



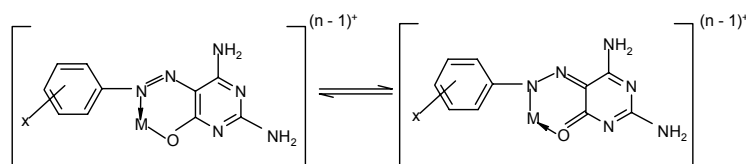
## COMPLEXES OF Cu(II), Co(II), Ni(II), Zn(II), Zr(IV), Ce(III), La(III) AND UO<sub>2</sub>(II) WITH ARYLAZO PYRIMIDINE DERIVATIVES

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Chelating behaviour of arylazo-2,6-diamino-4-pyrimidinol derivatives with Cu(II), Co(II), Ni(II), Zn(II), Zr(IV), Ce(III), La(III) and UO<sub>2</sub>(II) have been prepared and characterized on the basis of microanalysis, IR, <sup>1</sup>HNMR spectra. The analysis data indicate that the ligand acts as bidentate or tridentate mono-dibasic on chelation. IR, mass spectra and thermogravimetric analysis confirm the presence of coordinates water. The activation energy from the best fit line (TGA) and the enthalpy (DTA) are calculated. The 1:1 and 1:2 (M:L) ratios are suggested on the basis of spectrophotometric and conductometric data. It is concluded that the ligand L7 can act, as binuclear complexes 2:1 (M:L) species. The (M:L) complexes showed octahedral geometry.



### INTRODUCTION

The coordination chemistry of arylazo pyrimidine has attracted much attention in the recent years. The interest in this family of compounds arises from their potential biological activity<sup>1-6</sup> and capability to afford polynuclear metal complexes exhibiting a diversity of magnetic behaviour.<sup>7-18</sup> These ligands, in addition to having many potential coordination (donor) sites, can also exhibit tautomerism. Each tautomeric form may function as uni, bi- or tridentate ligand. Also, they can form a bridge between two metal atoms. The present work is aimed to study the coordination behaviour of the arylazo pyrimidine derivatives toward the metal ions. The aim of the present work therefore is to prepare and characterize the

complexes of some new arylazo-2,6-diamino-4-pyrimidine with Cu(II), Co(II), Ni(II), Zn(II), Zr(IV), Ce(III), La(III) and UO<sub>2</sub>(II) ions. The study involves characterization of these chelates by analytical, conductance, and electronic, IR, <sup>1</sup>H NMR spectral studies.

### RESULTS AND DISCUSSION

The recorded electronic absorption spectra of azo compounds (L1-L8) (Fig. 1) in pure ethanol exhibits mainly two bands located in the regions 207-210 nm and 221-250 nm can be attributed to the localization of  $\pi$ - $\pi^*$  electrons in pyrimidine ring and in the benzene ring. The third weak observed at 269-279 nm can be assigned to the

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excitation of the non-bonding electrons from the lone pair of a nitrogen atom to an  $\pi^*$  orbital of the ring.<sup>19</sup> In the visible region, the recorded spectra in ethanol show two broad bands within the range 321-382 nm and 404-449 nm (expected in case of L7,  $x = p\text{-NO}_2$  and L8,  $x = \text{-H}$ ). Thus, it can be suggested that these two bands are due to  $\pi\text{-}\pi^*$  transitions, *i.e.* intramolecular (CT) transitions.<sup>20</sup> This behavior can be explained by the fact that these compounds exist in hydroxyazo-quinoid hydrazone tautomeric equilibrium.<sup>21,22</sup> On comparing this band position with those of the chelated ligands (Figs. 2- 6) it is clear that the addition of the metal ion solution to the ligand solution causes a large red shift on complexation with the metal ions in the ranges Cu(II) 471-577

nm, Co(II) 421-607nm, Ni(II) 422-525 nm, Zn(II) 407-553, Zr(IV) 422-600 nm, Ce(III)421-602 nm, La(III) 408-610 nm and  $\text{UO}_2(\text{II})$  422-604 nm. On increasing the concentration of metal ion, the same band is still appearing in the spectra of binuclear (2M:L) complexes, but shows a more intense red shift. The observed red shift in the complex ligand can be ascribed to the expected easier intramolecular  $\text{L} \rightarrow \text{M}^{n+}$  CT interaction as a result of high positive charge of the coordinated metal ion relative to that in the free ligand. Careful examination of the  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values cited in Table 1. This may be attributed to the possible existence of the same complex in azo-hydrazone tautomeric equilibrium in solution as represented schematically by the following forms:

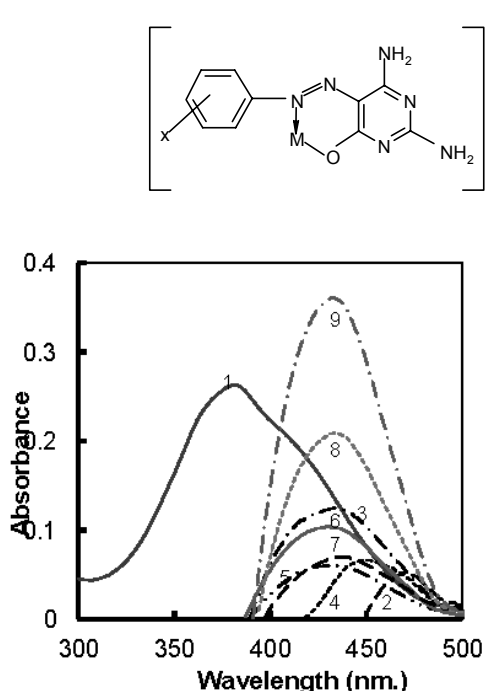


Fig. 1 – Electronic absorption spectra of  $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  of 5-( $x$ -arylo)-2,6-diamino-4-pyrimidinol in ethanol,  $x = p\text{-OH}$  (1);  $p\text{-HSO}_3$  (2);  $o\text{-COOH}$  (3); naphthyl (6);  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of compound,  $x = o\text{-CH}_3$  (4);  $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of compound,  $x = p\text{-N}(\text{C}_2\text{H}_5)_2$  (5) and  $2.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  of compounds,  $x = p\text{-NO}_2$  (7);  $\text{-H}$  (8).

The Cu(II), Co(II) and Ni(II) complexes of all ligands are characterized by high red shift in CT compared to the other complexes, indicating that  $\text{M}^{2+} \dots \text{N}$  bond are ionic.<sup>23</sup> The results reveal that the  $\lambda_{\text{max}}$  of  $o\text{-COOH}$  azo compounds of azo pyrimidine (in the case of Co(II), Zn(II) and Zr(IV)) is higher than that of the  $p\text{-OH}$  azo derivatives.<sup>24</sup> This indicates that the  $o\text{-COOH}$  group is involved in

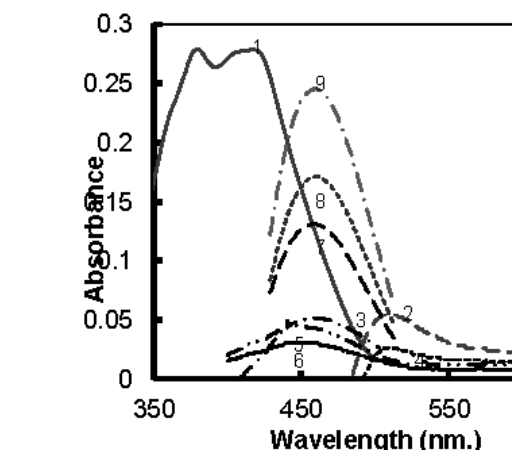
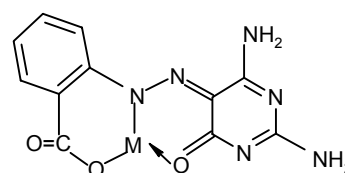


Fig. 2 – Electronic absorption spectra of  $2.5 \times 10^{-5}$  M solutions of  $\text{L}_1$ -complexes, (1) Free  $\text{L}_1$  ( $x = p\text{-OH}$ ) with  $2.0 \times 10^{-4}$  M of (2) Cu(II), (3) Co(II), (7) Ce(III);  $4.0 \times 10^{-4}$  M of (4) Ni(II);  $1.5 \times 10^{-4}$  M of (5) Zn(II);  $0.75 \times 10^{-4}$  M of (6) Zr(IV) and  $1.0 \times 10^{-4}$  M of (8) La(III), (9)  $\text{UO}_2(\text{II})$  in 1:1 ratio, using the same concentration of  $\text{L}_1$  as blank.

chelation giving rise to a bicyclic five-six member ring formation as represented below:



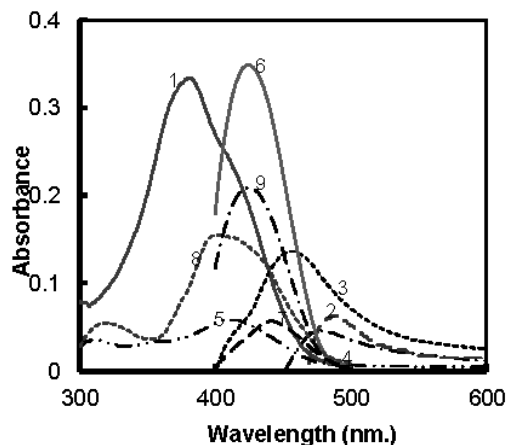


Fig. 3 – Electronic absorption spectra of  $2.5 \times 10^{-5}$  M solutions of  $L_2$ -complexes, (1) Free  $L_2$  ( $x = p\text{-HSO}_3$ ) with  $1.0 \times 10^{-4}$  M of (2) Cu(II), (5) Zn(II), (6) Zr(IV), (8) La(III), (9)  $\text{UO}_2(\text{II})$  and  $2.0 \times 10^{-4}$  M of (3) Co(II), (4) Ni(II), (7) Ce(III) in 1:1 ratio, using the same concentration of  $L_1$  as blank.

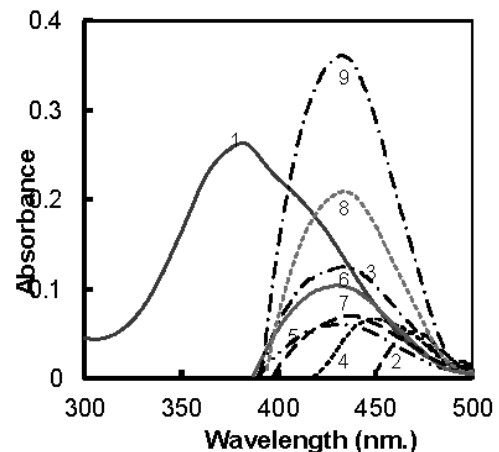


Fig. 4 – Electronic absorption spectra of  $5.0 \times 10^{-5}$  M solutions of  $L_4$ -complexes, (1) Free  $L_4$  ( $x = o\text{-CH}_3$ ) with  $2.0 \times 10^{-4}$  M of (2) Cu(II), (3) Co(II);  $2.5 \times 10^{-4}$  M of (4) Ni(II);  $1.0 \times 10^{-4}$  M of (5) Zn(II), (7) Ce(III), (8) La(III), (9)  $\text{UO}_2(\text{II})$  and  $5.0 \times 10^{-5}$  M of (6) Zr(IV) in 1 : 1 ratio, using the same concentration of  $L_4$  as blank.

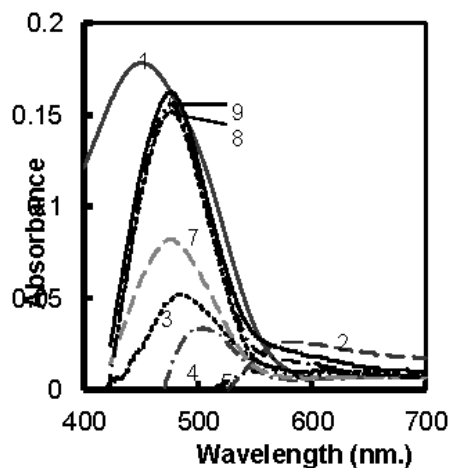


Fig. 5 – Electronic absorption spectra of  $1.0 \times 10^{-5}$  M solutions of  $L_6$ -complexes, (1) Free  $L_6$  ( $\text{Ar} = \text{naphthyl}$ ) with  $2.0 \times 10^{-4}$  M of (2) Cu(II), (3) Co(II), (4) Ni(II), (5) Zn(II) and  $1.0 \times 10^{-4}$  M of (6) Zr(IV), (7) Ce(III), (8) La(III), (9)  $\text{UO}_2(\text{II})$  in 1:1 ratio, using the same concentration of  $L_6$  as blank.

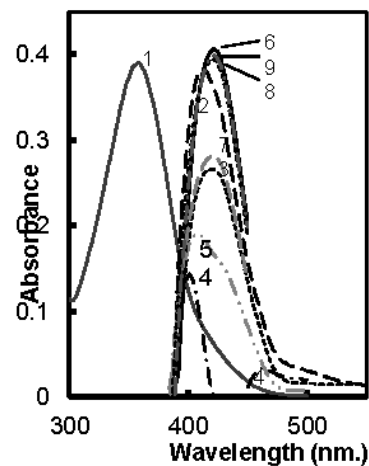


Fig. 6 – Electronic absorption spectra of  $6.25 \times 10^{-6}$  M solutions of  $L_8$ -complexes, (1) Free  $L_8$  ( $x = \text{-H}$ ) with  $2.0 \times 10^{-4}$  M of (2) Cu(II), (3) Co(II);  $4.0 \times 10^{-4}$  M of (4) Ni(II), (5) Zn(II) and  $1.0 \times 10^{-4}$  M of (6) Zr(IV), (7) Ce(III), (8) La(III), (9)  $\text{UO}_2(\text{II})$  in 1:1 ratio, using the same concentration of  $L_8$  as blank.

The formation of  $\text{M}^{2+} - \text{O}$  bond between the carboxylic oxygen and the metal ion increases ion-dipole interaction, because the  $\text{M}-\text{O}$  interaction results in increasing the polarity of the carboxylic oxygen atom. These presumably increase the ability of oxygen lone pair to enter the  $\pi$ -electron orbital of the system.<sup>25</sup>

This causes a displacement of CT band toward longer wavelength. It is clear from the obtained results (Table 1) that there is no correlation

between the  $\lambda_{\text{max}}$  values of the formed complexes and the basicity of substituents in the phenyl ring of the ligands. This may be attributed to some large size of groups which is produced from these substituents which make the pyrimidine moiety of the ligands deviate from planarity. Thus, the effect of molecule of bulky group over compensates the effect of increased basicity.<sup>26</sup>

The stoichiometry of the different metal complexes was determined by applying the

conventional spectrophotometric continuous variation methods,<sup>27,28</sup> using as blank, the same concentration of the ligand as in the test solution. Plots of absorbance values at fixed  $\lambda_{\max}$  of the formed complexes vs. the mole fraction  $C_L/C_M+C_L$  are shown in Figs. 7, 8. The obtained curves are characterized by two or three maxima. The maximum located at ligand mole fraction of 0.67 and 0.5 or 0.33 in all cases indicates the formation of 1:1 and 1:2 or 2:1 metal to ligand ratios. Moreover, the observed little increase in conductometric titration of Zr(IV) ion solution with all the ligands under study, Zn(II) ion solution with L<sub>3</sub>, L<sub>6</sub>, L<sub>7</sub> and L<sub>8</sub> can be attributed to the non liberation of hydrogen ions during complex formation. This behaviour clearly indicates that

molecules of the ligand and not their anions are coordinated to the metal ions. The data also show an increase in conductance values accompanied with the titration of Cu(II), Co(II), Ni(II), Ce(III), La(III) and UO<sub>2</sub>(II) solutions with all the ligands under study indicate liberation of high ionic mobil H<sup>+</sup> ions. The molar conductance values (Table 2) of the solid complexes in DMF solution ( $1 \times 10^{-5}$  mol dm<sup>-3</sup>) indicate that the metal chelates behave as 1:1 electrolytes. It is evident from the results that the molar conductance values of 1:1 complexes is in the range 2.48-6.8 mol<sup>-1</sup> cm<sup>2</sup>, which are commensurate with values characteristic for neutral complexes.<sup>29,30</sup> This reveals a non-electrolytic nature of the synthesized complexes.

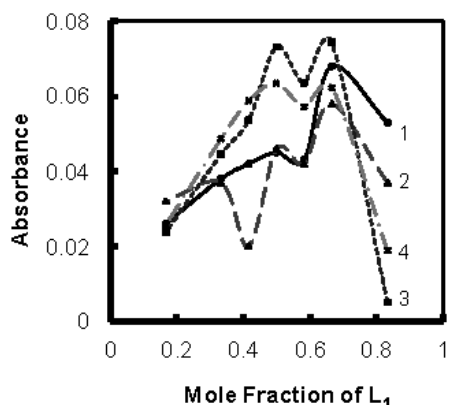


Fig. 7 – Continuous variation method for L<sub>1</sub>-M<sup>n+</sup> chelates: total concentration (L<sub>1</sub>-M<sup>n+</sup>) =  $2.4 \times 10^{-4}$  M of (1) Cu(II),  $\lambda = 509$  nm and  $2.4 \times 10^{-5}$  M, of (2) Co(II),  $\lambda = 459$  nm; (3) Zr(IV),  $\lambda = 446$  nm and (4) UO<sub>2</sub>(II),  $\lambda = 459$  nm.

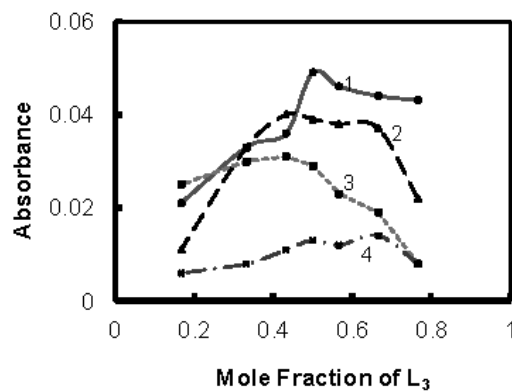


Fig. 8 – Continuous variation method for L<sub>3</sub>-M<sup>n+</sup> chelates: total concentration (L<sub>3</sub>-M<sup>n+</sup>) =  $3.0 \times 10^{-4}$  M, (1) Cu(II),  $\lambda = 496$  nm; (2) Co(II),  $\lambda = 492$  nm; (3) Zr(IV),  $\lambda = 493$  nm and (4) UO<sub>2</sub>(II),  $\lambda = 506$  nm.

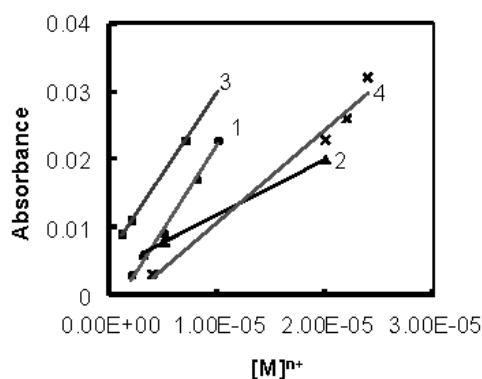


Fig. 9 – Validity of Beer's law of  $5 \times 10^{-5}$  M for L<sub>1</sub> (x = p-OH) with: (1) Cu(II),  $\lambda = 509$  nm; (2) Co(II),  $\lambda = 459$  nm; (3) Zr(IV),  $\lambda = 446$  nm and (4) UO<sub>2</sub>(II),  $\lambda = 459$  nm.

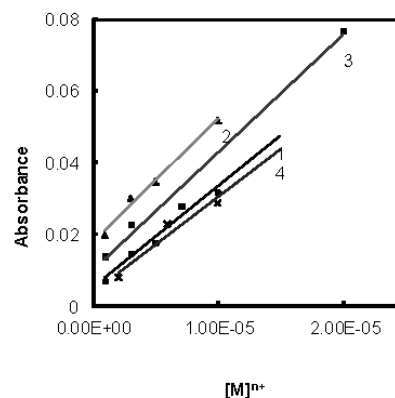


Fig. 10 – Validity of Beer's law of  $5 \times 10^{-5}$  M for L<sub>8</sub> (x = -H) with: (1) Cu(II),  $\lambda = 510$  nm; (2) Co(II),  $\lambda = 421$  nm; (3) Zr(IV),  $\lambda = 422$  nm and (4) UO<sub>2</sub>(II),  $\lambda = 422$  nm.

Table 1

Maximum wavelength ( $\lambda_{\max}$ , nm.) and extinction coefficient ( $\epsilon_{\max}$ ,  $10^3 \text{ mol}^{-1} \text{ cm}^2$ ) of the free ligands and their metal chelates

ligands	Free ligands		Cu(II)		Co(II)		Ni(II)		Zn(II)		Zr(IV)		Ce(III)		La(III)		UO <sub>2</sub> (II)	
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
L <sub>1</sub> (x = <i>p</i> -OH)	417	10.44	509	0.27	459	0.255	508	0.065	449	0.3	451	0.4	458	0.655	460	1.71	459	2.46
L <sub>2</sub> (x = <i>p</i> -HSO <sub>3</sub> )	382	3.44	487	0.63	456	0.815	478	0.23	410	0.59	425	3.49	440	0.285	408	1.55	425	2.09
L <sub>3</sub> (x = <i>o</i> -COOH)	412	376.0	496	0.07	492	0.105	495	0.105	486	0.025	493	0.055	439	0.125	435	0.215	496	0.02
L <sub>4</sub> (x = <i>o</i> -CH <sub>3</sub> )	381	10.52	471	0.261	434	0.625	449	0.264	430	0.605	429	2.08	438	0.7	434	2.09	433	3.61
L <sub>5</sub> (x = <i>p</i> -N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> )	445	6.575	554	0.615	515	0.495	514	0.295	500	0.31	533	0.99	552	0.85	548	1.015	555	1.04
L <sub>6</sub> (Ar = naphthyl)	449 –	48.1 –	– 577	– 0.13	484 607 <sub>sh</sub>	0.26 0.055	499 –	0.17 –	– 553	– 0.055	476 600 <sub>sh</sub>	1.63 0.18	475 602 <sub>sh</sub>	0.82 0.07	476 610 <sub>sh</sub>	1.52 0.1	477 604 <sub>sh</sub>	1.56 1.4
L <sub>7</sub> (x = <i>p</i> -NO <sub>2</sub> )	375	133.4	545	0.04	516	0.055	525	0.04	427	1.08	425	2.05	425	0.29	428	1.02	427	1.56
L <sub>8</sub> (x = -H)	359 –	97.12 –	422 510 <sub>sh</sub>	1.91 0.155	421 –	1.33 –	422 462	0.085 0.36	407 –	0.475 –	422 –	4.06 –	421 –	2.82 –	421 –	3.94 –	422 –	3.99 –

Table 2

Physical properties, analytical data, formula weight (F.W.) and molar conductance ( $\Lambda$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of the prepared complexes

Complexes	Color	m.p. (°C)	Found (Calcd.%)		N	M%	F.W.	$\Lambda_M$
			C	H			Found	
<b>M<sup>III</sup>-L<sub>1</sub> (x = p-OH)</b>								
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> ClCu.H <sub>2</sub> O]	GreenishYellow	279	36.12(36.76)	3.04(3.39)	25.11(25.72)	17.50	326.777	5.70
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> ClCo.H <sub>2</sub> O]	Deep Red	313	37.21(37.28)	3.08(3.44)	26.02(26.09)	16.50	322.170	6.07
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> ClNi.H <sub>2</sub> O]	ReddishBrown	316	36.59(37.31)	3.07(3.44)	26.35(26.10)	16.45	321.947	6.08
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> Cl <sub>3</sub> Zr].H <sub>2</sub> O	Red	313	26.10(24.21)	2.41(2.23)	16.23(16.94)	17.23	496.189	5.05
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> Ce].H <sub>2</sub> O	ReddishBrown	311	22.77(22.78)	2.12(2.10)	20.94(21.25)	26.60	527.368	3.76
[C <sub>10</sub> H <sub>9</sub> N <sub>6</sub> O <sub>2</sub> (CH <sub>3</sub> COO)UO <sub>2</sub> ].H <sub>2</sub> O	DeepYellow	321	24.31(24.33)	2.20(2.38)	14.16(14.19)	40.20	592.311	2.48
<b>M<sup>III</sup>-L<sub>3</sub> (x = o-COOH)</b>								
[C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub> Cu.2H <sub>2</sub> O]	Gray	303	35.54(35.54)	3.32(3.25)	22.64(22.60)	17.10	371.796	5.85
[C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub> Co.2H <sub>2</sub> O]	Brown	286	36.02(35.98)	3.22(3.29)	22.67(22.89)	16.08	367.189	6.23
[C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub> Ni.2H <sub>2</sub> O]	Brown	265	35.89(36.00)	3.25(3.30)	23.20(22.90)	16.02	366.966	6.25
[C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub> (NO <sub>3</sub> )Ce].3H <sub>2</sub> O	Orange	313	25.10(25.00)	2.44(2.47)	18.04(18.56)	32.99	528.397	3.77
[C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub> UO <sub>2</sub> ].3H <sub>2</sub> O	Orange	314	22.18(22.16)	2.22(2.37)	13.99(14.09)	38.68	596.301	2.50
<b>M<sup>III</sup>-L<sub>4</sub> (x = o-CH<sub>3</sub>)</b>								
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> OCICu.H <sub>2</sub> O]	Reddish Brown	305	36.68(36.67)	3.62(3.64)	23.40(23.33)	17.83	360.258	5.67
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> OCICo.H <sub>2</sub> O]	Brown	312	37.05(37.15)	3.66(3.68)	23.58(23.63)	16.58	355.651	6.03
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> O <sub>2</sub> ClNi.H <sub>2</sub> O]	Reddish Brown	281	37.16(35.57)	3.64(3.53)	23.61(22.63)	16.57	371.426	6.05
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> O <sub>2</sub> Cl <sub>3</sub> Zr].H <sub>2</sub> O	Deep Orange	286	27.80(27.82)	2.80(2.76)	17.37(17.70)	19.90	474.844	5.76
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> O(NO <sub>3</sub> ) <sub>2</sub> Ce].H <sub>2</sub> O	Orange	245	25.12(25.15)	2.46(2.49)	21.02(21.33)	26.72	525.396	3.75
[C <sub>11</sub> H <sub>11</sub> N <sub>6</sub> O(CH <sub>3</sub> COO)UO <sub>2</sub> ].H <sub>2</sub> O	Orange	317	26.31(26.45)	2.31(2.73)	14.30(14)	40.37	590.339	2.48

Table 3

Validity of Beer's law of ligands-chelates

System	$\lambda_{\max}$ (nm)	$\epsilon_{\max} \times 10^3$ ( $\text{mol}^{-1} \text{cm}^2$ )	$[\text{M}]^{n+}$ (ppm)
L <sub>1</sub> -Cu(II)	509	2.503	0.34
L <sub>1</sub> -Co(II)	459	0.794	0.71
L <sub>1</sub> -Zr(IV)	446	2.354	0.339
L <sub>1</sub> -UO <sub>2</sub> (II)	459	1.362	1.992
L <sub>3</sub> -Cu(II)	496	0.221	0.171
L <sub>3</sub> -Co(II)	492	0.789	0.71
L <sub>3</sub> -Zr(IV)	493	0.483	0.68
L <sub>3</sub> -UO <sub>2</sub> (II)	506	0.321	0.996
L <sub>7</sub> -Cu(II)	545	0.779	0.171
L <sub>7</sub> -Co(II)	516	0.401	0.71
L <sub>7</sub> -Zr(IV)	425	0.350	1.02
L <sub>7</sub> -UO <sub>2</sub> (II)	427	0.265	0.1
L <sub>8</sub> -Cu(II)	510	2.828	0.71
L <sub>8</sub> -Co(II)	421	0.512	2.38
L <sub>8</sub> -Zr(IV)	422	0.328	0.339
L <sub>8</sub> -UO <sub>2</sub> (II)	422	2.625	0.996

Table 4

Formation constants ( $K_f$ ,  $\text{L} \cdot \text{mol}^{-1}$ ) and free energy changes ( $\Delta G$  in  $\text{K cal mol}^{-1}$ ) for some complexes at 27°C

Ligands	Ratio M:L	Cu(II)		Co(II)		Zr(IV)		UO <sub>2</sub> (II)	
		$\log K_f$	$-\Delta G$	$\log K_f$	$-\Delta G$	$\log K_f$	$-\Delta G$	$\log K_f$	$-\Delta G$
L <sub>1</sub> (x = <i>p</i> -OH)	2:1	—	—	8.42	11.437	10.6	14.65	—	—
	1:1	6.38	8.81	5.67	7.83	5.86	8.1	5.42	8.43
	1:2	11.76	16.25	9.68	13.37	10.54	14.558	10.38	14.34
L <sub>3</sub> (x = <i>o</i> -COOH)	1:1	5.92	8.18	5.18	7.16	4.5	6.22	5.11	7.06
	1:2	11.35	15.68	9.41	13.00	6.96	9.615	9.34	12.90
L <sub>7</sub> (x = <i>p</i> -NO <sub>2</sub> )	2:1	—	—	—	—	—	—	9.81	13.55
	1:1	5.86	8.10	5.11	7.06	5.35	7.394	5.08	7.02
	1:2	11.20	15.47	9.38	12.96	9.626	13.299	9.42	13.01
L <sub>8</sub> (x = -H)	1:1	6.07	8.39	5.22	7.21	4.277	5.908	5.39	7.45
	1:2	11.60	16.03	9.59	13.25	7.91	10.98	9.70	13.40

The possibility of applying the spectrophotometric method for micro-determination of Cu(II), Co(II), Zr(IV) and UO<sub>2</sub>(II) ions is examined. Values of the absorbance obtained at  $\lambda_{\max}$  are

plotted against the tested metal ion concentration. The plots give linear relationships passing through the origin as shown in Figs. 9, 10 and this suggests a perfect validity of Beer's law (Table 3). The  $K_f$

values for complexes of Cu(II), Co(II), Zr(IV) and UO<sub>2</sub>(II) metals with different ligands decrease according to the order L1 (x = p-OH) > L8 (x = -H) > L7 (x = p-NO<sub>2</sub>) in accordance with the decreasing of the electron releasing character of the substituent in the same direction which results in the decrease in the basicity of the nitrogen atom of the ligand hydrazo group and consequently decrease of the tendency toward complexation<sup>31</sup> (Table 4). The K<sub>f</sub> values of the Cu(II) complexes are higher than those of Co(II) complexes and the K<sub>f</sub> values of Zr(IV) complexes are higher than those of UO<sub>2</sub>(II) complexes.<sup>32</sup> The K<sub>f</sub> values of L<sub>3</sub> (x = o-COOH) complexes are in general higher than those of L<sub>8</sub> (x=H) complexes. This is in line with the fact that the ligand L<sub>3</sub> can coordinate in a tridentate fashion through the nitrogen atom of the azo group, oxygen atom of the COOH group and either N(6) or O(6) exocyclic atom of pyrimidine ring, this leads to the stable formation of two six member chelated rings.<sup>33</sup>

The infrared spectral data also provide some significant results which support the proposed formula of each complex (Tables 5, 6). The vibration spectra of the free ligands exhibit broad band at around 3450 cm<sup>-1</sup> due to the ν<sub>OH</sub> and two sharp and at least of medium intensity bands in the region 3290-3035 cm<sup>-1</sup> assigned to the ν<sub>NH<sub>2</sub></sub> stretching vibration of C(2)-, C(4)-NH<sub>2</sub> of the pyrimidine ring. These bands can be attributed to the possible formation of intramolecular H-bond between the pyrimidine OH or NH<sub>2</sub> groups and the azo group.<sup>34</sup> One of the vibration modes of ν<sub>NH<sub>2</sub></sub> is absent while the other one is blue shifted in Cu(II) complexes or still remained in the same position in case of Ni(II) and Co(II) complexes. These data indicate that both nitrogen (amino) and oxygen (OH) atoms are active sites for complexation. Previous studies on similar compounds have revealed that the coordination through the exocyclic oxygen is preferable than the NH<sub>2</sub> group.<sup>35,36</sup> On the other hand, the strong bands

observed in complexes around 3300 cm<sup>-1</sup> weak with shoulder at ~3750 which have significantly different characteristics from the H-bonded ν<sub>N-OH</sub> vibrations. These bands are attributed to the presence of water molecules in the complexes prepared. Since, it was known that the free water absorb at 3520 cm<sup>-1</sup>.<sup>37</sup> One can suggest that water molecules in the prepared complexes are analyzed or exist as molecules of crystallization. Weak and medium bands at 3150 and 2840 cm<sup>-1</sup> region can be assigned to the ν<sub>NH</sub> stretching modes. The presence of these band suggests that the pyrimidine hetero-N atom at N(1) and N(3) may be protonated or due to the H-bonded NH of amino groups. This is based on the possible migration of proton from OH and NH<sub>2</sub> groups to the adjacent hetero nitrogen atom. This behaviour suggests that the studies compound can exist in keto-enol tautomeric equilibrium.<sup>38</sup> On complexation the ν<sub>C=N</sub> at 1610 and 1550 cm<sup>-1</sup> and ν<sub>C-N</sub> stretching vibrations at 1270 cm<sup>-1</sup> show lower shift which supports the involvement of NH<sub>2</sub> in chelate ring.<sup>39,40</sup> The observed blue shift in these bands may be due to the decrease of the bond order of carbon to the nitrogen link following the coordination of the imine nitrogen atom to metal ions. The observed shift of the ligand L<sub>3</sub> (x = o-COOH) bands at 2340 (ν<sub>OH</sub>), ν<sub>C-O</sub> (1276 cm<sup>-1</sup>), ν<sub>as</sub> (1320 cm<sup>-1</sup>), ν<sub>C-OH</sub> (1252 cm<sup>-1</sup>), γ<sub>OH</sub> (850 cm<sup>-1</sup>), γ<sub>O-C=O</sub> (680 cm<sup>-1</sup>) and γ<sub>C=O</sub> (620 cm<sup>-1</sup>) confirms the involvement of oxygen atom of o-COOH group in chelation.<sup>41</sup> The ligand (L<sub>3</sub>) acts in a tridentate fashion through the N(8) atom of the N=N group, O atom of COOH group and the exocyclic N(6) atom of the pyrimidine ring. This behaviour results in the formation of two six membered rings having in common M-N(8) bond.<sup>42,43</sup> The planarity of phenyl and pyrimidine rings enhanced the involvement of OH of the o-CO<sub>2</sub>H group in chelation. The structure of the L<sub>3</sub> chelates is suggested as follows:

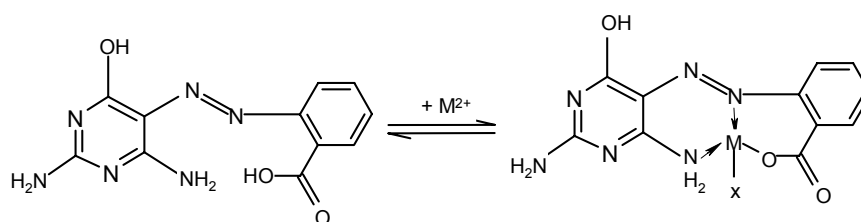




Table 5

Fundamental infrared and far infrared bands ( $\text{cm}^{-1}$ ) of L1 (x = p-OH) and Its (1:1) chelates

Ligand	Complexes						Assignments
	Cu(II)	Co(II)	Ni(II)	Zr(IV)	Ce(III)	UO <sub>2</sub> (II)	
–	3751.8 w	3751.9 w	3751.8 w	3751.4 w,sh	3752.9 w	3751.6 w	$\nu$ (OH), $\nu$ (H <sub>2</sub> O) stretching
–	–	3673.9 w	–	3675.9 w	3677.4 w	–	$\nu$ (OH), $\nu$ (NH) stretching
3450.7 b	3418.9 s,b	3391.8 s,b	3368.7 s,b	3363.9 s,b	3381.7 s,b	3394.4 s,b	$\nu$ (OH), $\nu$ (NH), $\nu$ (NH <sub>2</sub> ) stretching
3232.6 m,b	–	3130.7 m	3160.0 m	3171.2 s,b	–	–	$\nu$ (NH <sub>2</sub> ), $\nu$ (NH) stretching
–	–	–	–	–	2434.4 w	2431.8 m	$\nu$ (NH) stretching
–	–	–	2132.6 w,b	–	2278.5 vw	–	$\nu$ (C=N) stretching
1622.8 vvs	1601.2 vs,sh	–	1600.5 s,sh	1597.5 vs,sh	1597.0 s,sh	1599.0 s,sh	$\delta$ NH stretching
1535.5 s	–	–	1544.1 sh	1561.0 s,sh	–	–	$\nu$ (C=N) stretching
1495.5 vvs	–	–	1452.9 s,b	–	1452.3 s	–	$\nu$ (C=C), $\nu_{as}$ (N=N), $\nu$ (C=N)
1329.0 s	–	1320.2 vs	–	–	–	1334.1 m	$\nu$ (C–N), $\delta$ (CCN), $\nu$ (CN)
1253.3 vs	1253.3 vs	–	1259.9 m	1256.2 m,sh	–	1271.4 m,b	$\nu$ (C–OH) stretching
–	–	–	1100.9 w	1111.8 w,sh	–	–	$\nu$ (CO), $\nu$ (CN)
910.1 m	880.6 m,sh	–	–	881.4 m,sh	–	–	$\nu$ (N–H), $\nu$ (NH <sub>2</sub> )
–	842.0 s,sh	851.1 m,sh	841.4 m,sh	838.1 m,sh	835.4 m,sh	834.8 s,sh	$\nu$ (H <sub>2</sub> O) stretching
–	628.8 s,b	–	666.7 m,b	659.0 m,b	661.7 w	676.0 w	$\delta$ (NCC), $\delta$ (CCN), $\gamma$ (C=O)
–	500.0 w	515.4 w	530.4 w	537.5 m	524.8 vw	533.7 w	$\nu$ (MO) stretching
–	458.1 w	430.5 w	412.6 w	425.5 w	418.6 w	416.3 w	$\nu$ (MN)
–	–	–	–	–	391.9 m	–	$\nu$ (M–N=N)
–	–	–	–	377.3 s	376.4 s	377.4 m	$\nu$ (MO) + $\delta$ (COM)
–	368.3 vw	365.5 vw	367.9 vw	365.9 m	363.7 m	363.6 s	$\nu$ (MO) + $\delta$ (CN <sub>a</sub> N) + $\delta$ (CCN <sub>a</sub> )
357.2 vs	–	–	–	350.7 m	–	353.8 m	$\nu$ (MO) + $\delta$ (CN <sub>a</sub> N) + $\delta$ (CNN <sub>a</sub> ) + $\delta$ (CCN <sub>a</sub> )
333.9 m	–	–	339.9 s	334.4 m	336.8 w	336.3 vw	$\nu$ (MO) + $\delta$ (CNN <sub>a</sub> ) + $\delta$ (CCO)
314.8 vs	318.8 m	–	317.8 w	321.4w	314.5 m	313.1 m	$\nu$ (MO) + $\delta$ (CCO) + $\delta$ (CNN <sub>a</sub> )
–	–	306.9 m	–	–	–	–	$\nu$ (MO) + $\delta$ (CCO) + $\delta$ (CNN <sub>a</sub> )
–	282.8 m	–	288.1 m	293.6 m	292.0 m	296.8 m	$\nu$ (MO)
–	–	–	–	275.3 w	276.9 w	278.8 w	$\nu$ (MO)
–	264.7 w	–	–	–	261.7 m	270.0 w	$\nu$ (MO)
253.6 m	–	257.8 m	254.9 w	257.9 m	–	258.2 m	$\nu$ (MO)
–	–	–	–	248.4 w	246.6 m	245.7 w	$\delta$ (NMN) + $\nu$ (MN) + $\nu$ (MO) + $\delta$ (COM)
238.9 m	–	–	–	–	–	233.6 m	$\nu$ (MN) + $\delta$ (COM) + $\nu$ (MO)
225.5 m	–	–	–	225.3 w	222.8 m	221.4 w	$\nu$ (MO) + $\nu$ (MN <sub>a</sub> ) + $\delta$ (CNNC)
–	210.2 m	218.5 m	–	217.2 w	–	–	$\nu$ (MN <sub>a</sub> ) + $\nu$ (MO) + $\delta$ (CNNC) + $\delta$ (OMN)
–	–	–	–	204.6 vw	203.3 m	203.0 w	$\delta$ (NMO) + $\delta$ (NMN)

vs = very strong; s = strong; m = medium; w = weak; b = broad.

Table 6

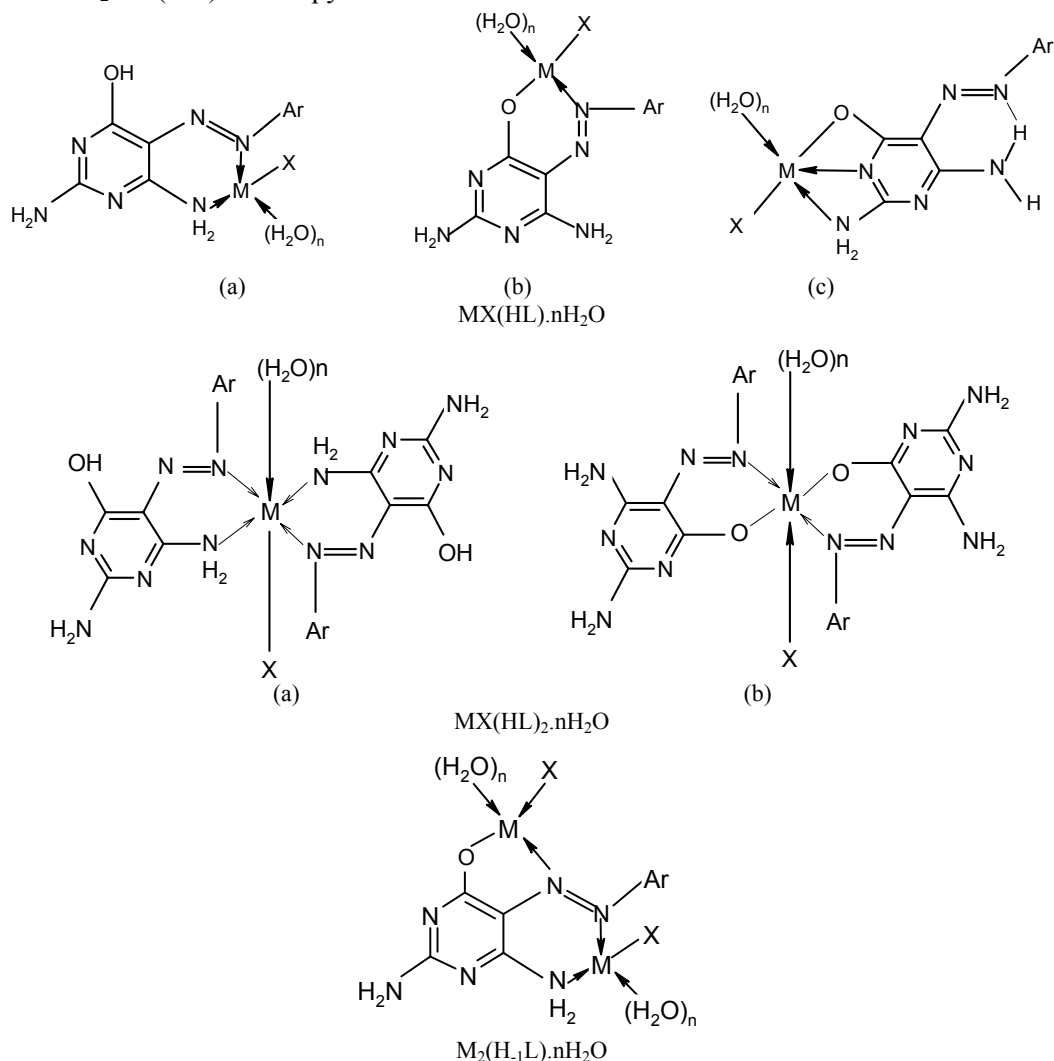
Fundamental infrared and far infrared bands ( $\text{cm}^{-1}$ ) of L3 ( $x = \text{o-COOH}$ ) and its (1:1) chelates

Ligand	Complexes Cu(II)	Co(II)	Ni(II)	Zr(IV)	Ce(III)	UO <sub>2</sub> (II)	Assignments
–	–	3708.5 vw	–	–	–	–	v (OH), v (H <sub>2</sub> O) stretching
3653.0 w	3674.5 vw	–	3674.9 vw	3672.1 vw	–	–	v (OH), v (NH) stretching
3460.6 b	–	3419.4 vs,b	–	3417.2 vs,b	3420.0 vs,b	3442.8 vs,b	v (OH), v (NH), v (NH <sub>2</sub> ) stretching
3311.6 s,b	3337.9 s,b	–	3318.7 s,b	–	–	–	v (NH <sub>2</sub> ), v (NH) stretching
3161.5 s,b	3037.0 s,b	–	–	3136.6 b	–	–	v (NH) stretching
2340.4 w	2341.3 m,sh	2340.0 w,sh	2341.2 m,sh	2350.9 s,b	2350.0s,b	2341.1 w,sh	v (COOH) stretching
–	–	2195.3 w,b	–	–	2125.0 m,b	–	v (C=N) stretching
1655.3 vs	1624.4 s,sh	–	1632.5 s,sh	1652.0 s,sh	1638.1 vs,b	1639.2 s,b	$\delta$ (NH), v (NH <sub>2</sub> ) stretching
1595.9 vs	–	1595.4 s,sh	–	1588.5 s,sh	–	1588.2 s,sh	v (C=N), (ring stretching)
1558.0 vs	1545.1 vs,b	1556.7 vs,b	1539.3 vs,sh	–	1543.1 s,sh	–	v (C=N) stretching
1498.9 vs	–	1453.8 s,sh	–	–	–	–	v (C=C), v <sub>as</sub> (N=N)
–	–	–	1402.1 s,sh	1405.4 s,sh	1398.2 vs,b	–	v <sub>as</sub> (N=N)
1320.2 vs	1363.8 vs,b	1387.8 vs,b	1364.4 vs,sh	1359.5 s,sh	–	1382.3 vs,sh	v (C–N), v (COOH)
1276.6 w	–	–	–	–	–	–	v (C–O) stretching
1252.1 vs	1239.0 s,sh	–	1243.6 m,sh	1252.7 m,sh	–	–	v (C–OH) stretching
1147.3 w	1151.0 s,sh	1148.7 m,b	1150.7 m,b	1181.8 m,sh	1149.6 m,sh	1185.6 m,sh	v (CN), $\gamma$ (C=C), v (CCC)
1081.5 m	1109.0 s,sh	–	1089.6 m,sh	1092.2 w,sh	–	1085.7 w,sh	v (CO), v (CN)
886.9 s	–	–	–	885.1 w,sh	888.1 w,sh	904.2 m,sh	v (N–H), v (NH <sub>2</sub> )
–	827.2 w,sh	–	818.4 m,sh	845.7 m,sh	826.0 m,sh	–	v (H <sub>2</sub> O) stretching
682.8 m	699.3 m,sh	–	698.3 m,sh	692.5 m,sh	690.6 m,sh	691.5 w,sh	$\gamma$ O–C=O
621.8 m	635.9 w,sh	646.0 m,sh	634.2 m,sh	–	614.6 m,sh	–	$\delta$ (NCC), $\delta$ (CCN), v (C=O)
–	541.7 m,sh	541.5 m,sh	539.6 m,sh	551.0 m,sh	538.2 m,sh	533.6 m,sh	v (MO) stretching
–	410.9 vw	414.0 vw	412.3 vw	419.1 m,sh	416.3 m,sh	405.1 w,sh	v (MN)
–	–	394.1 m	–	–	391.8 m	–	v (MO)
–	382.5m,b	382.0 m	382.1 m	379.2m	379.5m	380.3 m	v (M–N=N)
–	–	360.8 m	365.6 m	366.9 m	364.6 m	363.2 m	v (MO) + $\delta$ (CN <sub>a</sub> N) + $\delta$ (CCN <sub>a</sub> )
–	–	–	–	–	353.5 s	353.1 s	v (MO) + $\delta$ (CN <sub>a</sub> N) + $\delta$ (CNN <sub>a</sub> ) + $\delta$ (CCN <sub>a</sub> )
340.0 m	342.2 m,b	–	–	–	–	–	v (MO)
–	–	336.8 m	336.1 vw	336.3 w	336.1 m	336.7 w	v (MO) + $\delta$ (CNN <sub>a</sub> ) + $\delta$ (CCO)

The medium hands located in the regions  $540-500\text{ cm}^{-1}$  and  $443-416\text{ cm}^{-1}$  can be tentatively attributed to the  $\nu_{M-N}$  and  $\nu_{M-O}$  respectively.<sup>44,45</sup> The  $\delta_{M\leftarrow N=N}$  bending vibration appeared in the range  $400-370\text{ cm}^{-1}$ .

It is also suggested that the ligands can acts in a N,N or N,O bidentate manner through the N-(or OH) atom of  $\text{NH}_2$  or (OH) of the pyrimidine and

N(8)-atom of N=N groups. In Co(II) (M:L) complexes and in 2M:L, these ligands can also acts as N,N,N tridentate through the two nitrogen of  $\text{NH}_2$  and one hetero nitrogen atom of the pyrimidine ring. The structure of 1:1, 1:2 and 2:1 (M:L) chelates of Cu(II), Co(II) and Ni(II) can be represented schematically by the following forms:



The bands around  $1030\text{ cm}^{-1}$  observed in the spectra of Ce(III) complexes which may be assigned to the coordinated  $\text{NO}_3$  group to metal ion.<sup>46,47</sup> The  $\text{UO}_2(\text{II})$  complexes show strong bands at around  $910$  and  $805\text{ cm}^{-1}$  assignable to  $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$  ( $\text{O}=\text{U}=\text{O}$ ) modes respectively. This indicates that linearity of  $\text{O}=\text{U}=\text{O}$  is retained in complexes. Moreover, the two new bands located at around  $570-430\text{ cm}^{-1}$  can be attributed to  $\nu_{M-N}$  stretching mode.<sup>48,49</sup> It is noticed that the stretching frequency values of  $\nu_{M-N}$  follows the order  $\text{Zr(IV)} > \text{Ce(III)} > \text{UO}_2(\text{II})$ .<sup>50</sup> The change in

the bond order of M-L is probably due to the formation of  $\pi$ -orbital within the chelate ring and also to the change in electronegativity of metal ions. Generally, all above IR data pointed that in Zr(IV), Ce(III) and  $\text{UO}_2(\text{II})$  complexes, the azo ligands act as tridentate. The coordination positions are both nitrogen atoms of the two  $\text{NH}_2$  and amide groups forming two fused rings, as represented by structures (a), (b) and (c) shown below. The two fused four membered chelate rings are well characterized in similar azopyrimidines.<sup>51</sup>

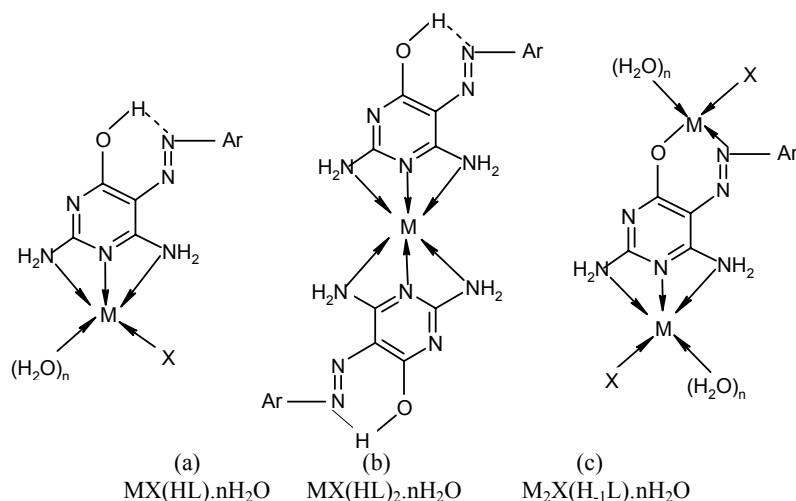


Table 7

Proton  $^1H$  NMR spectral of ligands and some of their complexes in DMSO

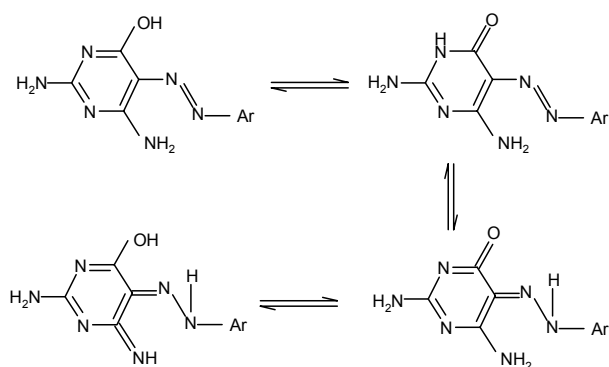
Compounds	$\delta_{H_2O}$	$\delta_{NH_2}$	$\delta(\text{ring protons})$	$\delta_{NH}$	$\delta_{OH}$
$L_1$	-	5.889	6.800–7.585	10.032	-
$L_1-Cu^{2+}$	3.438	-	6.981–7.702	-	-
$L_1-(UO_2)^{2+}$	3.426	-	6.790–7.468	10.034	8.478
$L_2$	-	-	7.530–7.680	10.212	8.480
$L_3$	-	5.210	7.310–7.740	-	9.011
$L_3-Cu^{2+}$	3.367	-	6.659–7.604	-	8.414
$L_3-(UO_2)^{2+}$	3.598	-	6.998–7.760	-	8.409
$L_4$	-	5.860	7.095–7.580	11.081	8.113
$L_4-Cu^{2+}$	3.512	-	6.610–7.608	-	8.409
$L_4-(UO_2)^{2+}$	3.439	-	7.129–7.770	10.273	8.487
$L_5$	-	5.245	6.841–7.803	11.070	8.094
$L_6$	-	5.862	6.860–7.740	11.075	9.048
$L_6-Cu^{2+}$	3.538	-	7.360–7.740	-	8.995
$L_6-(UO_2)^{2+}$	3.615	-	6.505–7.134	-	8.409

The far IR spectra in the range  $400-200\text{ cm}^{-1}$  for the free ligands and some of their complexes are shown in Tables 5, 6. However, tentative assignments of few modes are proposed on basis of normal coordination analysis for complexes containing "N,O" ligands.<sup>52</sup> According to Gupta,<sup>53</sup> the band around  $205\text{ cm}^{-1}$  is taken to represent the  $\nu_{OH-N}$  mode due to intermolecular hydrogen bonding. The broad bands located at  $395\text{ cm}^{-1}$  are assigned to the OH torsion frequency ( $\nu_t$ ). The magnitude of  $\nu_t$  has been shown to be direct measure of  $\pi$ -electron density at C-atom in the C-OH group and thus the rotation of OH group about the C-O bond.<sup>54</sup> The far-IR suggests that the chlorine atom is involved in coordination share of metal chloride complexes, since the data display a band at around  $260\text{ cm}^{-1}$  assignable to the M-Cl stretching vibration. The new bands observed in all complexes under study at  $336-258\text{ cm}^{-1}$  and  $236-$

$258$  are tentatively assigned to  $\nu_{M-O}$  and  $\nu_{M-N}$  respectively. In Ce(III) complexes the only one  $\gamma_{M-N}$  modes is located at around  $260\text{ cm}^{-1}$ .

The proton  $^1H$  NMR spectral data for the free ligands and some of their complexes are used to confirm the complexes structure in Table 7. It is clear that the proton signals are that appearing in the spectra of the free ligands very low field ( $\delta = 10.03-11.08\text{ ppm}$ ) which arise from the NH proton associated to the pyrimidine ring N(1), N(3) and hydrazone NH proton.<sup>55-57</sup> The signal at 8.11-9.01 ppm range is in the same position previously observed for the hydrogen bonded OH proton of pyrimidine C(6) ring. The presence of the above two signals suggested that the ligands under study do not exclusively exist in hydroxy azo structure, but they contain some amount of azoquinone hydrazone tautomers. The  $^1H$  NMR spectra of  $L_1$  ( $x = p-OH$ ) show a peak at 4.84 ppm attributed to

the p-OH proton associated to the phenyl ring. This signal still presents in spectra of complexes revealing the non-involvement of this group in complexation. On the other hand, the signal observed at 6.1 ppm for the  $\delta_{\text{OH}}$  of the COOH group of the phenyl moiety of  $L_3$  ( $x = \text{o-COOH}$ ) is shifted downfield by  $\sim 0.5$  ppm implying a possible coordination of metal via oxygen atom of the carboxylic group of  $L_3$ . The  $\text{NH}_2$  protons of the free ligands appear as split signals between 4.42 [C(2)- $\text{NH}_2$ ] and 5.89 [C(6)- $\text{NH}_2$ ] ppm. The non equivalence of the hydrogen atoms of the  $\text{NH}_2$  groups could be attributed to the  $\text{NH}\cdots\text{N}$  hydrogen bonding formation. Owing to this bond, the resonances of the two  $\text{NH}_2$  groups of the pyrimidine ring, occur in different chemical shifts. Moreover, the higher field  $\text{NH}_2$  group is assigned to the C(6)  $\text{NH}_2$  protons because its nearby azo group has deshielding effect. These data confirm the suggestion that the studied compounds can exist in azo-hydrazone tautomer as a result of the following prototropic equilibrium:



The peaks of p- $\text{SO}_3\text{H}$  ( $L_2$ ), o- $\text{CH}_3$  ( $L_4$ ) and p- $\text{N}(\text{C}_2\text{H}_5)_2$  ( $L_5$ ) protons located at  $\sim 4.0$ , 2.56 and 1.48 ppm respectively show little shift downfield in the spectra of the chelates indicating some sort of deshielding as a result of complexation. The proton of arylazo system appear as broad multi signal at 6.5 to 7.77 ppm. The multiplet nature of this signals can be attributed to the shielding effect of  $\text{N}=\text{N}$  group.<sup>58</sup>

It is worth mentioning that the dissociation of H-bond in  $L_3$  ( $X = \text{o-COOH}$ ) and  $L_7$  ( $X = \text{p-NO}_2$ ) occurs at higher temperature than other ligands. This suggested that the function groups are related to the strength of this band, *i.e.*, the electron withdrawing groups in arylphenolic moiety increase the thermal stability of H-bond. The curve finally shows two exothermic peaks at 225 and 516  $^\circ\text{C}$ , which may result from thermal loss of remaining part of heterocyclic ring. The

endothermic peak and 297  $^\circ\text{C}$  indicates the melting of this compound.<sup>59</sup> The  $E^*$  values of these decomposition steps are 9.28 and 11.685  $\text{KJmol}^{-1}$  and enthalpy change values are 9.45 and 18.072  $\text{Jmol}^{-1}$ . The endothermic peak at 297 $^\circ\text{C}$  indicates the melting of this compound.

The mass spectrum of  $L_1$ -Cu(II) complexes has  $M/e = 361.98$ , as mass lost of one molecule of coordinated water and weight loss of 93 (9.03%;  $M^{2+}$ , 10.87%;  $M^{4+}$ , 19.18%) due to the molecular ions peaks of phenol radical and the chelate is still appeared. The copper oxide is formed with  $M/e = 79.48$  (4.69%) after losing the reminder part of organic reagent  $M/e = 171.5$  (-4H; 21.67%). In case of  $L_1$ -Ni(II) complexes the observed  $M/e = 357.21$  may lose both coordination water and amino group and give  $M/e = 323.21$  ( $M^{4+}$ , 3.3%). This is followed by the elimination of HCl and the phenol radical leaving the  $\text{N}=\text{N}$  and o-OH groups attached to the metal ion ( $M/e = 194.71$ , 3.53%). Finally, the residual part of the ligand is eliminated ( $M/e = 120$ ;  $M^+$ , 5.97%) giving NiO ( $M/e = 74.71$ , 8.4%).  $L_1$ -Co(II) complexes show different fragmentation, the mass of  $M/e = 357.43$  lost one molecule of coordinated water and one molecule of HCN giving  $M/e = 312.43$  (1.95%). Losing of mass 52.5 (11.5%) is related to the loss of amino group and HCl. The weight loss 186 (5.66%) is corresponding to the residual part of the azo and the metal formed its oxide with  $M/e = 74.93$  (19.28%). All the solid complexes have the same degradation as the phenyl ring is breaking first or its substituent after losing the water of coordination while the chelate still exists. Finally, a stable metal oxide is formed after losing the residual part of organic reagent.

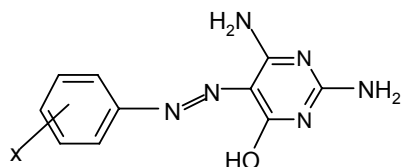
Electronic absorption spectra of the complexes in DMF solution are characterized by one or more broad band in the 29000-24000  $\text{cm}^{-1}$  region, corresponding to an intermolecular CT transition from the antibonding level of the ligand to the vacant orbital of metal ion ( $L \rightarrow M$  CT). This behaviour is normally expected for the octahedral or distorted octahedral geometry.<sup>60-62</sup> The longer wavelength visible bands observed in the spectra of some chelates below 23000  $\text{cm}^{-1}$  can be ascribed to f-f transitions of Ce(III) and  $\text{UO}_2(\text{II})$  ions or due to d-d electronic transition of the d-transition elements.<sup>63-67</sup> The disappearance of this band in the spectra of some chelates is due to its head with the broad  $L \rightarrow M$  CT that spread over the whole visible region or the possibility for the metal d-orbital to overlap and mix with orbitals or the free ligand.

This behaviour is in accord with suggested distorted octahedral geometry. Depending on the splitting of  $^2D$ -ground state of Cu(II) into two levels, it is expected that copper ion is characterized by large distortions from octahedral symmetry.<sup>68</sup> Accordingly the d-d transition of its distorted octahedral configuration is due to  $^2E_{2g} \rightarrow ^2T_{2g}$  transitions. Moreover, the absence of any absorption below  $10,000 \text{ cm}^{-1}$  eliminates the possibility of tetrahedral geometry for the investigated solid complexes.<sup>69</sup>

## EXPERIMENTAL

### Ligand synthesis and reagents

Preparation of the arylazo Pyrimidine ligand and their metal complexes can be represented as follows:



$x = p\text{-OH}$  ( $L_1$ ),  $p\text{-HSO}_3$  ( $L_2$ ),  $o\text{-COOH}$  ( $L_3$ ),  $o\text{-CH}_3$  ( $L_4$ ),  $p\text{-N}(\text{C}_2\text{H}_5)_2$  ( $L_5$ ),  $p\text{-NO}_2$  ( $L_7$ ),  $\text{-H}$  ( $L_8$ ) and  $\text{Ar} = \text{naphthyl}$  ( $L_6$ )

The azo were synthesized by coupling the alkaline pyrimidines – ethanol mixture with the appropriate diazonium salt.<sup>70</sup> The diazotate were prepared by appropriate method for each amine. The formed compounds were purified by repeated crystallisation of the crude products from ethanol and dried in vacuum over silics gel. The solid chelates were prepared by refluxing an ethanolic solution of each ligand and metal salt for about one hour. The metal chelate products were separated after cooling and crystallized from ethanol and dried in a over silica gel.

### Spectral measurements

Stock solutions ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) of the azo compounds and metal salts  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $(\text{CH}_3\text{COO})_2\text{UO}_2 \cdot 6\text{H}_2\text{O}$  were prepared by dissolving the accurate weight of the crystallized product in pure absolute ethanol. Stock solutions of  $\text{ZrCl}_4$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  were prepared by dissolving the needed amount of  $\text{ZrCl}_4$  or  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in a mixture of 80% ethanol-water (v/v). The electronic spectral measurements of the chelates formed in solution were performed on Shimadzu UV-1650 PC, UV-Visible Recording Spectrophotometer using 1 cm silica cell. The infrared and far infrared spectra of the ligands, as well as their solid chelated were recorded as PEAK Y ( $4000\text{-}400 \text{ cm}^{-1}$ ) threshold 2.00%; emission based on a Perkin-Elmer 983 B IR, recording spectrophotometer as KBr discs. The proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded with a Varian EM-390 spectrophotometer at 90 MHz in DMSO. TMS were used as internal reference. The mass spectra were analysed by the EI technique at 80 eV, threshold output = 0.8 V and peak detection = 0.02 V.

## CONCLUSIONS

Stoichiometry of the metal complexes formed in solution were determined by spectrophotometric and conductometric methods. It was found that 1:1 and 1:2 (M : L) mononuclear chelates are formed in solution. The observed increase in conductance during the titration indicates the liberation of  $\text{H}^+$  during complexation. The molar conductance value of the solid complexes in DMF solutions indicates that the complexes are nonelectrolyte. The values of the apparent constant  $K_f$  of the formed chelates species in solution were determined from the spectrophotometric continuous variation. The  $K_f$  values for complexes of Cu(II), Co(II), Zr(IV) and  $\text{UO}_2(\text{II})$  metals with different ligands as order:

$L_1 (x = p\text{-OH}) > L_8 (x = \text{-H}) > L_7 (x = p\text{-NO}_2)$

The  $K_f$  values of the Cu(II) complexes are higher than those of Co(II) complexes and the  $K_f$  values of Zr(IV) complexes are higher than those of  $\text{UO}_2(\text{II})$  complexes.

## REFERENCES

1. R. Zrenner, M. Stitt, M. Sonnewald and R. Boldt, *Annu. Rev. Plant Biol.*, **2006**, 57, 805.
2. D. Das, I. Chakraborty and A. Chakravorty, *Polyhedron*, **2003**, 22, 901.
3. M. Candida, T. A. Vaz and J. J. R. Frausto, *J. Inorg. Nucl. Chem.*, **1981**, 43, 1573-1255.
4. J. Asceno, M. Condido, T. A. Vaz and J. J. R. Frausto, *J. Inorg. Nucl. Chem.*, **1981**, 43, 3043
5. W. M. Willingham and J. R. J. Sorenson, *Biochem. Bioph. Res. Co*, **1988**, 150, 252.
6. C. Heidelberger and F. J. Ansfield, *Cancer Res*, **1963**, 23, 1226.
7. B. Chand, U. Roy, P. K. Santra, G. Mostafa, T. H. Lu and C. Sinha, *Polyhedron*, **2003**, 22, 120.
8. A. S. Amin, T. Y. Mohammed and A. A. Mousa, *Spectrochim Acta*, **2003**, 59, 2577.
9. A. S. Amin and T. Y. Mohammed, *Talanta*, **2001**, 54, 611.
10. M. S. Masoud, S. A. Abouel-Enein and H. M. Kamel, *J. Indian Chem. Soc.*, **2002**, 41, 297.
11. S. Senapoti, P. K. Santra and C. Sinha, *Transit Metal Chem.*, **2002**, 27, 888.
12. P. K. Santra, U. Roy, S. Pal and C. Sinha, *Inorg. Chem. Commun.*, **2001**, 4, 269.
13. P. K. Santra, C. Sinha, W. J. Sheen, F. L. Liao and T. H. Lu, *Polyhedron*, **2001**, 20, 599.
14. Z. M. Zaki, *Spectrochim. Acta A*, **2000**, 56, 1917.
15. J. M. Moreno, J. Ruiz, J. M. Dominguez-Vera and E. Calacio, *Inorg. Chem. Acta*, **1993**, 208, 111.
16. A. J. Barnes, M. A. Stuckey and L. LeGall, *Spectrochim Acta A*, **1984**, 40, 419.
17. E. S. Bamberger, G. G. Black, C. A. Fewson and M. Gibbs, *J. PlantL Physiol.*, **1963**, 38, 482.

18. M. S. Goher, M. S. Masoud, and A. M. Heriba, *Pol J Chem.*, **1981**, 55, 1491.
19. R.S. Becker, A.B.F. Duncan, F.A. Matsen, D.R. Scott and W. West, "Chemical Application of Spectroscopy", 2<sup>nd</sup> edition, Wiley, New York, 1968, 605.
20. A. H. Amrallah, N. A. Abdalla and E. Y. El-Haty, *J. Chin. Chem. Soc. Taip.*, **2007**, 54, 1629.
21. M. T. El-Haty, A. H. Amrallah and M. A. Selim, *Bull. Soc. Chim. Fr.*, **1991**, 128.
22. A. A. Khalifa, R. H. Issa and S. H. El-Shafi, *Rev. Rom. Chim.*, **1977**, 22, 1251.
23. N. Shashikala, E. G. Leelamani and G. K. Reddy, *J. Indian Chem.*, **1982**, 21, 743.
24. M. T. El-Haty and F.A. Adam, *Bull. Soc. Chim. Fr.*, **1983**, 129.
25. A. Buraway and E. Spinner, *J. Chem. Soc.*, **1955**, 2557.
26. J.H. Grimes, A. J. Huggard and S.P. Wilford, *J. Inorg. Nucl. Chem.*, **1963**, 25, 1225.
27. P. Job, *Comp. Rend (Paris)*, **1952**, 180, 928.
28. M. J. Herak, M. Janko, B. Tamhina, *Microchim Acta*, **1973**, 61, 783.
29. W. J. Geaory, *Coordin Chem Rev.*, **1971**, 7, 81.
30. J. F. Loetzee, and G. P. Cunningham, *J. Am. Chem. Soc.*, **1965**, 87, 2529.
31. M. S. Masoud, S. A. Abou -Ali, G. Y. Ali and I. M. Abed, *Thermochim. Acta*, **1987**, 122, 209.
32. M. I. Ismail, *Collect. Czech. Chem. C.*, **1992**, 57, 2042.
33. A. F. Wells, "Structural Inorganic Chemistry", 4<sup>th</sup> edition, Oxford Univ. Press, New York, 1975, 723.
34. M.S. Masoud, E.A. Khalil and A.R. Youssef, *Synth. React. Inorg. & Met.-Org. Chem.*, **1990**, 20(6), 793- 807.
35. M. I. Arriortua, J. L. Pizarro, J. Ruiz, J. M. Moreno and E. Colacio, *Inorg. Chim. Acta*, **1995**, 231-103.
36. E. Colacio, J.M. Dominguez-Vera, A. Escuer, R. Kivekas, and A. M. Romersa, *Inorg. Chim.*, **1994**, 33, 3914.
37. L.G. Theriot, G. O. Carlisle and H.J. Hu, *J. Inorg. Nucl. Chem.*, **1969**, 31, 3303.
38. J. Ruiz, E. Calacio, J. D. López-González, M. Sundberg and R. Kivekäs, *J. Chem. Soc. (Dalton Trans.)*, **1990**, 9, 2747.
39. M. S. Masoud, M. A. El-Dossouky, F. A. Aly and S. A. Abouel Enein, *Transit Metal Chem.*, **1990**, 15, 443.
40. M.S. Masoud, O.H.A. Elhamid and Z.M. Zaki, *Transit Metal Chem.*, **1994**, 19, 12.
41. G.R. Burns, *J. Inorg. Chem.*, **1988**, 7, 277.
42. E. Colacio, J. M. Dominguez-Vera, J. Costes, R. Kivekäs, J. Laurent, J. Ruiz and M. Sundberg, *J. Inorg. Chem.*, **1992**, 1, 774.
43. E. Colacio, J. Ruiz, J. M. Moreno, R. Kivekäs, M. R. Sunderg, J. M. Dominguez-Vera and J. P. Laurent, *J. Chem. Soc., Dalton Trans.*, **1993**, 1, 157.
44. J. R. Kincaid and K. Nakamoto, *Spectrochim Acta*, **1976**, 32, 277.
45. G. C. Percy, *Spectrochim Acta*, **1976**, 32, 1287.
46. J. I. Bullock, *J. Inorg. Nucl. Chem.*, **1967**, 29, 2257.
47. N. F. Curtis and Y. M. Curtis, *Inorg. Chim.*, **1965**, 4, 804.
48. A. S. Amin and A.A. Gouda, *Talanta*, **2008**, 76, 1241.
49. A. S. Amin, *Spectrochim. Acta A*, **2002**, 58, 1831.
50. E. C. Okafor, *Spectrochim Acta*, **1981**, 37, 951.
51. M. S. Masoud, A. S. Abou-Enein, M. E. Ayad and A. S. Goher, *Spectrochim. Acta*, **2004**, 60, 77.
52. J. R. Kincaid and K. Nakamoto, *Spectrochim Acta*, **1976**, 32, 277.
53. S. P. Gupta, S. Sharma and R. K. Goel, *Spectrochim Acta*, **1986**, 42, 1171.
54. I. Iweibo and J. A. Faniran, *Spectrochim Acta*, **1981**, 37, 373.
55. H. G. Beaton, G. R. Willey and M. G. B. Drew, *J. Chem. Soc., Perkin Trans.*, **1987**, 2, 469.
56. M. G. B. Drew, *J. Chem. Soc., Perkin Trans.*, **1982**, 2, 1297.
57. F. Kaberia, B. Vickery, G. R. Willey and M. G. B. Drew, *J. Chem. Soc., Perkin Trans.*, **1980**, 2, 1622.
58. E. C. Okafor, *Spectrochim Acta*, **1982**, 38, 981, 45.
59. P. D. Beer, Z. Chen, M. G. B. Drew and P. A. Gale, *J. Chem. Soc. Chem. Comm.*, **1995**, 1851.
60. C. Duval, "Inorganic Thermogravimetric Analysis", 2<sup>nd</sup> edition, Elsevier Publishing Company, Amsterdam, New York, London, 1963, 691.
61. K. C. Dash, *J. Ind. Chem. Soc.*, **1989**, 66, 562.
62. S. A. Zaidi, S. N. Rehani and M. Eslam, *Polyhedron*, **1985**, 4, 365.
63. G. P. Pokhariyal, *J. Ind. Chem. Soc.*, **1985**, 62, 416.
64. M. Abraham and P. K. Radhakrishnan, *J. Ind. Chem. Soc.*, **1990**, 67, 243.
65. N. K. Kaushik, B. Bhushan and G. R. Chalwal, *J. Inorg. Nucl. Chem.*, **1980**, 42, 457.
66. M. Mohan, J. P. Tandon and N. S. Gupta, *Inorg. Chem. Acta*, **1989**, 111, 187.
67. A. K. Rana and J. R. Shah, *J. Ind. Chem.*, **1981**, 20A, 615.
68. M. R. Mahmoud, A. M. Hammam, S. A. El-Gyar and S. A. Ibrahim, *Monatsh. Chem.*, **1986**, 117, 313.
69. L. W. Laue and L. T. Tuylor, *J. Coord. Chem.*, **1973**, 2, 295.
70. A. H. Amrallah, N. A. Abdalla and E. Y. El-Haty, *Monatsh. Chem.*, **1997**, 128, 1073.

