously described⁹, followed by EDTA titration¹⁰.

The infrared spectra of the chelates were obtained by applying the KBr disc technique using a Perkin-Elmer 1430 infrared spectrometer. The visible spectra of the 8-(arylazo)chromones and their chelates were measured by applying the Nujol mull technique using a Perkin Elmer Lambda 4B spectrophotometer. with 1 cm matched silica cells. Thermogravimetric analyses (of some chelates which contain water molecules) were achieved using a Shimadzu thermal analyzer (Japan). The weight loss was measured from ambient temperature up to 1000° C ramped at 10° C/min. The conductivity measurements were carried out in DMF solution using a conductivity bridge model CM-1K-TOA company (Japan). The magnetic moments were measured using a Johnson-Mathey susceptometer devised by F. Evans (USA).

RESULTS AND DISCUSSION

The analytical data for the metal chelates with 8-(arylazo) derivatives of 5,7dihydroxy-2,6-dimethylchromones, and 5,7-dihydroxy-6-formyl-2-methylchromones, $(H_k L^{1-8})$ are listed in Table I. The obtained data showed that the stoichiometries of the 1:1 and 2:1 (M:Ligand). The chelates are suggested formulas are $[MH_{k-1}LX_m(H_2O)_m]$, yH_2O or $[M_2H_{k-2}LX_m(H_2O)_m]$, yH_2O , where X = OH or Cl, m = 1 or 2, n = 1-3 or 6, y = 1-3 or 5, M represents Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) ions; and H₂L represents the 8-(arylazo)chromones, the complex formation may be represented by the following equations:

For the 1:1 chelates:

 $M^{2+} + H_kL + mX + (n+y)H_2O \rightarrow [MH_{k-1}LX_m(H_2O)_n].yH_2O + H^+$

For the 2:1 chelates:

 $2M^{2+} + H_kL + mX + (n+y)H_2O \rightarrow [M_2H_{k-2}LX_m(H_2O)_n].yH_2O + 2H^+$

It is observed from Tables I and II that the analytical data are in good agreement with the calculated values according to the proposed structural formulas of the chelates. The molar conductivities of the chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) with the azo dyes (H_kL^{1-8}) at 25° C in DMF solvent are in the 3.80-33.00 ohm⁻¹ cm² mole⁻¹ range indicating a non-electrolytic nature for all the chelates¹¹.

Infrared Spectra

The infrared spectra of the metal chelates, in comparison with those of the free ligands, display certain changes which give an idea about the types of bonds and their structures. IR band assignments are given in Table II.

In the 1:1 (M:H_kL) chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) with 8-(arylazo) chromone, the band due to the chromone carbonyl in position

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43.0 (42.50)4.4 (4.38)5.4 (5.83) [13.01 (13.23) 7.2 (7.40) 27.3 (27.79)4.2 (3.72(4.5 (3.72) 27.85 (28.31) 8.8 (9.44) \overline{O} 51.2 (51.12)4.5 (4.01)6.5 (7.02) 13.70 (13.78) 50.7 (50.65)4.2 (3.97)7.4 (6.95) 14.75 (14.57) [50.0 (49.83)]4.5 (3.91)[6.7 (6.48)]15.70 (15.97) 64.7 (64.69)4.3 (4.12)7.0 (6.41) 13.40 (13.50) 44.6 (44.93) 5.3 (4.85) 5.2 (6.16) 12.56 (12.33) 47.3 (47.11)4.4 (4.15)7.1 (6.46) 12.83 (12.70) 48.7 (47.95)4.8 (3.76)5.7 (6.58) 15.50 (15.37) (3.05)5.5 (4.74) 35.96 (36.03) **48.5 (48.72)4.2 (3.82)5.9 (6.69) 14.22 (14.02)** 46.6 (46.20)|4.2 (4.07)|7.3 (6.34) |14.42 (14.38) Σ z Η F.W. |Yield|Found (Calcd) % 34.6 (34.55)2.9 \circ 75 65 80 75 80 75 65 80 65 75 2 % 65 454.16 480.30 591.13 399.21 433.23 441.83 403.01 437.23 419.01 424.61 734.09 409.61 Empirical Formula C₁₇H₂₆Cl₂N₂O₁₂Pd₂ C₁,H₂₁CICuN₂O₈ C₁,H₁₆MnN₂O₆ C₁₇H₁₈N₂O₈Pd₂ $Mn(H_{J}L^{2})(OH)(H_{2}O)].H_{2}O|C_{17}H_{18}MnN_{2}O_{8}$ Co(H₂L²)(OH)(H₂O)].H₂O C₁₇H₁₈CoN₂O₈ $Fe(HL^{1})(OH)(H_{2}O)_{3}].H_{2}O[C_{17}H_{22}FeN_{2}O_{6}]$ C₁₇H₁₆NiN₂O₆ C₁₇H₁₆N₂O₆Zn Cu(H₂L²)(OH)(H₂O)].H₂O C₁₇H₁₈CuN₂O₈ C₁₇H₁₆N₂O₇Zn C₁₇H₁₆NiN₂O₇ [Pd₂(HL²)Cl₂(H₂O)].6H₂O Cu(HL¹)Cl(H₂O)].3H₂O Mn(HL¹)(OH)(H,O)] $Zn(H_2L^2)(OH)(H_2O)]$ Pd₂(L¹)(OH)₂(H₂O)₂] $Ni(H_2L^2)(OH)(H_2O)]$ Ni(HL¹)(OH)(H,O)] [(0,H)(H)(H)(H,0)] Chelate L¹ Derivatives H₁L² Derivatives

Table I. Elemental Analyses of Metal Chelates of 8-(Arylazo)-5,7-dihydroxy-2,6-dimethylchromone Derivatives (H,L¹⁻⁸)

(continued)

CHELATES WITH 8-(ARYLAZO)CHROMONES

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Table I continued

H ₃ L ³ Derivatives								
$[Mn_2(HL^3)(OH)_2(H_2O)_2]$	$C_{18}H_{18}Mn_2N_2O_{10}$	532.14	80	40.8 (40.60)3.	5 (3.38)6.	1 (5.26)	20.45 (20.67)	
[Co(H ₂ L ³)Cl(H ₂ O) ₃].H ₂ O	C ₁₈ H ₂₁ CICoN ₂ O ₁₀	519.71	75	42.1 (41.57)4.	4 (4.04)6.	1 (5.39)	11.20 (11.36)	6.5 (6.83)
$[Ni(H_2L^3)(OH)(H_2O)]$. 3H ₂ O	C ₁₈ H ₂₂ O ₁₁ NiN ₂	501.07	65	34.4 (34.14)4.	8 (4.39)6.	3 (5.59)	11.90 (11.72)	
$[Cu(H_2L^3)Cl(H_2O)].5H_2O$	C ₁₈ H ₂₅ ClCuN ₂ O ₁₂	560.34	70	38.9 (38.57)4.	5 (4.46)5.	6 (5.00)	11.45 (11.34)	5.8 (6.34)
[Zn(H ₂ L ³)(OH)(H ₂ O)]	C ₁₈ H ₁₆ N ₂ O ₈ Zn	453.62	75	47.8 (47.64)4.	1 (3.53)5.	3 (6.18)	14.70 (14.42)	
$[\mathrm{Pd}_2(\mathrm{HL}^3)\mathrm{Cl}_2(\mathrm{H}_2\mathrm{O})_2]$	$C_{18}H_{16}Cl_2N_2O_8Pd_2$	672.02	80	31.9 (32.14)2.	5 (2.38)3.	95 (4.17)	31.4 (31.67)	10.5 (10.56)
H ₄ L ⁴ Derivatives								
[Mn ₂ (H ₂ L ⁴)Cl ₂ (H ₂ O) ₂].H ₂ O	$C_{17}H_{10}AsCl_2Mn_2N_2O_{10}$	666.94	65	30.8 (30.59)3.0	0 (2.85)3.	5 (4.20)	16.30 (16.50)	10.8 (10.65)
$[Co_2(H_2L^4)Cl_2(H_2O)_2].H_2O$	C ₁₇ H ₁₉ AsCl ₂ Co ₂ N ₂ O ₁₀	674.94	70	30.3 (30.23)3.	7 (2.82)3.	6 (4.15)	17.41 (17.48)	10.7 (10.52)
[Ni ₂ (H ₂ L ⁴)Cl ₂ (H ₂ O) ₂] 3H ₂ O	C ₁₇ H ₂₃ AsCl ₂ Ni ₂ N ₂ O ₁₂	710.57	80	28.2 (28.72)4.:	3 (3.34)3.	5 (3.94)	16.40 (16.53)	10.6 (9.99)
$[Cu_2(H_2L^4)Cl_2(H_2O)_2].5H_2O$	$C_{17}H_{27}AsCl_2Cu_2N_2O_{14}$	756.20	75	26.4 (26.98)4.	1 (3.57)4.	2 (3.70)	16.65 (16.80)	8.8 (9.39)
$[Zn_2(H_2L^4)(OH)_2(H_2O)_2]$	C ₁₇ H ₁₉ AsN ₂ O ₁₁ Zn ₂	632.84	75	33.2 (32.24)3.	7 (3.00)3.	8 (4.43)	20.35 (20.67)	
$[Pd_{2}(H_{2}L^{4})(OH)_{2}(H_{2}O)_{2}]$	C ₁₇ H ₁₉ AsN ₂ O ₁₁ Pd ₂	715.04	70	28.7 (28.53)3.	3 (2.66)3.	4 (3.94)	30.05 (29.79)	
H ₂ L ⁵ Derivatives								
[Mn(HL ⁵)(OH)(H ₂ O)]	C ₁₇ H ₁₄ MnN ₂ O ₇	413.29	75	49.2 (49.39)3.9	9 (3.39)7.	3 (6.78)	13.60 (13.32)	

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[Co ₂ (L ⁵)Cl ₂ .(H ₂ O) ₂].H ₂ O	$C_{17}H_{16}Cl_2Co_2O_8N_2$	565.16	65	36.2 (36.10)	3.1 ()	2.83)	.2 (4.96)	20.75 (20.88)	11.8 (12.56)
[(0 ² H)(HO)(₂ TH)!N]	C ₁₇ H ₁₄ O ₇ NiN ₂	416.99	80	48.2 (48.95)	4.3 ()	3.36)	1.0 (6.72)	13.80 (14.08)	
$[Cu_{2}(L^{5})(OH)_{2}(H_{2}O)_{2}]$	$C_{17}H_{16}Cu_2N_2O_9$	519.30	65	40.0 (39.31)	4.2 (;	3.80)4	.6 (5.39)	24.75 (24.47)	
[(O ⁷ H)(HO)(₇)]	C ₁₇ H ₁₄ N ₂ O ₇ Zn	423.59	75	48.7 (48.18)	3.0 (3.31)7	.4 (6.61)	15.60 (15.44)	
[Pd(HL ⁵)(OH)(H ₂ O)]	C ₁ ,H ₁₄ N ₂ O,Pd	464.69	70	43.8 (43.92)	3.4 (;	3.01)	6.03) 0.0	22.50 (22.92)	
H ₃ L ⁶ Derivatives									
[Mn(H ₂ L ⁶)(OH)(H ₂ O)]	C ₁₇ H ₁₄ MnN ₂ O ₈	429.19	80	48.0 (47,55)	17	3.26)4	.0 (6.53)	12.65 (12.82)	
[Fe ₂ (HL ⁶)(OH) ₂ (H ₁ O) ₆].3H ₂ O	$C_{17}H_{30}Fe_2N_2O_{17}$	646.02	75	31.4 (31.57)	4.3 (4	4.33)4	.2 (4.33)	17.56 (17.33)	
[Co ₂ (HL ⁶)(OH) ₂ (H ₂ O) ₂]	C ₁₇ H ₁₆ Co ₂ N ₂ O ₁₀	526.11	75	39.1 (38.78)	3.4 ()	3.04)6	.1 (5.32)	22.8 (22.43)	
$[(0_{1}H_{2}H)(HO)(_{2}H)(H_{2}O)]$	C ₁₇ H ₁₄ O ₈ NiN ₂	432.99	80	47.3 (47.15)	3.6 (3.24)6	.6 (6.47)	13.80 (13.56)	
$[Cu_2(HL^6)(OH)_2(H_2O)_2]$	C ₁₇ H ₁₆ Cu ₂ N ₂ O ₁₉	535.31	65	38.2 (38.13)	3.2 (3	5(66.3	.2 (5.23)	23.40 (23.74)	
$[Zn(H_2L^6)(OH)(H_2O)]$.H ₂ O	C ₁₇ H ₁₆ N ₂ O ₉ Zn	457.69	65	45.1 (44.60)	3.3 (3	3.50)5	.8 (6.12)	14.45 (14.29)	
[Pd(H ₂ L ⁶)(OH)(H ₂ O)]	C ₁₇ H ₁₄ N ₂ O ₈ Pd	480.69	70	42.2 (42.46)	3.2 (3	5(16.2	.4 (5.83)	22.33 (22.15)	
H ₃ L ⁷ Derivatives									
$[Mn_2(HL^7)(OH)_2(H_2O)_2]$	C ₁₈ H ₁₆ O ₁₁ Mn ₂ N ₂	546.12	65	39.3 (39.56)	3.4 (5	2.93)6	.0 (5.13)	20.35 (20.14)	
$[Fe(H_2L^7)(OH)(H_2O)_3]H_2O$	C ₁₈ H ₂₀ FeN ₂ O ₁₂	512.15	70	42.8 (42.18)	1 .2 (3	3.91)5	.6 (5.47)	11.10 (11.33)	

CHELATES WITH 8-(ARYLAZO)CHROMONES

[Co ₂ (HL ⁷)(OH) ₂ (H ₂ O) ₂]H ₂ O	C ₁₈ H ₁₈ Co ₂ N ₂ O ₁₂	572.19	70	38.4 (37.76)	3.6 (3	3.15)	.5 (4.90)	20.30 (20.63)	
$[Ni_2(HL^7)(OH)_2(H_2O)_2]$	C ₁₈ H ₁₆ O ₁₂ Ni ₂ N ₂	553.72	65	40.0 (39.03)	3.0 (2	2.89)6	6.0 (5.06)	20.90 (21.20)	
[Cn(H ² L ¹)(OH)(H ² O)].H ₂ O	C ₁₈ H ₁₆ CuN ₂ O ₁₀	483.82	75	44.3 (44.67)	3.5 (3	3.31)	;.7 (5.80)	13.35 (13.13)	
[Zn(H ₂ L ⁷)(OH)(H ₂ O)].H ₂ O	C ₁₈ H ₁₆ N ₂ O ₁₀ Zn	485.72	75	44.5 (44.50)	3,4 (2	3.30)	6.0 (5.76)	13.4 (13.47)	
$[Pd(H_2L^7)(OH)(H_2O)]$.H ₂ O	C ₁₈ H ₁₆ N ₂ O ₁₀ Pd	526.72	80	41.0 (41.03)	3.5 (3	3.04)4	1.7 (5.32)	20.06 (20.22)	
H ₄ L ⁸ Derivatives									
[(Mn(H ₃ L ⁸)(OH)(H ₂ O)]	$C_{17}H_{15}AsMnN_2O_{10}$	537.14	80	38.6 (37.99)	3.7 (2	<u>, 79)</u>	6.0 (5.21)	10.20 (10.24)	
[Co ₂ (H ₂ L ⁸)Cl ₂ (H ₂ O) ₂].2H ₂ O	$C_{17}H_{19}AsCl_2Co_2N_2O_{12}$	706.64	65	28.6 (28.86)	3.5 (2	2.69)4	1.5 (3.69)	16.90 (16.69)	9.2 (10.00)
$[Ni_2(H_2L^8)Cl_2(H_2O)_2] 5H_2O$	C ₁₇ H ₂₅ AsCl ₂ Ni ₂ N ₂ O ₁₅	760.58	70	26.0 (26.86)	4.7 (3	3.29)4	1.2 (3.68)	15.4 (15.46)	9.2 (9.35)
[Cn ² (H ² T ₈)Cl ² (H ² O) ²]	C ₁₇ H ₁₅ AsCl ₂ Cu ₂ N ₂ O ₁₀	680.10	75	30.2(30.00)	3.1 (2	2.50 4	t.0 (4.18)	18.75 (18.68)	10.2 (10.44)
[Zn(H ₃ L ⁸)(OH)(H ₂ O)]	$C_{17}H_{15}AsN_2O_{10}Zn$	547.50	75	37.0 (37.27)	3.4 (2	2.74)	5.2 (5.11)	12.20 (11.59)	
$[Pd_2(H_2L^8)Cl_2(H_2O)_2] 3H_2O$	$C_{17}H_{21}AsCl_2N_2O_{13}Pd_2$	819.95	70	25.7 (24.88)	3.1 (2	2.37)	3.5 (3.49)	26.40 (26.55)	8.4 (8.83)

Table I continued

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CHELATES WITH 8-(ARYLAZO)CHROMONES

Free	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Pd ²⁺	Band assignment
ligand								
8-(Phen	ylazo)ch	romone	(H ₂ L ¹)	derivativ	/es	L	L	
3421	3440	3420	-	3414	3450	3440	3450	ν(OH) b
1120	1111	1110	-	1129	1120	1120	1115	δ(OH) m
1658	6300	1642	-	1654	1640	1640	1648	v(C=O) (chromone) s
1419	1440	1420	-	1442	1440	1450	1390	ν(N=N) w
-	475	510	-	443	490	430	550	v(M-O) w
-	-	-	-	-	-	-	385	v(M-N) w
847	762	830	-	763	840	755	765	γ(OH) m
-	-	-	-	-	350	-	-	v(M-Cl) m
8-(2-Hy	droxyph	enylazo)chromo	one (H ₃ I	$\frac{1}{2}$ derivative	atives	1	<u> </u>
3418	3420	-	3410	3410	3420	3460	3330	v(OH) b
1141	1145	-	1140	1140	1140	1130	1120	δ(OH) m
1657	1648	-	1640	1645	1638	1645	1645	v(C=O) (chromone) s
1426	1440	-	1430	1410	1430	1435	1390	v(N=N) w
-	570	-	470	470	485	500	490	v(M-O) w
-	-	-	-	-	-	-	385	v(M-N) w
849	755	-	810	750	840	845	820	γ(OH) m
-	-	-	-	-	-	-	350	v(M-Cl) m
8-(2-Ca	rboxyph	enylazo)chromo	one (H ₃ L	$\frac{1}{2}$) deriva	atives		• • • • • • • • • • • • • • • • • • •
3431	3410	-	3411	3385	3428	3460	3460	ν(OH) b
1157	1115	-	1157	1096	1155	1150	1110	δ(OH) w
1651	1640	-	1642	1645	1641	1645	1645	v(C=O) (chromone) s
1700	-	-	1730	1740	1762	1730	-	v(C=O) (COOH) s
1409	1395	-	1449	1448	1447	1430	1390	v(N=N) w

Table II. IR Bands^a of 8-(Arylazo)chromones (H_kL¹⁻⁸) Chelates.

(continued)

-	495	-	464	564	460	450) 42	0	v(M-O) w		
-	370	-	-	-	-	-	38	0 \	v(M-N) w		
800	785	-	765	763	766	785	5 76	5 γ	(OH) m		
-	-	-	343	-	344	-	34	0 \	v(M-Cl) m		
8-(2-Ar	sonoph	enylaz	o)chron	none (H	L ⁴) deriv	atives					
3400	3420	-	342	0 336	n 338	0 334	10 34	10	v(OH) b		
1118	1120	-	112	0 109	0 109	0 109	95 11	40 E	5(OH) w		
1658	1640	-	164	8 164	2 163	8 164	10 16	45 v	v(C=O) (chromone) s		
1415	1390	-	140	139	0 140	140)5 13	98 \	v(N=N) m		
-	465	-	475	500) 495	470) 43	0	v(M-O) w		
-	375	-	380	370) 375	395	5 38	0	v(M-N) w		
840	835	-	820	755	835	810) 76	5 γ	y(OH) m		
-	350		340	340) 350) -	-	, ,	v(M-Cl) m		
8-(Pher	8-(Phenylazo)chromone (H ₂ L ⁵) derivatives										
357	7 3	410		3423	3414	3446	3440	346	50 ν(OH) b		
1114	4 1	085		1119	1118	1112	1118	111	5 δ(OH) w		
164	7 1	650		1619	1653	1630	1651	165	50 ν(C=O) (CHO) s		
1662	2								(C=O) (chromone)		
1432	2 1	420		1491	1450	1447	1449	144	10 v(N=N) s		
		465		519	451	427	463	51	1 ν(M-O) w		
841		765		760	761	764	761	820	0 γ(OH) m		
						350			v(M-C)I w		

Table II continued

8-(2-Hydrox	yphenyl	azo) chr	omone (H₃L ⁶) de	erivative	s		
3577	3385	3413	3389	3411	3236	3424	3437	v (OH) b
1114	1121	1084	1119	1117	1083	1078	1120	δ(OH) w
1636	1643	1631	1630	1651	1630	1647	1650	v(C=O) (CHO) s
1662								(C=O) (chromone) s
1432	1464	1424	1465	1467	1389	1461	1430	v(N=N) s
	515	465	507	454	425	459	545	v(M-O) w
853	780	765	755	761	755	757	757	γ(OH) m
			345	350	340		350	v(M-Cl) w
8-(2-Carbox	yphenyl	azo)chro	omone (l	H_3L^7) de	rivatives	3		
3577	3380	3389	3415	3414	3420	3410	3420	v(OH) b
1115	1120	1113	1122	1117	1115	1112	1110	δ(OH) w
1647	1646	1650	1646	1634	1645	1655	1650	v(C=O) (CHO) s
1662								v(C=O) (chromone) s
1700		1731		1719	1740	1730	1700	v(C=O) (COOH) s
1436	1400	1401	1400	1444	1456	1430	1450	ν(N=N) s
	428	454	518	458	470	508	486	v(M-O) w
	380		390					v(M-N) w

Table II continued

(continued)

848	780	762	766	764	830	870	835	γ(OH) m
			340		344		340	v(M-Cl) w
8-(2-Arsono	phenyla	zo)chror	none (H	₄L ⁸) deri	vatives			
3500	3420		3480	3450	3380	3380	3290	v(OH) b
1115	1100		1120	1110	1120	1110	1110	δ(OH) w
1650	1650		1640	1642	1640	1650	1645	v(C=O) (CHO) s
1680								(C=O) (chromone) s
1440	1410		1430	1430	1430	1430	1420	v(N=N) s
	485	-	515	455	420	479	460	v(M-O) w
855	755		785	845	755	755	825	γ(OH) w
	350		340	340	350			v(M-Cl) w

Table II continued

^ab = broad, s = strong, m = medium, w = weak

four (Fig. 1) (1662-1680 cm⁻¹) has disappeared. This suggests the involvement of this group in chelation.

The existence of water of hydration or coordination in all chelates renders it difficult to draw conclusions from the v(OH) band of the hydroxyl group of the free ligands which would overlap with those of water molecules. The participation of the hydroxyl group in the chelation is confirmed by the appearance of new bands related to the v(M-O) vibration.

The 1409-1440 cm⁻¹ band due to the N=N vibration and the 1700 cm⁻¹ band of the carboxylic carbonyl of the free ligands are not affected on chelation in case of the 1:1 chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) ions with

8-(arylazo)chromones. Whereas, the carboxylic carbonyl stretching vibration (1700 cm⁻¹) disappeared upon chelation of the 2:1 (M:L⁵⁻⁸) complexes of Mn(II) and Co(II) with the ligand H_3L^7 , this same vibration merely shifted to lower frequency upon chelation of the Mn(II) and Pd(II) complexes with the ligand H_3L^3 . This suggests involvement of this group in chelation.

The stretching vibration at 1636-1650 cm⁻¹ due to the formyl carbonyl in position six for 8-(arylazo)-5,7-dihydroxy-6-formyl-2-methylchromone derivatives (H_kL^{5-8}) is shifted to lower frequency in the 2:1 chelates of Fe(II), Ni(II), Cu(II) and Pd(II) ions suggesting the participation of this group in coordination. On the other hand, this band is not affected by chelation in case of the 2:1 Mn(II) and Co(II) chelates with H_3L^7 . Meanwhile, the bands due to the stretching frequency of the carboxylic carbonyl as well as the azo group disappeared in the 2:1 (M:L) chelates of Mn(II) and Co(II) with ligand H_3L^7 . These same bands disappeared in the Mn(II) and Pd(II) chelates with ligand H_3L^3 , indicating the involvement of these groups in chelation with the metal ion.

The appearance of a new band at 417-570 cm⁻¹ in the IR spectra of the chelates indicates the presence of M-O vibrations¹². The IR spectra of the 2:1 Mn(II) and Co(II) chelates with H_3L^7 , the Mn₂-IIL³, Mn₂-II₂L⁴, Co₂-H₂L⁴, Ni₂-H₂L⁴, Cu₂-H₂L⁴, Zn₂-H₂L⁴ and Pd₂-H_{k-2}L¹⁻⁴ chelates display a band at 370-395 cm⁻¹, corresponding to the M-N vibration¹³. The band at 340-350 cm⁻¹ in the IR spectra of the 1:1 Cu(II)-HL¹, Co(II)-H₂L³ and 2:1 Mn(II), Co(II), Ni(II), and Cu(II) chelates with H₄L⁴ is attributed to the M-Cl vibration¹⁴.

Electronic Spectra and Magnetic Measurements

The magnetic moment values and the absorption bands for the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) chelates with the ligands (H_kL^{1-8}) are given in Tables III and IV. The magnetic moments are comparable to those expected for tetrahedral, square-planar or octahedral geometries, respectively.

The electronic absorption spectra of the free ligands display a shoulder at 320-330 nm (31250-30303 cm⁻¹) for ($H_{\rm k}L^{5-8}$) and 300-314 nm (33333-31847 cm⁻¹) for ($H_{\rm k}L^{1-4}$) which is attributed to the electronic transition within the chromone ring. On

	H_2L^1	μ eff.	H ₃ L ²	μ eff.	H ₃ L ³	μ eff.	H ₄ L ⁴	μ eff.
	$v (cm^{-1})$	B.M.	$v(cm^{-1})$	B.M.	$v (cm^{-1})$	B.M.	v(cm ⁻¹)	B.M.
	32786,		33333,		32258		31847	
	26315		28368		28392		22222	
Mn	22296	5.93 tet	18611	5.84 tet	22222	5.4 tet	23809	5.15 tet
Fe	24582	0.00 oct	-	-	24509	0.00 oct	-	-
Co	-	-	20898	2.45 sq	22691	2.60 sq	14900	3.60 tet
Ni	22815	0.00 sq	21113	0.00 sq	21739	0.00 sq	21796	0.00 sq
Cu	22784	1.81 sq	19459	1.86 sq	22893	1.87 sq	22614	1.46 sq
Zn	24015	0.00 tet	19257	0.00 tet	22431	0.00 tet	21326	0.00 tet
Pd	22614	0.00 sq	19853	0.00 sq	22002	0.00 sq	22614	0.00 sq

Table III. Electronic Bands and Magnetic Moments of the Metal Chelates of 8-

Table IV. Electronic Bands and Magnetic Moments of the Metal Chelates of 8-(Arylazo)-5,7-dihydroxy-6-formyl-2-methylchromones (H_kL⁵⁻⁸).

				-				
	H ₂ L ⁵	μeff.	H ₃ L ⁶	μeff.	H_3L^7	μ eff.	H_4L^8	μ eff.
	v (cm ⁻¹)	B.M.	v (cm ⁻¹)	B.M.	v (cm ⁻¹)	B.M.	v (cm ⁻¹)	B.M.
Mn	22075	5.88 tet	18832	5.85 tet	22431	5.22 tet	22568	5.79 tet
Fe	-	-	22356	0.00 oct	22386	0.00 oct	-	-
Co	-	-	21326	2.27 sq	22675	2.45 sq	-	-
Ni	22537	0.00 sq	-	-	22075	0.00 sq	22614	0.00 sq
Cu	22371	1.52sq	19379	1.43 sq	22492	1.80 sq	22583	1.49 sq
Zn	-	-	19689	0.00 tet	-	-	22462	0.00 tet
Pd	21987	0.00sq	19948	0.00 sq	22076	0.00 sq	21958	0.00 sq

the other hand, the bands at 352-450 nm (28392-22222 cm⁻¹) may be due to the $\pi - \pi^*$ transition of the azo moiety influenced by intramolecular charge transfer within the ligand molecules.

The electronic spectra of the chelates $Co(II)-H_{k-1}L^{1.3.6.7}$, Ni(II) with the ligands H_kL^{1-8} and Pd(II) with the ligands H_kL^{1-8} show bands in the 19948-22691 cm⁻¹ range

which can be assigned to the ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition and the Cu(II) chelates with ligands $H_{k}L^{1-8}$ exhibit bands in the 19379-22893 cm⁻¹ range corresponding to the ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transition. The intensity of the bands and the magnetic moment values support square- planar geometry for these chelates^{14, 15}.

The Mn(II) chelates with the ligands $H_k L^{1-8}$ and Zn(II) chelates with the ligands $H_k L^{1-4}$. ^{6,8} exhibit bands in the 18611-23809 cm⁻¹ range corresponding to the ${}^2A_1 \rightarrow {}^2T_1$ transition and the Co(II) chelate with ligand $H_4 L^4$ display a band at 14900 cm⁻¹ which is assigned to the 4A_2 (F) $\rightarrow {}^4T_1$ (P) transition, therefore, a tetrahedral structure is suggested for these chelates^{16, 17}.

The electronic spectra of the Fe(II) chelates with the ligands $H_k L^{1.6.7}$ display bands in the 22356-24582 cm⁻¹ range, this can be attributed to the ${}^{5}T_2g \rightarrow {}^{5}Eg$ transition. The high intensity of the bands and the diamagnetic nature support octahedral geometry for these chelates¹⁸.

Thermogravimetric Analysis

TG analyses were carried out for the chelates of $[Fe_2(HL^6)(OH)_2(H_2O)_6]$.3H₂O, $[Co_2(L^5)Cl_2(H_2O)_2]$.H₂O, $[Cu(H_2L^7)(OH)(H_2O)]$.H₂O, $[Zn(H_2L^7)(OH)(H_2O)]$.H₂O, $[Mn(HL^1)(OH)(H_2O)]$ and $[Cu_2(H_2L^4)Cl_2(H_2O)_2]$.5H₂O $[Fe_2(HL^6)(OH)_2(H_2O)_6]$.3H₂O. From the TG curves, the weight losses were calculated for the different steps and compared with those theoretically calculated for the suggested formulae based on the results of the elemental analyses in Table I. The first weight loss at a temperature up to 160° C is attributed to the loss of hydrated water molecules. Whereas, the second weight loss within the 160-250° C temperature range may be assigned to coordinated water molecules in the metal chelates.

For the 1:1 (M:Ligand) chelates of Cu(II) and Zn(II) with the ligand H_3L^7 and the 2:1 (M:Ligand) $[Co_2(L^5)Cl_2(H_2O)_2].H_2O$ chelate, the weight losses are about 4.40, 3.20 and 3.60%, respectively, and this can be attributed to the loss of one water molecule that is eliminated at a temperature up to 160 C. The weight losses of 9.20 and 11.60% for the 2:1 (M:Ligand) $[Fe_2(HL^6)(OH_2(H_2O)_6].3H_2O$ and $[Cu_2(H_2L^4)Cl_2(H_2O)_2].5H_2O$ chelates represent the removal of three and five water molecules, respectively, within the 140-160° C temperature range. On the other hand, the weight losses for the $[Cu(H_2L^7)(OH)(H_2O)].H_2O$, $[Zn(H_2L^7)(OH)(H_2O)].H_2O$, and $[Mn(HL^1)(OH)(H_2O)]$

chelates amounting to 4.00, 3.50, and 5.00%, respectively, may be assigned to the removal of one coordinated water molecule within the 150-250° C temperature range. Moreover, the weight losses in case of the $[Co_2(L^5)Cl_2(H_2O)_2]$. H₂O and $[Cu_{2}(H_{2}L^{4})Cl_{2}(H_{2}O)_{2}].5H_{2}O$ chelates are 6.80 and 4.50%, respectively, due to two coordinated water molecules within the 150-250 C temperature range. The weight loss of the [Fe₂(HL⁶)(OH)₂(H₂O)₆].3H₂O chelate is 16.20%, corresponding to six coordinated water molecules in the temperature range 140-250° C. From TG curves, one can suggest the formation of the metal oxide as the end product at a temperature ranging from 500-1000° C. Also, the percentages of the metal oxide found experimentaly for $[Cu(H_{1}L^{7})(OH)(H_{2}O)]$, H₂O, $[Zn(H_{1}L^{7})(OH)(H_{2}O)]$, H₂O and $[Mn(HL^{1})(OH)(H_{2}O)]$ amounted to 18.00, 18.10 and 20.80%, respectively, and the corresponding calculated values are 17.39, 17.41 and 21.80%, respectively. The metal oxide percentages of the $[Co_2(L^5)Cl_2(H_2O)_2]$. H₂O, $[Fe_2(HL^6)(OH)_2(H_2O)_6]$. 3H₂O and $[Cu_2(H_2L^8)Cl_2(H_2O)_2]$ chelates were found to be 26.00, 24.00 and 34.80%, respectively, which are in good agreement with the calculated ones for the suggested formulas in Table V. The TG curve of the $[Cu_2(H_2L^4)Cl_2(H_2O)_2]$.5H₂O chelate shows that the residue is a mixture of As₂O₃ and metal oxide. The following equations may be suggested for the thermal decomposition of the 1:1 chelates with Mn, Cu and Zn (L = Ligand)

 $\begin{bmatrix} MH_{k-1}L(OH)(H_2O) \end{bmatrix} H_2O \xrightarrow{up \text{ to } 160^\circ \text{ C}} \begin{bmatrix} MH_{k-1}L(OH)H_2O \end{bmatrix} + H_2O$ $\begin{bmatrix} MH_{k-1}L(OH)H_2O \end{bmatrix} \xrightarrow{160-250^\circ \text{ C}} \begin{bmatrix} MH_{k-1}L(OH) \end{bmatrix} + H_2O$ $\begin{bmatrix} MH_{k-1}L(OH) \end{bmatrix} \xrightarrow{250-400^\circ \text{ C}} \text{ Unstable intermediate}$ $\xrightarrow{>400^\circ \text{ C}} \text{ Metal oxide (MnO_2, CuO and ZnO)}$

Whereas, for the 2:1 (M:Ligand) Fe, Co and Cu chelates, the following equations may be suggested:

$$[M_{2}H_{k-2}LX_{2}(H_{2}O)_{n}].yH_{2}O \xrightarrow{up to 160^{\circ}C} [M_{2}H_{k-2}LX_{2}(H_{2}O)_{n}] + yH_{2}O$$

$$[M_{2}H_{k-2}LX_{2}(H_{2}O)_{n}]. \xrightarrow{160-250^{\circ}C} [M_{2}H_{k-2}LX_{2}] + nH_{2}O$$

$$[M_{2}H_{k-2}LX_{2}] \xrightarrow{250-400^{\circ}C} Unstable intermediate$$
intermediate
$$\xrightarrow{>400^{\circ}C} Metal \text{ oxide } (Fe_{2}O_{3}, CoO \text{ and } CuO)$$

$$(X = OH, \text{ or } CI, n = 2 \text{ or } 6 \text{ and } y = 1, 3 \text{ or } 5)$$

Table V. Thermogravimetric An	alysis	Results of	f Metal Cl	ielates with {	8-(Aryla	izo)chrom	ones				
Chelate	M:L	Water of I	hydration	No. of H ₂ O	Temp	Wat	er of	No. of H ₂ O	Temp	Metal oxic	le residu
		weigh	it loss	molecules	dn (C)	coordi	ination	molecules	(°C)	%)	(9
		~~~~			to	wcigl	ht loss		up to		
						0`	~				
		Found	(Calcd)			Found	(Calcd)			Found	(Calcd)
[Co ₂ (L ⁵ )Cl ₂ (H ₂ O) ₂ ].H ₂ O	2:1	3.60	(3.18)		150	6.80	(6.37)	2	150-250	26.00	(26.54)
$[Fe_2(HL^6)(OH)_2(H_2O)_6].3H_2O$	2:1	9.20	(8.36)	m m	140	16.20	(16.72)	9	140-250	24.00	(24.76)
[Cu(H ₂ L ⁷ )(OH)(H ₂ O)].H ₂ O	1:1	4.40	(3.72)	-	150	4.00	(3.72)	1	150-210	18.00	(17.39)
$[Zn(H_2L^7)(OH)(H_2O)].H_2O$	1:1	3.20	(3.71)		150	3.50	(3.71)	1	150-250	18.10	(17.49)
[Mn(HL ¹ )(OH)(H ₂ O)]	1:1	1		1	1	5.00	(4.51)	1	150-250	20.80	(21.80)
$[Cu_2(H_2L^4)Cl_2(H_2O)_2].5H_2O$	2:1	11.60	(11.90)	s.	160	4.50	(4.76)	2	160-250	34.80	(34.12)

do/onohe V / 0 dtie tol Chalate f NA. 1 ρ . Ē 11 -Ĥ

^a L = ligand



Fig. 2. Suggested Structure of the 1:1 Complexes of Fe(II) lons with the ligands  $H_2L^1$ and  $H_3L^7$  (X = H, Y = CH₃) and (X = COOH, Y = CHO), respectively.



Fig. 3. Suggested Structures of the Chelates of the Metal Ions Co(II), Ni(II), Cu(II) and Pd(II) with the ligands H₄L^{1-3, 5-8}.



M = Mn or Zn, X = H, OH or AsO(OH)₂, Y = CHO M = Mn or Zn, X = H, OH or COOH, Y = CH₃

Fig. 4. Suggested Structures of the Mn(II) and Zn (II) Chelates with  $H_{t}L^{1-3, 5, 6, 8}$ 



Fig. 5. Suggested Structural Formula of the Binuclear Complex of Fe₂-HL⁶.

#### **Geometrical Structures of the Metal Chelates**

It is suggested, based on the elemental analysis data, thermogravimetric analysis, spectral data and magnetic moment measurements of the metal chelates of 8-(arylazo)chromones ( $H_k L^{1-8}$ ) that the geometrical structures of these chelates are as illustrated below.



- Z = OH or Cl
- $M = Ni, X = COOH \text{ or } AsO(OH)_2$
- M = Co, X = H or OH
- $M = Cu, X = H, OH \text{ or } AsO(OH)_2$

Z = OH or Cl  $M = Ni \text{ and } Cu, X = AsO(OH)_2$  $M = Pd, X = H \text{ or } AsO(OH)_2$ 



Z = OH or CI, M = Co or Pd

Fig. 6. Suggested Structural Formula of the  $Co_2-H_{k,2}L^{5, 6}$ ,  $Ni_2-H_{k,2}L^{7, 8}$ ,  $Cu_2-H_{k,2}L^{5, 6, 8}$ ,  $Co_2-HL^3$ ,  $Ni_2-H_2L^4$ ,  $Cu_2-H_2L^4$  and  $Pd_2-H_{k,2}L^{1, 3, 4}$  Chelates.



 $Y = CH_3$  or CHO; M = Mn, Co and Zn,  $X = AsO(OH)_2$ ; Z = OH or Cl Fig. 7. Suggested Structure of the Mn(II), Co(II) and Zn(II) Chelates with  $H_kL^{3.4.7}$ .

The electronic spectral data and magnetic moment values of the 1:1 (M:Ligand) Fe(II) chelates with  $H_3L^7$  and  $H_2L^1$  show an octahedral geometry e.g., Fig. 2.

The stereochemistry, electronic spectral and magnetic data of the Co(II), Ni(II), Cu(II), and Pd(II) with the ligands  $H_k L^{1-3, 5-8}$  are in good agreement with a square planar structure e.g., Fig. 3

A tetrahedral configuration structure [see Fig. 4] was suggested for Mn(II) and Zn(II) chelates with  $H_{\nu}L^{1-3, 5, 6, 8}$  based on their electronic spectra.

The electronic spectrum of the binuclear chelate of  $Fe_2$ -HL⁶ shows an octahedral geometry, Fig. 5.

The electronic spectral data of the  $\text{Co}_2\text{-H}_{k-2}\text{L}^{5.6}$ ,  $\text{Ni}_2\text{-H}_{k-2}\text{L}^{7.8}$ ,  $\text{Cu}_2\text{-H}_{k-2}\text{L}^{5.6.8}$ ,  $\text{Co}_2\text{-HL}^3$ ,  $\text{Ni}_2\text{-HL}^4$ ,  $\text{Cu}_2\text{-H}_2\text{L}^4$  and  $\text{Pd}_2\text{-H}_{k-2}\text{L}^{1.3.4}$  chelates show the squarc-planar configuration e.g. Fig. 6.

The electronic spectral data of the divalent Mn, Co and Zn chelates with  $H_3L^7$  and  $H_kL^{3-4}$  exhibit tetrahedral structure e.g., Fig. 7.

The most important conclusions drawn from this investigation is that the monobasic bidentate ligands are coordinated to the metal ion through the chromone carbonyl at position 4 and the oxygen anion in position five in the 1:1 chelates of the 8-(arylazo)chromones ( $H_k L^{1-8}$ ). In the binuclear chelates, the ligands behave as dibasic tetradentates and chelate to the metal ions through the chromone carbonyl in position

four and oxygen anion in position five (see Figs.1-7). In addition, chelation may take place at the formyl carbon in position six and the oxygen anion in position seven or through the azo group and any acidic substituent positioned <u>ortho</u> to it in the arylazo moiety. Finally, chelation could also occur through the azo group and oxygen anion in position seven.

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Referee I: J. W. Owens Referee II: P. R. Singh