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Thermodynamic Parameters of Complexes of Bivalent Transition Metal Ions with 3-(4′-Chlorophenyl)-1-(2′-Hydroxynaphthyl)-2-Propen-1-One

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The stability constants of UO_2^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+} complexes of 3-(4′-chlorophenyl)-1(2′-hydroxynaphthyl)-2-propen-1-one (CPHNO) have been determined in 75% (v/v) dioxane-water, acetone-water and 2-ethoxy ethanol-water mixtures using the Bjerrum-Calvin pH titration technique as developed by Irving and Rossottii. The stability constants are in fair agreement with Irving-Williams order. The results obtained are compared with the data available in the literature. Abnormal behaviour of the chelates was observed in acetone-water medium. The thermodynamic parameters such as free energy, ethalpy and entropy changes involved in complexation have been calculated.

INTRODUCTION

Among the various *o*-hydroxy carbonyl compounds, *o*-hydroxy chalcones form a distinct category which can form chelates with metal ions with low spin square-planar configuration. These chelates are reluctant to form adducts and this has been attributed to the presence of extensive conjugation[1]. Chalcones were found to be physiologically and pharmacologically active. They were also found to have germicidal[2], bactericidal[3], fungicidal[4] and carcinogenic activity[5]. The present investigation deals with the determination of stability constants and the thermodynamic parameters of the complexes of UO^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} Ni^{2+} and Mn^{2+} with 3-(4′-chlorophenyl))-1-(2′-hydroxynaphthyl)-2-propen-1-one (CPHNO) at different temperatures employing Calvin-Bjerrum pH titration technique[6-8] as modified by Irving and Rossottii[9].

EXPERIMENTAL

The ligand 3-(4′-chlorophenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (CPHNO) was prepared by the condensation of 2-hydroxy-1-acetonaphthone with chloro benzaldehyde employing the method reported earlier[10]. It was recrystallized from ethanol m. pt. 137°C (found C-73.89%, H-4.23%, required C-73.91%, H-4.21%). The solution of the ligand was prepared using dioxane, acetone and 2-ethoxy-ethanol as solvents. The metal nitrate solutions were prepared in CO_2-free doubly distilled water and were standardized by standard methods. Dioxane, acetone, and 2-ethoxy ethanol were purified before ure. An Elico (<I-120) digital pH meter was used for pH measurements.

Procedure

The experimental method consisted of pH titrations of the following carbonate free solutions of 50 ml at the desired temperatures against standard sodium hydroxide (0.1213 M).

(a) 5 ml of 0.1 M KNO_3 + 37.5 ml organic solvent + 5 ml 0.01 M HNO_3 + 2.5 ml water.
(b) 5 ml of 0.1 M KNO_3 + 1 ml of 0.1 M ligand in pure organic solvent + 36.5 ml organic solvent + 5 ml 0.01 M HNO_3 + 2.5 ml water.
(c) 5 ml of 0.1 M KNO_3 + 1 ml of 0.1 M ligand solution + 36.5 ml organic solvent + 5 ml 0.01 M HNO_3 + 0.5 ml of (0.01 M) metal solution + 2 ml water.

The pH values (B) were corrected in all the aquo-organic mixtures by the method of Van Uitert and Hass[11] ($-\log [H^+] = B + \log UH$) and others[12]. Under the present conditions the following log U_H values were obtained in different media under consideration: 0.36 (75% aq dioxane), 0.29 (75% aq. acetone), 0.24 (75% aq. 2-ethoxy ethanol).

RESULTS AND DISCUSSION

The dissociation constant (K_L) of the ligand is obtained from the formation curve of the proton ligand system. The formation curve is constructed by plotting $\bar{n}_A$ values versus pH. From the titration curves using the solutions (a) and (b) $\bar{n}_A$ values were calculated[9] at various pH values and the values obtained at different temperatures. For a ligand with one dissociable proton log K_L becomes equal to the pH corresponding to $\bar{n}_A = 0.5$ Proton ligand formation constants of the ligand in 75% aq. dioxan at 30°, 35° and 40°C are 12.70, 12.49, 12.30 (Fig. 1–3) respectively. In 75% aq. acetone and 75% aq. 2-ethoxy-ethanol at 30°C are 12.25, 11.30 (Fig. 4 & 5) respectively.

From the titration curve of solution of (b) and (c), $\bar{n}$ and P_L values were calculated[6,7,9]. The stepwise formation constants were corrected by least squares method[9] and are presented in Table 1.

The formation of metal chelates takes place by replacement of hydrogen of the 2-hydroxynaphthyl group and coordination occurs through the oxygen of the ketonic group. The acid dissociation constant of the ligand was found to increase in different media in the order 2-ethoxy ethanol < acetone < dioxane. A plot of PK_L against 1/D is linear (where D is the dielectric constant). However in acetone-water solvent the dissociation constant of the ligand is less than the expected value and it may be attributed to the non-ideal behaviour of acetone-water solvent. The order of stability of the metal chelates observed in all the three mixed solvents studied is $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$.

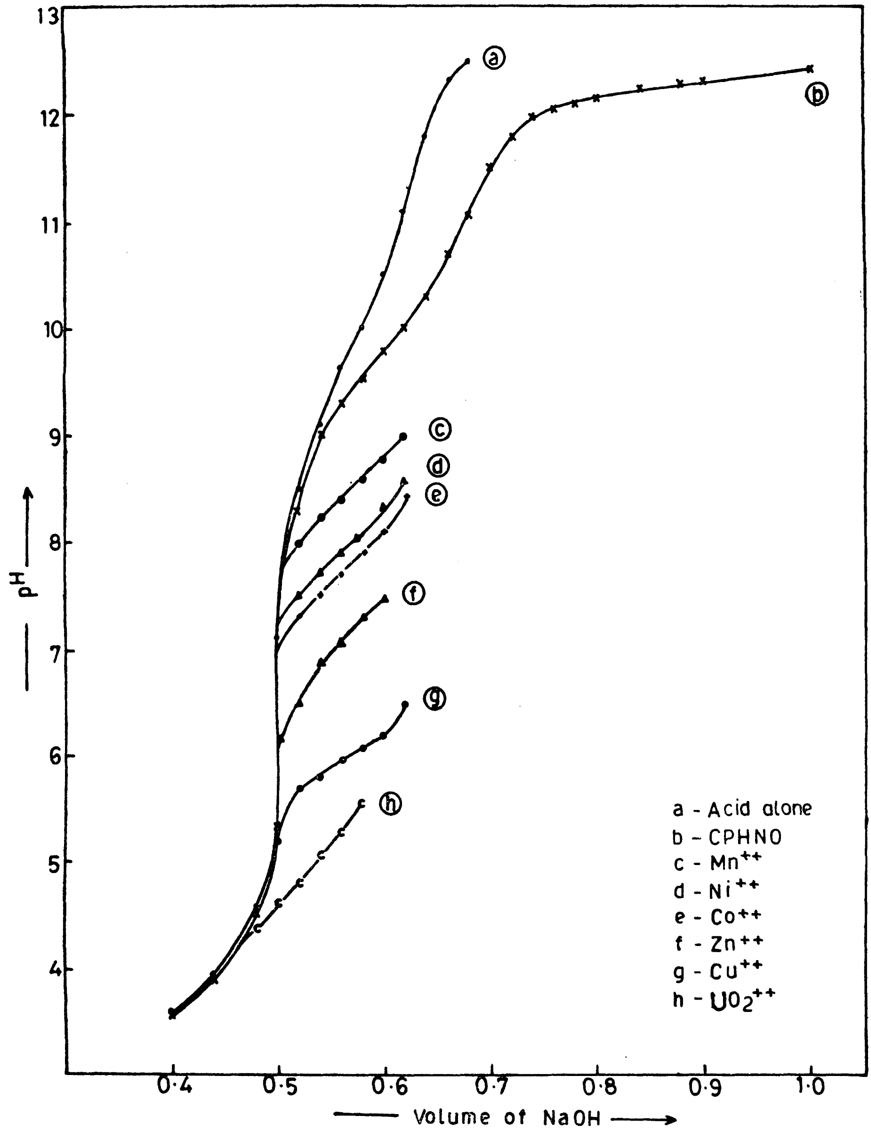

Fig. 1 pH titration curves at 30°C in 75% (v/v) aqueous dioxan

This order of stability follows the Irving-Williams[13] natural order except Co(II) leading to the conclusion that the ligand used in the present investigation is weak field one. The greater stability of Co(II) chelate when compared to Ni(II) chelate may be attributed to the additional stabilization due to Jahn-Teller distortion present in the former case.

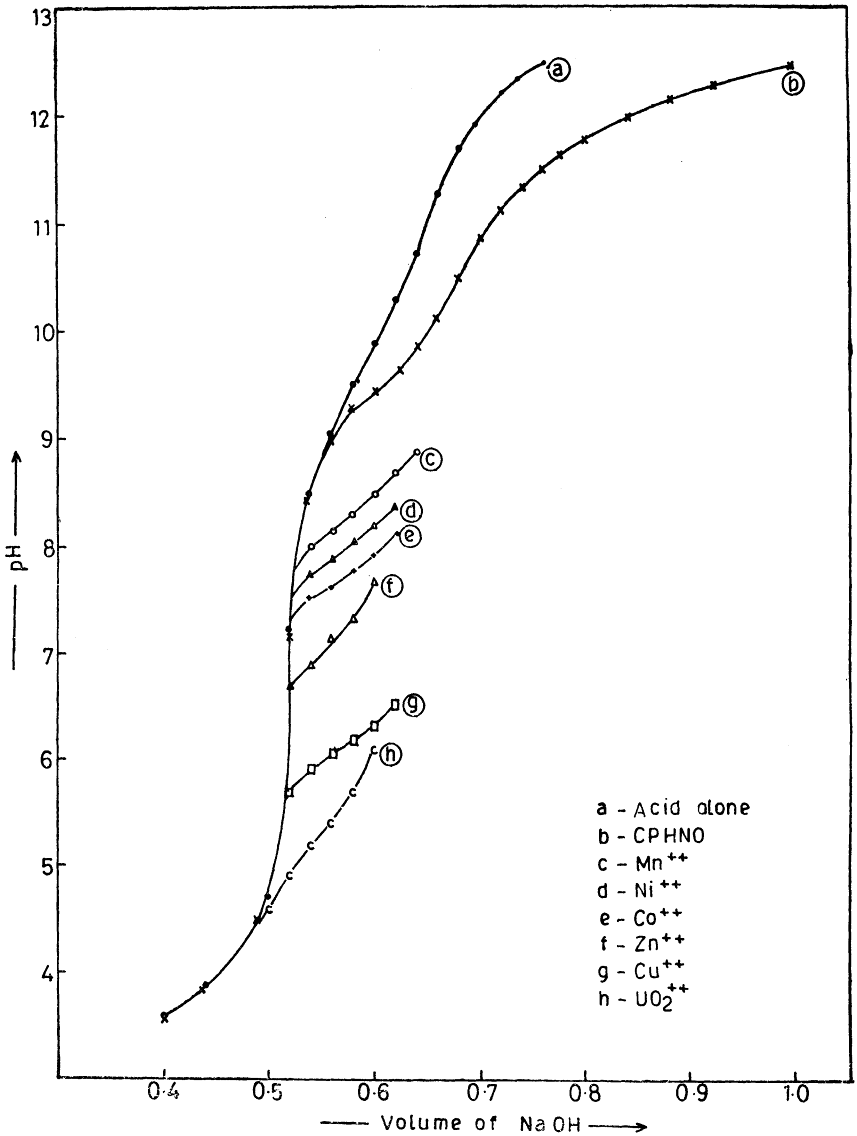

Fig. 2. pH titration curves at 35°C in 75% aqueous dioxane

The order Co(II) > Ni(II) has been reported for some other ligands also *viz.*, 4-nitro-2-amino phenol[14] 8-hydroxy-2-methyl quinolinol[15] and 2-hydroxychalcone[16]. The values of log β for Zn(II) chelates are greater than those for Ni(II). The order Zn(II) > Ni(II) has been observed earlier also[18-20] where the relative low value for Ni(II) has been attributed to

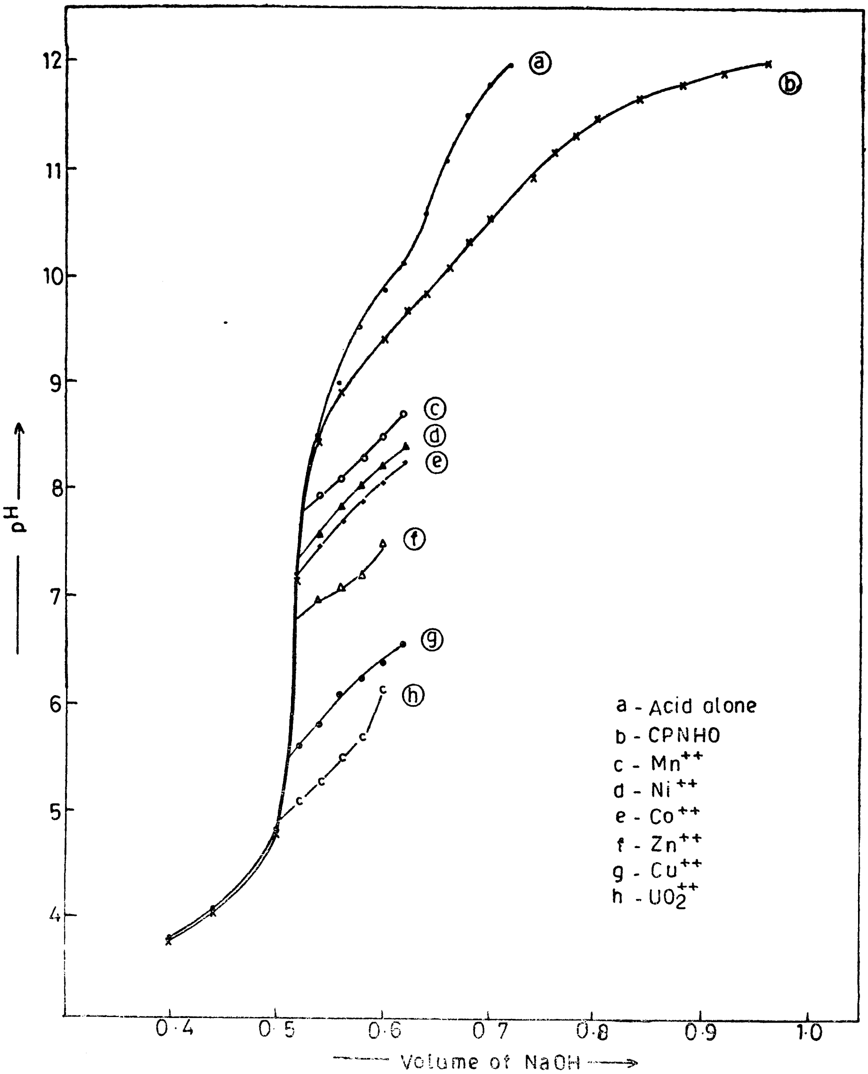

Fig. 3. pH titration curves at 40°C in 75% (v/v) aqueous dioxane

the presence of a square planar structure. Further the hydrolysis constant of Zn(II) chelate is greater than that for Ni(II) indicates a greater affinity of Zn(II) for OH ions. This factor seems to be accurate for the order Zn(II) > Ni(II). The order of stability of complexes with respect to the solvent is dioxane > acetone > 2-ethoxy-ethanol. The dielectric constants for the pure as well as mixed solvent are in the order acetone > 2-ethoxy ethanol > dioxane. This also shows the abnormal behaviour of acetone-

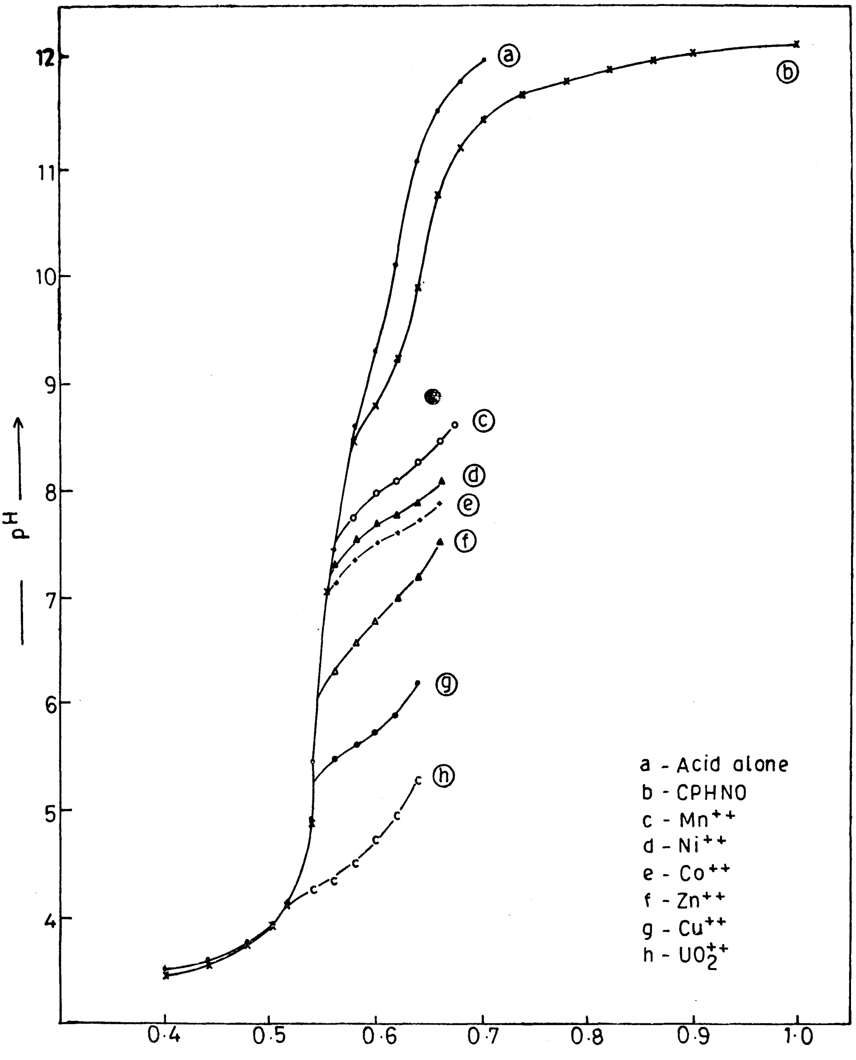

Fig. 4. pH titration curves at 30°C in 75% (v/v) aqueous Acetone

water mixture, similar abnormality was reported in the literature[17,18]. A pot of log β_2 versus ionisation potential shows that the stabilities of the complexes can be better correlated with the second ionisation potential rather than the first.

The data presented in Table 1 shows that the difference between log K_1 and log K_2 values are small and the ratio of log K_1/log K_2 is

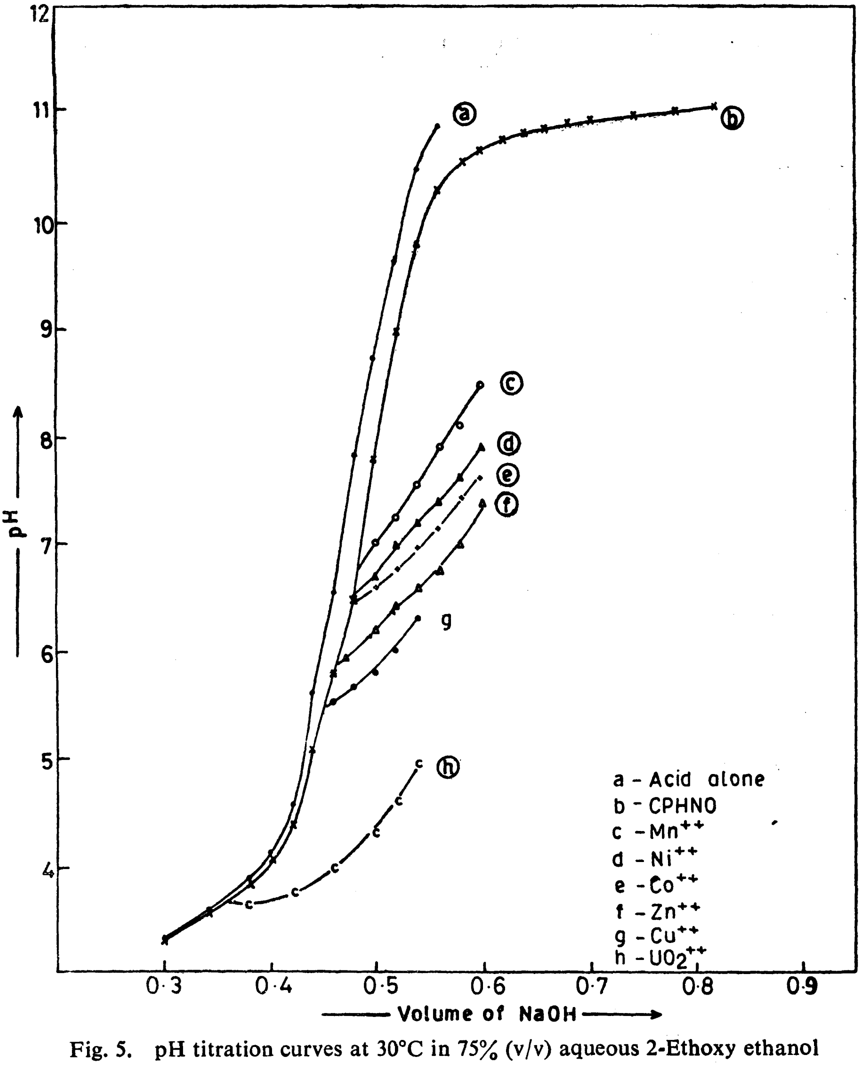

Fig. 5. pH titration curves at 30°C in 75% (v/v) aqueous 2-Ethoxy ethanol

positive in all cases indicating that there is little (or) no steric-hindrance to the addition of the second ligand molecule[19]. It is also evident from the values of log K_1 and log K_2 that there is almost equal tendency for the formation of neutral complex species ML_2 as for the species ML^+.

The stability constant values decrease with increase in temperature (Table 1) which is in agreement with the conclusions reached by Pitzer[20]. The thermodynamic parameters free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change have been calculated[21] from the stability constants of the metal complexes determined at three different temperatures in 75% dioxane, and are given in Table 2.

TABLE 1

STABILITY CONSTANTS OF BIVALENT TRANSITION METAL COMPLEXES WITH CPHNO AT DIFFERENT TEMPERATURES AND DIFFERENT SOLVENT MEDIA

(Ionic Strength 0.1 M)

		75% Dioxane			75% Acetone	75% 2-Ethoxy ethanol
		30°C	35°C	40°C	30°C	30°C
UO_2^{2+}	log K_1	10.85	10.40	10.10	10.50	10.22
	log K_2	10.10	9.70	9·58	10.08	10.04
	log β_2	20.95	20.10	19.68	20.60	20.26
Cu^{2+}	log K_1	9.70	9.40	9.28	9.38	9.38
	log K_2	9.26	9.05	8.70	9.13	8.68
	log β_2	18.96	18.45	17.96	18.51	17.98
Zn^{2+}	log K_1	8.68	8.18	8.08	8.30	8.24
	log K_2	7.84	7.74	7.64	8.02	7.62
	log β_2	16.52	15.94	15.72	16.32	15.86
Co^{3+}	log K_1	7.85	7.70	7.48	7.50	7.20
	log K_2	7.29	7.12	7.04	7.13	6.85
	log β_2	15.14	14.82	14.52	14.64	14.05
Ni^{2+}	log K_1	7.40	7.31	7.24	7.40	7.10
	log K_2	7.12	7.00	6.88	7.04	6.63
	log β_2	14.52	14.31	14.12	14.44	13.73
Mn^{2+}	log K_1	7.35	7.10	7.05	7.30	6.88
	log K_2	6.84	6.68	6.38	6.52	6.05
	log β_2	14.19	13.76	13.43	13.82	12.93

TABLE 2

THERMODYNAMIC PARAMETERS OF TRANSITION METAL COMPLEXES WITH CPHNO IN 75% DIOXANE

Metal	$-\Delta G$ K. J. mole^{-1}	$-\Delta H$ K. J. mole^{-1}	$+\Delta S$ J. deg^{-1} mole^{-1}
UO_2^{2+}	121.29	109.42	39.17
Cu^{2+}	110.04	87.05	75.87
Zn^{2+}	95.88	70.73	82.93
Co^{2+}	87.86	52.84	92.48
Ni^{2+}	84.29	54.58	97.18
Mn^{2+}	81.02	53.06	98.02
	ΔG values at 30°C		

Error limits are: ±0.01 for ΔG and ΔH; and ±0.1 for ΔS

The ΔG values are all negative and suggest that complexation is a spontaneous process. These values become less negative at higher temperatures indicating that low temperature favours complexation. The negative ΔH values for complex formation indicate the release of energy during the interaction of metal ions with ligand. The ΔH values of the complex formation of CPHNO with metal complexes follows the order $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$, in agreement with the natural order of the stability constants. The values of ΔS are positive for all the system, indicating that entropy is favourable for the complex formation.

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