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ORIGINAL ARTICLE

Physical characterization of some complexes of organic nitrogen donor compounds

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Abstract The stability constants of the complexes of cyanopyridine and aminoantipyrine with some divalent transition metal chlorides were determined at different temperatures. The thermodynamic parameters were calculated; the obtained data reveal that the complexation is an endothermic process. Also it was found that the type of bonding between the ligands and the corresponding metal ion is mainly ionic in nature. The stoichiometry of the formed complexes was found to be M:L and M:2L. The structure of some prepared complexes was confirmed by IR, ^{1}H NMR spectra as well as elemental analysis. Thermal stability was studied using TGA technique.

1. Introduction

Organic compounds containing nitrogen and oxygen donor atoms attract the attention of many researchers due to their biological activity and industrial applications (Darian et al., 1999; Khare and Mishra, 2000). Cyanopyridine acts as antibacterial agent (Alder et al., 1995). Aminoantipyrine has both antitumor effect and anti-inflammatory activity (Alice and Prabharan, 1990; Abd El Missih, 1994).

The coordination chemistry of nitrogen donor ligands is an activate area of research. Therefore, many aminopyridine, cyanopyridine and aminoantipyrine derivatives as well as their metal complexes were prepared (Tsintsadze et al., 1998; Sultana et al., 1995; Mohamed and El-Gamel, 2004; Emori et al., 1990; Santana et al., 1998; Sanmartin et al., 1993; Maurya et al., 1997). The obtained data reveal that the formation of the metal complexes is a spontaneous process, endothermic in nature and entropically favourable. The stoichiometric ratio of the complexes were 1:1 and 1:2 (metal:ligand). Also the structure of the complexes is confirmed by spectroscopic studies.

This work is aimed to calculate the stability constants and the related thermodynamic functions of the complexes of 2-aminopyridine (APy); 4,6-dimetly-3-cyanopyridin-2-one (CNPy-one) and 1-aminoantipyrine (AAP) with Mn (II),

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Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Fe (III) and Cr (III) ions. The structure and composition of the complexes are confirmed using conductometric titration, spectral (IR, ^{1}H NMR) spectra, elemental analysis and thermal studies as described early (Abd El Wahed et al., 2008a,b,c,d).

2. Experimental

All chemicals and reagents are of the pure laboratory grade provided by Aldrich. The stability constants of different complexes at a constant ionic strength (1.0 M KCl), are determined potentiometrically at 288, 298, 308 and 318 K by using Irving–Rossotti pH-titration technique (Abd El Wahed et al., 2006). Three titrations, viz. titration of (i) 1.5 ml 0.01 M HCl, (ii) 1.5 ml 0.01 M HCl + 2.0 ml 0.01 M ligand and (iii) 1.5 ml 0.01 M HCl + 2.0 ml 0.01 M ligand + 0.5 ml 0.01 M metal ion are carried out against 0.01 M KOH. A digital pH-meter, Consort P-907 provided with a glass calomel electrode is used. All calculations were computed using an excel-computer program.

To ascertain the probable stoichiometric ratio of the complexes; conductometric titration technique was employed. The conductance values were measured during titration of 0.001 M metal ion solution against 0.01 M ligand solution using a digital conductometer, 5800-50 solution analyzer, Cole-Parmer, provided with a platinum conductivity cell.

Solid complexes of aminopyridine are prepared by addition of metal ion solution slowly to a solution of the ligand, with a constant stirring for 10 min. Aminoantipyrine solid complexes are synthesized by adding slowly a hot aqueous solution of metal ion to hot aqueous solution of the ligand with a constant stirring for 1.0–2.0 h. The complexes formed were filtered, washed with hot water and ethanol and dried over anhydrous $CaCl_2$. The melting point of all prepared complexes is above 360 °C. In order to verify that the chlorides are counter ions, i.e., outside the coordination sphere of metal ions, $AgNO_3$ solution is added to the dissolved complexes. A white precipitate was obtained for all samples suggesting that the chloride ions are outside the coordination sphere of the metal ion, i.e., cationic nature was observed. In order to suggest the correct formula for complexes under investigation, elemental analysis for C, H and N are carried out. Elemental analysis results are collected in Table 1. Structure of the complexes is confirmed by using IR (KBr disc technique; Mattson 5000 FT-IR spectrometer) and ^{1}H NMR spectra which are recorded on Vardin 200 MHz using deuteriated dimethyl sulphoxide (D-DMSO) as a solvent. The thermal stability of complexes is carried out in the range 20–800 °C using Shimadzu TDG (50 Hz) with a uniform heating rate 15 °C/min.

3. Results and discussion

From the three potentiometric titration curves, the proton-ligand, pK, metal-ligand, log K as well as stability constants are determined using the standard expression:

$$n_a = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)T_L}$$

where V_1 and V_2 are the volumes of alkali required to reach the same pH value in titrations of acid alone and acid with ligand, respectively, V° is the initial volume of the titrated solution (25.0 ml), T_L represents the total ligand concentration, Y is the total number of dissociable protons attached to the ligand molecule and N° and E° is the normality of alkali and free acid (0.01 M), respectively.

To evaluate the successive stability constants, the average number of ligand associated with metal ion, $\bar{n}$, and the free ligand exponent (PL), are calculated using the two equations listed below (Abd El Wahed et al., 2001,1997):

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)nT_M}$$

and

$$PL = \log\left[\frac{\sum\limits_{n=0} \beta\left[\frac{1}{anti\log\beta}\right]^n}{T_L - \bar{n}T_M}\right]\frac{V^\circ + V_3}{V^\circ}$$

where T_M is the total concentration of the metal ion in solution and the other terms have their usual meaning. β is the overall proton-ligand stability constant.

The calculated stability constants are reported in Tables 2–4. The data indicate that more than one of the complexed ligand are present, and thus two successive stability constants are obtained, i.e., M:L and M:2L. The stability values for APy decrease with increasing temperature indicating an exothermic nature of the complexing process, but, in the case of other ligands the stability values increase with increasing temperature indicating an endothermic nature of the formed complexes.

Thermodynamic functions are computed with the help of the following relations:

$$\Delta G^\circ = -2.30RT\log K = \Delta H^\circ - T\Delta S^\circ$$

and

$$\Delta H^\circ = 2.303R\left(\frac{T_1T_2}{T_1 - T_2}\right)\log\left(\frac{K_2}{K_1}\right)$$

The thermodynamic data are given in Tables 5–7. The data reveal that the formed complexes, accompanied by negative free energy change (ΔG°) values, indicating that the complex

Table 1 Elemental analysis data of some prepared solid complexes.

Complex	Colour	C (%)		H (%)		N (%)	
		Found	Calcd	Found	Calcd	Found	Calcd
$[Co–(C_5H_4N_2)H_2O]Cl$	Green	23.60	23.26	3.72	4.65	9.52	10.85
$[Ni–(C_5H_4N_2)_2H_2O]2H_2O$ Cl	Greenish yellow	22.50	23.20	3.80	4.60	9.48	10.80
$[Cd–(C_5H_4N_2)4H_2O]Cl_2$	Dirty white	16.55	17.32	2.88	3.04	7.79	8.08
$[Ni–C_{11}H_{11}N_3O)_26H_2O]Cl$	Dirty white	43.64	43.7	4.55	4.6	13.50	13.90
$[Cu–C_{11}H_{11}N_3O)_24H_2O]H_2O$ Cl	Black	47.3	46.11	2.94	3.08	13.89	14.6

Table 2 Formation and stability constants of 2-aminopyridine and its complexes at different temperatures.

Compounds		Temperature			
		288 K	298 K	308 K	318 K
Free ligand	Log K_H	11.00	10.90	10.50	10.00
1-Mn-complex	Log K_1	5.31	5.15	4.91	4.72
	Log K_2	[5.03]	[4.77]	[4.48]	[4.22]
2-Co-complex	Log K_1	5.73	5.45	5.09	4.74
	Log K_2	[5.36]	[5.03]	[4.68]	[4.32]
3-Ni-complex	Log K_1	6.09	5.71	5.26	4.8
	Log K_2	[5.55]	[5.15]	[4.75]	[4.36]
4-Cu-complex	Log K_1	6.34	6.10	5.85	5.60
	Log K_2	[5.55]	[5.17]	[4.8]	[4.52]
5-Zn-complex	Log K_1	6.00	5.75	5.45	5.18
	Log K_2	[5.85]	[5.60]	[5.34]	[5.06]
6-Cd-complex	Log K_1	5.42	5.19	4.95	4.73
	Log K_2	[5.35]	[5.10]	[4.61]	[4.18]
7-Fe-complex	Log K_1	6.50	6.30	6.09	5.85
	Log K_2	[6.15]	[5.95]	[5.76]	[5.59]

Table 3 Formation and stability constants of 4,6-dimethyl-3-cyano pyridin-2-one and its complexes at different temperatures.

Compounds		Temperature			
		288 K	298 K	308 K	318 K
Free ligand	Log K_H	9.58	9.70	10.00	10.10
1-Mn-complex	Log K_1	3.85	4.07	4.34	4.59
	Log K_2	[3.35]	[3.56]	[3.87]	[4.20]
2-Co-complex	Log K_1	3.95	4.21	4.49	4.77
	Log K_2	[3.74]	[3.95]	[4.30]	[4.66]
3-Ni-complex	Log K_1	5.08	5.25	5.50	5.70
	Log K_2	[3.80]	[4.10]	[4.51]	[4.80]
4-Cu-complex	Log K_1	6.48	6.72	7.00	7.25
	Log K_2	[5.96]	[7.18]	[6.53]	[6.80]
5-Zn-complex	Log K_1	5.00	5.28	5.64	6.00
	Log K_2	[4.71]	[4.78]	[4.95]	[5.10]
6-Cd-complex	Log K_1	4.10	4.40	4.71	5.01
	Log K_2	[3.20]	[3.30]	[3.45]	[3.58]
7-Cr-complex	Log K_1	7.65	7.80	7.96	8.20
	Log K_2	[6.60]	[6.90]	[7.25]	[7.55]
8-Fe-complex	Log K_1	7.95	8.08	8.26	8.50
	Log K_2	[6.30]	[6.50]	[6.75]	[6.98]

Table 4 Formation and stability constants of 4-amino antipyrine and its complexes at different temperatures.

Compounds		Temperature			
		288 K	298 K	308 K	318 K
Free ligand	Log K_H	9.98	10.08	10.12	10.30
1-Mn-complex	Log K_1	4.20	5.00	5.80	7.00
	Log K_2	[3.05]	[3.50]	[3.65]	[5.40]
2-Co-complex	Log K_1	4.15	4.60	5.30	5.80
	Log K_2	[3.20]	[3.90]	[4.60]	[5.15]
3-Ni-complex	Log K_1	4.30	5.08	5.25	5.65
	Log K_2	[3.40]	[4.50]	[4.60]	[4.75]
4-Cu-complex	Log K_1	7.00	7.21	7.45	7.85
	Log K_2	[6.30]	[6.50]	[6.95]	[7.05]
5-Zn-complex	Log K_1	6.50	6.68	6.91	7.03
	Log K_2	[5.15]	[5.50]	[5.92]	[6.20]
6-Cd-complex	Log K_1	4.20	4.50	4.90	6.00
	Log K_2	[4.10]	[4.17]	[4.30]	[4.45]
7-Fe-complex	Log K_1	6.30	6.85	7.10	7.40
	Log K_2	[5.00]	[5.70]	[6.35]	[7.00]

Table 5 Thermodynamic parameters of 2-aminopyridine complexes at 298 K.

Compounds	*Log K* [Log K_2]	$-\Delta G°$ (KJ/mol)	$-\Delta H°$ (KJ/mol)	$-\Delta S$ (J/mol deg)
1-Mn-complex	5.15	29.38	34.46	17.04
	[4.77]	[27.21]	[53.61]	[88.57]
2-Co-complex	5.45	31.09	65.10	114.10
	[5.03]	[28.70]	[61.27]	[109.29]
3-Ni-complex	5.71	32.58	76.58	147.67]
	[5.15]	[29.38]	[76.58]	[158.40]
4-Cu-complex	6.1	34.80	45.95	37.40
	[5.17]	[29.49]	[49.78]	[68.06]
5-Zn-complex	5.75	32.80	57.44	82.66
	[5.6]	[31.95]	[49.78]	[59.83]
6-Cd-complex	5.19	29.61	42.12	41.98
	[5.1]	[29.09]	[57.44]	[95.10]
7-Fe-complex	6.3	35.94	42.12	20.72
	[5.95]	[33.94]	[38.29]	[14.57]

Table 6 Thermodynamic parameters of 4,6-dimethyl-3-cyano-pyridin-3-one complexes at 298 K.

Compounds	Log K_1 [Log K_2]	$-\Delta G°$ (KJ/mol)	$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol deg)
1-Mn-complex	4.07	23.22	45.95	232.13
	[3.56]	[20.31]	[49.78]	[235.21]
2-Co-complex	4.21	24.02	49.78	247.66
	[3.95]	[22.53]	[53.61]	[255.53]
3-Ni-complex	5.25	29.95	42.12	241.87
	[4.10]	[23.39]	[55.52]	[264.83]
4-Cu-complex	6.72	38.34	59.35	327.85
	[6.18]	[35.26]	[57.44]	[311.08]
5-Zn-complex	5.28	30.12	55.52	287.42
	[4.78]	[27.27]	[28.72]	[187.90]
6-Cd-complex	4.40	25.10	49.78	251.30
	[3.30]	[18.82]	[28.72]	[159.56]
7-Cr-complex	7.80	44.50	38.29	277.85
	[6.90]	[39.37]	[57.44]	[324.87]
8-Fe-complex	8.08	46.10	42.12	296.06
	[6.50]	[37.08]	[38.29]	[252.96]

Table 7 Thermodynamic parameters of 4-amino antipyrine complexes at 298 K.

Compounds	Log K_1 [Log K_2]	$-\Delta G°$ (KJ/mol)	$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol deg)
1-Mn-complex	5.00	28.52	174.06	679.84
	[3.50]	[19.97]	[172.32]	[645.28]
2-Co-complex	4.60	26.24	114.88	473.58
	[3.90]	[22.25]	[134.03]	[524.43]
3-Ni-complex	5.08	28.98	87.03	389.32
	[4.50]	[25.67]	[121.84]	[495.03]
4-Cu-complex	7.21	41.13	38.29	266.55
	[6.50]	[37.08]	[42.54]	[267.22]
5-Zn-complex	6.68	38.11	38.29	256.40
	[5.50]	[31.38]	[87.03]	[397.36]
6-Cd-complex	4.50	25.67	136.76	545.10
	[4.17]	[23.79]	[51.54]	[252.82]
7-Fe-complex	6.85	39.08	57.44	323.91
	[5.70]	[32.52]	[134.03]	[558.90]

formation is a spontaneous process. In the case of (APy) the negative $\Delta H°$ values prove that the complexing process is exothermic in nature, while the positive $\Delta H°$ values for (CNPy-one) and (AAP) indicate that the complexing process is endothermic. The great positive values of $\Delta S°$ reveal that the complexes are highly disordered and very stable.

Table 8 Electrostatic and non-electrostatic parts of thermodynamic data of 2-amio pyridine complexes at 298 K.

Compounds	$-\Delta G^\circ_{non}$	ΔG°_{ele}	$-\Delta H^\circ_{non}$	ΔH°_{ele}	ΔS°_{ele}
1-Mn-complex	25.89	−3.46	35.83	1.40	16.32
	[31.80]	[4.61]	[51.68]	[−1.87]	[−21.76]
2-Co-complex	48.15	17.08	58.09	−6.94	−80.63
	[37.67]	[8.99]	[57.55]	[−3.65]	[−42.46]
3-Ni-complex	56.74	24.19	66.68	−9.83	−114.17
	[48.74]	[19.39]	[68.63]	[−7.88]	[−91.52]
4-Cu-complex	35.62	0.85	45.56	−0.34	−4.01
	[29.74]	[0.27]	[49.62]	[−0.11]	[−1.27]
5-Zn-complex	43.20	10.42	53.14	−4.23	−49.21
	[30.44]	[−1.47]	[50.33]	[0.59]	[6.94]
6-Cd-complex	31.40	1.81	41.34	−0.73	−8.58
	[35.06]	[5.99]	[54.94]	[−2.43]	[−28.29]
7-Fe-complex	33.22	−2.68	43.17	1.08	12.65
	[22.55]	[−10.28]	[42.43]	[4.17]	[48.51]

Table 9 Electrostatic and non-electrostatic parts of thermodynamic data of 4,6-dimethyl-3-cyano pyridin-2-one complexes at 298 K.

Compounds	ΔG°_{non}	$-\Delta G^\circ_{ele}$	ΔH°_{non}	ΔH°_{ele}	ΔS°_{ele}
1-Mn-complex	33.01	56.20	23.06	22.83	265.25
	[43.63]	[63.93]	[23.75]	[25.97	[301.70]
2-Co-complex	35.49	59.49	25.55	24.17	280.77
	[45.71]	[68.23]	[25.83]	[27.72]	[321.99]
3-Ni-complex	28.34	58.27	18.40	23.67	274.99
	[46.82]	[70.20]	[26.94]	[28.52]	[331.28]
4-Cu-complex	38.16	76.47	28.22	31.07	360.88
	[44.76]	[79.99]	[24.88]	[32.50]	[377.49]
5-Zn-complex	37.81	67.91	27.87	27.59	320.49
	[26.66]	[53.91]	[6.78]	[21.90]	[254.43]
6-Cd-complex	35.18	60.26	25.24	24.48	284.40
	[29.10]	[47.91]	[9.22]	[19.46]	[226.12]
7-Cr-complex	21.42	65.88	11.48	26.77	310.93
	[43.57]	[82.90]	[23.69]	[33.68]	[391.26]
8-Fe-complex	23.68	69.74	13.74	28.33	329.12
	[30.63]	[67.68]	[10.75]	[27.50]	[319.42]

The above conclusion is confirmed by analyzing the conventional thermodynamic functions in terms of electrostatic and non-electrostatic components (Abd El Wahed et al., 2005):

$$\Delta G^\circ = \Delta G^\circ_{ele} + \Delta G^\circ_{non} = nRT\ln M + Rc(a + eT/\theta)$$

$$\Delta H^\circ = \Delta H^\circ_{ele} + \Delta H^\circ_{non} = Rc[a + (1 + T/\theta)eT/\theta]$$

and

$$\Delta S^\circ = \Delta S^\circ_{ele} + \Delta S^\circ_{non} = -nRT\ln M - (Rc/\theta)eT/\theta$$

where θ is the characteristic temperature of the solvent and M is its mobility. The obtained data were listed in Tables 8–10. A comparison of the calculated values of the change in the free energy show that in the case of (APy) the negative values of ΔG°_{non} compared to the positive value of ΔG°_{ele} suggest that the non-electrostatic forces are stronger than the electrostatic forces, i.e., the covalent character is predominant. But in the case of (CNPy-one) and (AAP) the negative values of ΔG°_{ele} compared to positive value of ΔG°_{non} suggest that the ionic character is predominant. The enthalpic data also support the above consideration. Large positive ΔS°_{ele} values for most complexes, show that the complexing reaction is mainly entropically favoured (Murakami and Yo Shino, 1981).

One of the most frequent uses of conductometric titration is the qualitative determination of molar ratio of complexes (Martell, 1997). It is well known that the measured conductance value is directly proportional to the concentration and mobility of one or more ions of interest at a given temperature. Thus, the replacement of some ions by others during complex formation is accompanied by a change in the measured quantity. Straight or nearly straight lines intersecting at the required ratio of complexing process were obtained. A common behaviour of the conductograms of all studied ligands was a reduction in the conductance values. The decrease in conductance continues until the desired stoichiometric ratio is attained. The obtained conductograms exhibit two obvious breaks at M:L and M:2L.

In order to illustrate the bonding site, the IR and ^{1}H NMR spectra of each free ligand as well as those of their metal complexes showed be compared. APy has the characteristic bands shown in Fig. 1: stretching frequency of NH2 group at 3189 cm^{-1}, bending band of NH2 group at 1624 cm^{-1} and that

Table 10 Electrostatic and non-electrostatic parts of thermodynamic data of 4-amino antipyrine complexes at 298 K.

Compounds	ΔG°_{non}	$-\Delta G^{\circ}_{ele}$	ΔH°_{non}	ΔG°_{ele}	ΔS°_{ele}
1-Mn-complex	122.48	150.98	112.54	61.34	712.52
	[130.78]	[150.73]	[110.90]	[61.24]	[711.35]
2-Co-complex	81.10	107.32	71.16	43.60	506.47
	[102.92]	[125.15]	[83.042]	[50.85]	[590.63]
3-Ni-complex	60.52	89.48	50.58	36.35	422.29
	[93.28]	[118.93]	[73.39]	[48.32]	[561.25]
4-Cu-complex	22.39	63.49	12.45	25.79	299.64
	[33.65]	[70.70]	[13.77]	[28.72]	[333.67]
5-Zn-complex	23.27	61.34	13.32	24.92	289.50
	[66.90]	[98.25]	[47.02]	[39.92]	[463.68]
6-Cd-complex	96.80	122.46	86.86	49.75	577.91
	[43.88]	[67.65]	[24.00]	[27.49]	[319.29]
7-Fe-complex	36.59	75.63	26.65	30.73	356.94
	[99.95]	[132.45]	[80.07]	[53.81]	[625.06]

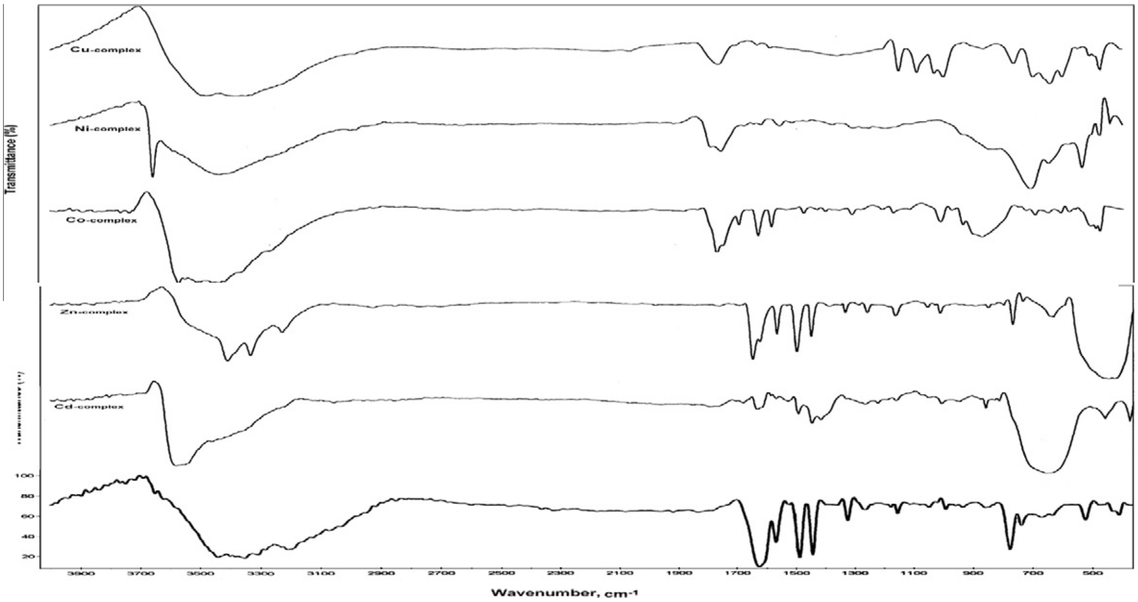
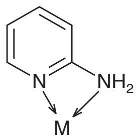


Figure 1 Infrared spectrum of 2-aminopyridine and its metal complexes.

of C═N group at 1566 cm^{-1}. The IR spectra of its metal complexes show that there are shift in frequency bands of NH2 and C═N groups in all complexes (Nakamoto, 1997). This indicates that the amino group and N of pyridine ring participate in coordination compounds. The structure of the studied complexes is represented as:



^{1}H NMR spectra of the free ligand has signals of the aromatic ring protons at $\delta = 7.9, 7.4, 6.8, 6.3$ ppm, and NH_2 group signal at $\delta = 4.0$ ppm Pretch et al., 1983. During compexation there is a shift of amino group signal to $\delta = 3.4$ ppm in the case of Cd-complex and to $\delta = 3.7$ ppm in the case of Co-complex as shown in Fig. 2. This indicates that the amino group is a site of bonding with metal ions.

The characteristic IR bands for free aminoantipyrine and its metal complexes show that the free ligand has characteristic bands at: Stretching frequency bands at 3432, 3325 cm^{-1} corresponding to NH_2. Also two bands at 3325, 3181 cm^{-1} due to stretching of aromatic C–H; two bands at 2989, 2913 cm^{-1} due to stretching of CH_3 group, finally one band at 1678 cm^{-1} due to C═O group as observed in Fig. 3. For the complexed molecules the characteristic band for amino group is slightly shifted to higher frequency indicating that the amino group takes place in the complexing process (Nakamoto, 1997). The characteristic band of (C═O) is shifted to lower frequency indicating that it is the second site of bonding with metal ion. The structure of the complexes is listed below:

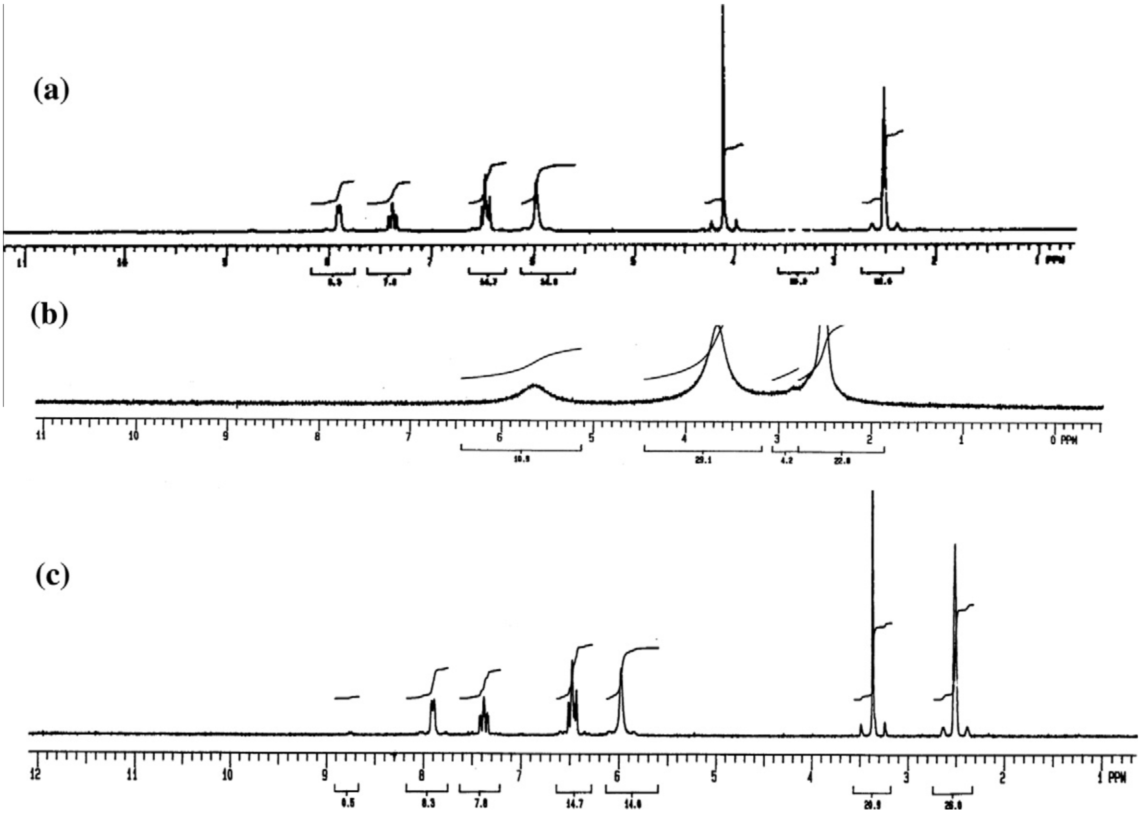
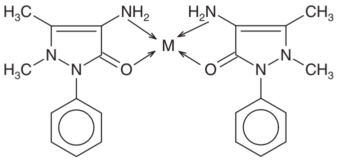
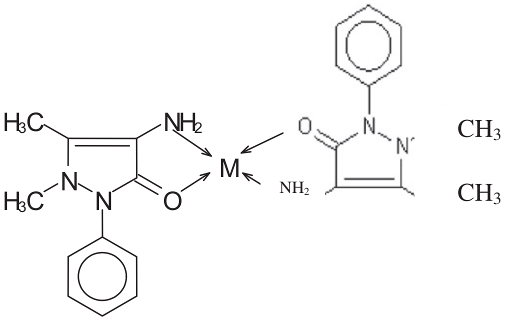


Figure 2 ^{1}H NMR spectra for: (a) 2-Aminopyridine, (b) cobalt complexes and (c) cadmium complex.



or



The ^{1}H NMR of the free aminoantipyrine has the following characteristic signals: The aromatic ring has a signal at $\delta = 7.4$ ppm, amino group signal is at $\delta = 3.81$ ppm and methyl protons at $\delta = 2.09$ ppm as shown in Fig. 4. On complexation with zinc it is found that there are two bands of NH at $\delta = 9.54$, 5.7 ppm indicating that this complex exist in *cis* and *trans* form as described early from IR data.

Thermal studies and spectral analyses provided more information about the structure of complexes. The presence of water molecules (solvent) outside or inside the coordination sphere of the complexes is determined by thermal analysis (weight loss). The existence of H_2O inside the coordination sphere was confirmed by the presence of sharp peak at ca 180–270 °C, as shown in Figs. 5 and 6. The decomposition starts at 180 °C and is completed at ca 400–600 °C leaving the metal oxide as a final product.

From thermogravimetric analysis, the activation energies of the decomposition were calculated. Assuming a first order decomposition reaction Coats–Redfern equation may be written in the form (Coats and RedFern, 1964):

$$\log F(\alpha)/T^2 = \log[AR/\theta E^*(1 - 2RT/E^*)] - E^*/2.303RT$$

where A is the pre-exponential factor, R is the gas constant, E^* is the activation energy in J mol^{-1} and θ is the heating rate. The function $F(\alpha) = -\log(1 - \alpha)$ and α equal weight loss at temperature T/total weight loss at each step of decomposition. Since $(1 - 2RT/E^*) \approx 1$, a plot of $-\log[-\log(1 - \alpha)/T^2]$ Vs $1/T$ resulted in a straight line of slope $= -E^*/2.303R$. Thus, E^* was calculated from the slope and A was calculated from the intercept.The activation entropy ΔS°, the activation enthalpy ΔH°, and the free energy of activation ΔG° were calculated from the following equation:

$$\Delta S^\circ = 2.303(\log Ah/KT)R$$

$$\Delta H^\circ = E^* - RT$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

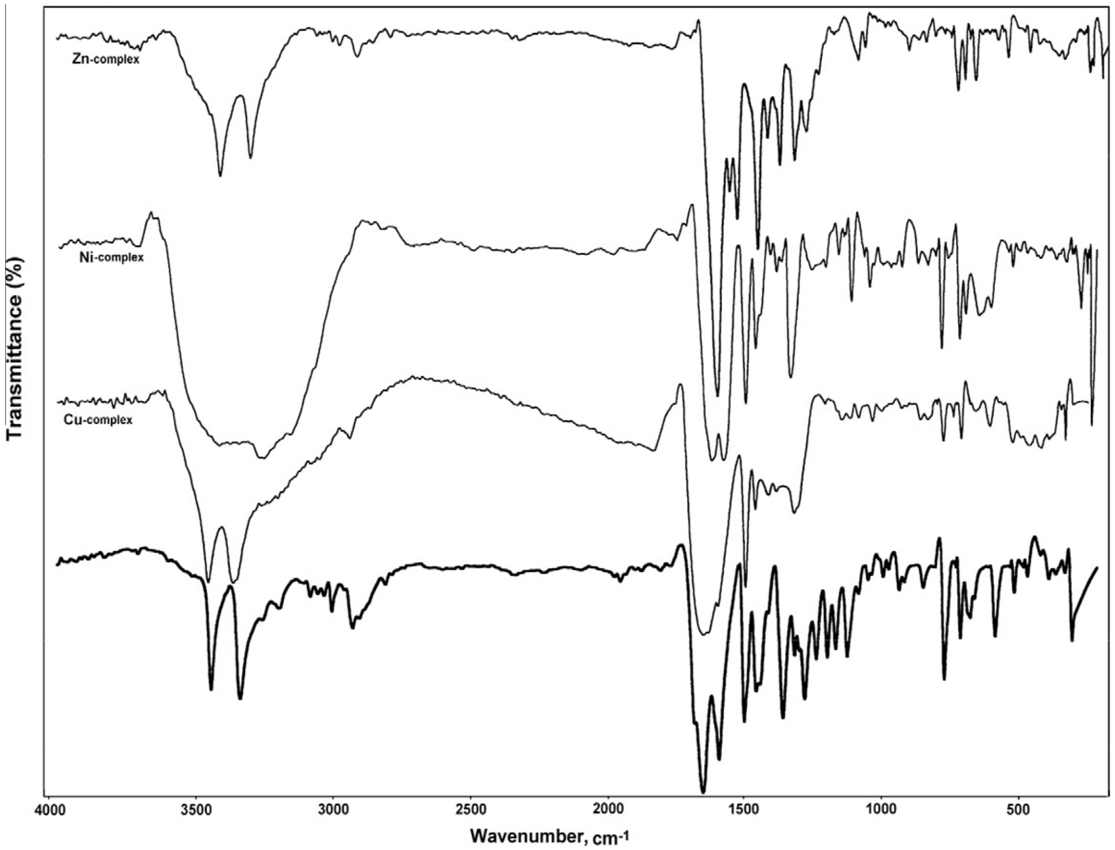


Figure 3 Infrared spectrum of 4-aminoantipyrine and its metal complexes.

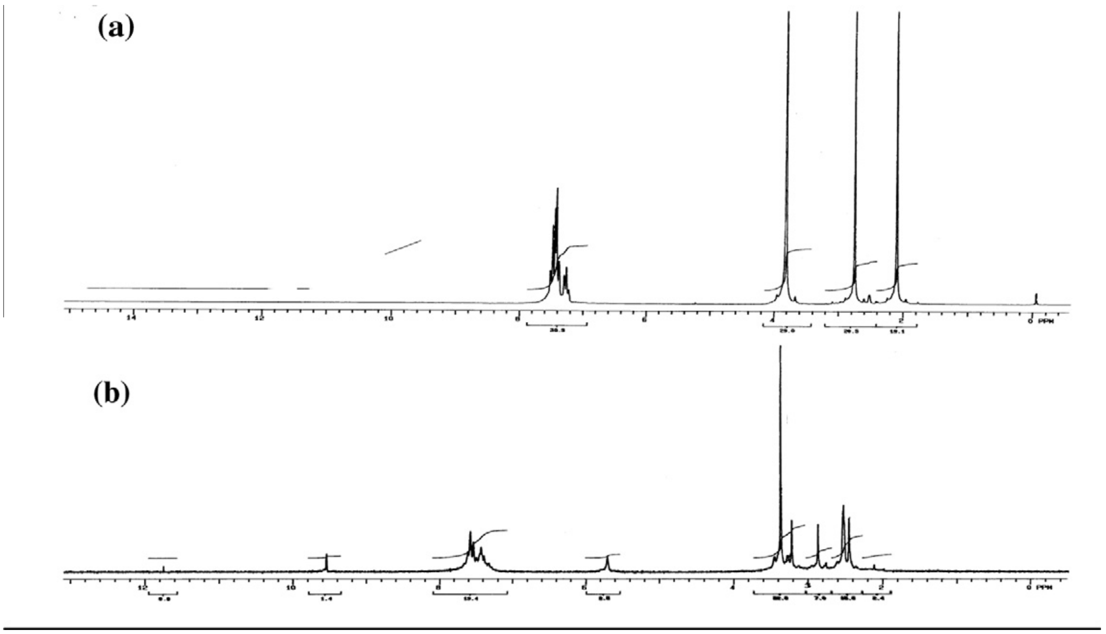


Figure 4 ^{1}H NMR spectra for: (a) 4-Aminoantipyrine and (b) zinc complex.

where K is Boltzman constant, 1.368×10^{-23} J K^{-1} and h is Plank constant 6.626×10^{-34} J S. The calculated values of E^*, $\Delta S°$, $\Delta H°$ and $\Delta G°$ for the decomposition steps for the complexes are given in Tables 11 and 12.

It is clear that the enthalpy values of $\Delta H°$ for most complexes have the same trend as those of the activation energy values E^*. The negative values of the activation entropies $\Delta S°$ in most steps of decomposition indicated that the

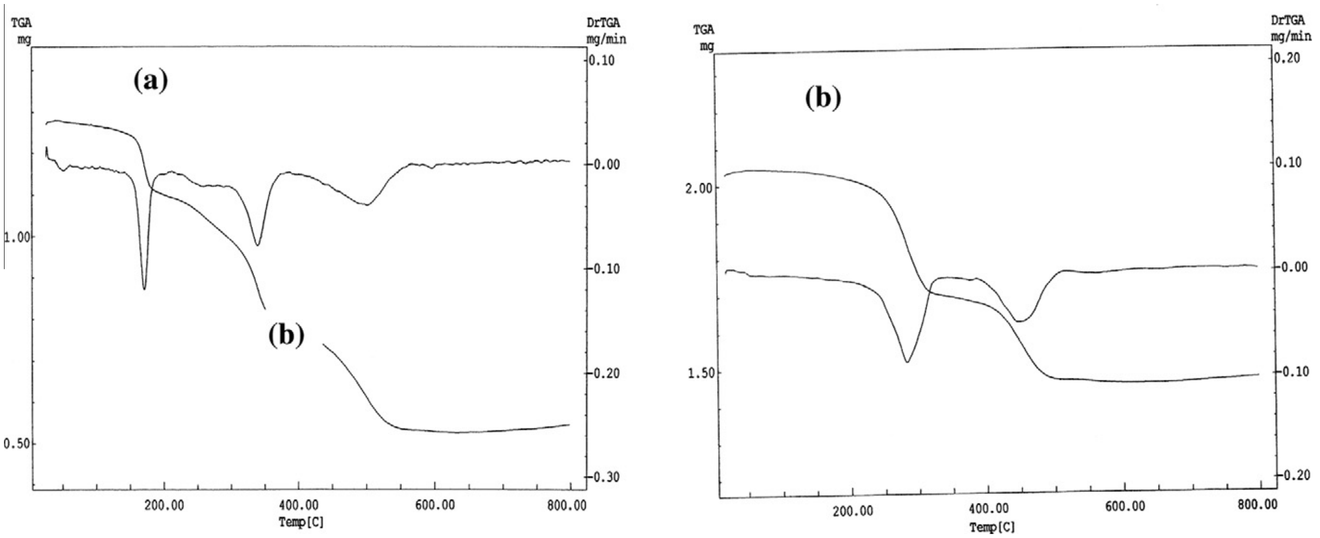


Figure 5 TGA of 2-aminopyridine with (a) nickel complex and (b) copper complex.

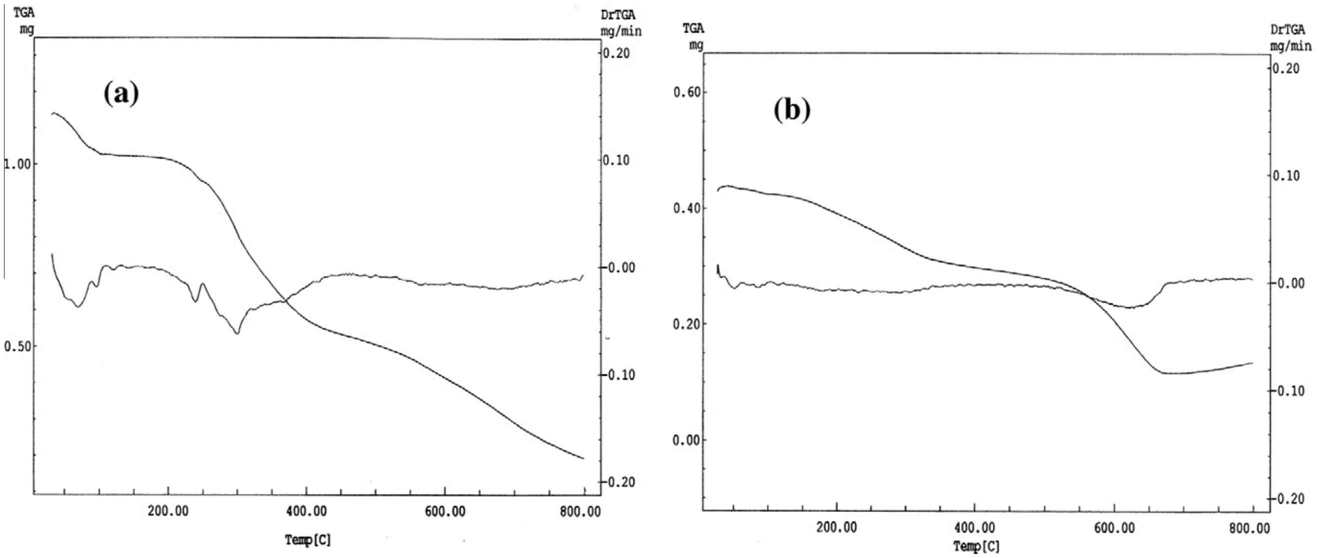


Figure 6 TGA of 4-aminoantipyrine with (a) nickel complex and (b) copper complex.

Table 11 Kinetic data of the thermal decomposition of 2-aminopyridine complexes.

Complexes	Decomp. steps (°C)	E^* (KJ/mol)	$\Delta S°$ (JK mol^{-1})	$\Delta H°$ (KJ/mol)	$\Delta G°$ (KJ/mol)
Ni-complex	148.54–214.54	152.79	−55.96	151.37	160.96
	217.17–304.36	62.95	−292.4	60.74	138.56
	304.36–394.47	303.55	99.62	300.73	266.98
	394.47–54.83	139.85	−212.4	135.85	238.08
Cu-complex	226.03–328.89	227.36	9.31	225.02	222.4
	393.37–508.19	302.94	22.6	299.2	289.0

activated complex has a more ordered structure than the reactants (Frost and Person, 1961). Also, $\Delta H°$ values for most steps of decomposition had opposite sign compared to the values obtained early from potentiometric calculation. The positive values of $\Delta G°$ for most steps of decomposition indicate that the decomposition process is non spontaneous in nature.

4. Conclusions

The complexes of cyanopyridine and aminoantipyrine with some divalent transition metal are stable. The thermodynamic parameters reveal that the complexation is an endothermic in nature. Also it was found that the type of bonding between

Table 12 Kinetic data of the thermal decomposition of 4-aminoantipyrine complexes.

Complexes	Decomp. steps (°C)	E^* (KJ/mol)	$\Delta S°$ (JK/mol)	$\Delta H°$ (KJ/mol)	$\Delta G°$ (KJ/mol)
Ni-complex	41.38–101.22	111.16	−145.00	−2.83	46.78
	211.78–268.69	84.36	−251.62	80.09	209.35
	268.69–377.3	−107.2	−111.3	−112.1	−46.84
	378.89–572.16	217.92	96.66	211.87	141.53
	573.9–792.79	1446	822.14	−7.80	788.09
Cu-complex	42.58–131.20	4.20	−386.28	1.32	135.02
	240.53–385.21	208.11	−33.54	203.41	222.40
	534.37–679.63	939.50	1262.62	−7.34	−1122.28

the ligands and the corresponding metal ion is mainly ionic in nature. The stoichiometry of the formed complexes was found to be M:L and M:2L. Aminoantipyrine is bidentate and coordinate with metal ions via the amino and carbonyl groups as confirmed by IR, ^{1}H NMR spectra as well as elemental analysis. The results reveal that these complexes have high thermal stability.

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