Thermodynamics of Substituted Pyrazolone VIII. Potentiometric, Spectrophotometric, and Conductometric Studies of 4-(4-Nitrophenylazo)-3-methyl-1-(2-hydroxy-3-morpholinopropan-1-yl)-2-pyrazolin-5-one and its Metal Complexes

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Proton—ligand dissociation constant of 4-(4-nitrophenylazo)-3-methyl-l-(2-hydroxy-3-morpholinopropan-1-yl)-2-pyrazolin-5-one (NAMP) and metal—ligand stability constants of its complexes with some transition metal ions were measured potentiometrically in 0.1 M-KCl and 40 vol. % ethanol—water. The order of stability constants was found to be

$$K(UO_2^{2+}) > K(Ce^{3+}) > K(La^{3+}) > K(Mn^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}) > K(Zn^{2+})$$

The dissociation constant pK_1^H of NAMP and the stepwise stability constants log K of its complexes were determined at different temperatures (298 K, 308 K, and 318 K). The corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed. The dissociation process is nonspontaneous, endothermic, and entropically unfavourable. The formation of the complexes was found to be spontaneous, exothermic or endothermic (depending on the metal) and entropically favourable. The stoichiometries of the complexes were determined spectrophotometrically and conductometrically and indicate the formation of n(metal):n(ligand) = 1:1 and 1:2 complexes.

In recent years there has been considerable interest in the coordination chemistry of the azopyrazolone donor. In part, this interest has arisen because of the biological importance of this donor system [1]. A number of metal complexes containing azopyrazolone donors have been characterized [2—4].

In continuation of our earlier work [5—8] on the metal complexes, we report herein the dissociation constant of 4-(4-nitrophenylazo)-3-methyl-l-(2-hydroxy-3-morpholinopropan-1-yl)-2-pyrazolin-5-one (NAMP), and the stability constants for its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} at different temperatures are determined potentiometrically. The corresponding thermodynamic parameters are derived and discussed. Moreover, the stoichiometries of these complexes are determined spectrophotometrically and conductometrically.

EXPERIMENTAL

NAMP was prepared according to the method [4, 5]. Its purity (m.p. = 175 °C) was checked by elemental analysis, IR, and ^{1}H NMR spectra.

Metal-ion solutions ($c = 0.001$ mol dm^{-3}) were prepared from AnalaR metal chlorides in bidistilled water and standardized with EDTA [9]. The ligand solution ($c = 0.01$ mol dm^{-3}) was prepared by dissolving the accurate mass of the solid in ethanol (AnalaR). Solution of 0.01 M-HCl and 1 M-KCl was also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40 vol. % ethanol—water was used as titrant and standardized against AnalaR oxalic acid.

The absorption spectra of NAMP were recorded in the wavelength region of 200—600 nm on a Perkin—Elmer Lambda 2 apparatus equipped with a thermostatted cell holder using a 1 cm quartz cell.

Solutions of 10^{-4} mol dm^{-3} metal ions were titrated with 10^{-3} mol dm^{-3} NAMP. These titrations were performed using YSI model 32 conductivity meter at 298 K.

Table 1. Potentiometric Thermodynamic Functions for the Dissociation of NAMP in 40 vol. % Ethanol—Water and 1 M-KCl at Different Temperatures

T/K	Dissociation constant pK_1^H	Free energy change ΔG_1/(kJ mol^{-1})	Enthalpy change ΔH_1/(kJ mol^{-1})	Entropy change $-\Delta S_1$/(J mol^{-1} K^{-1})
298	7.50	42.79		
308	7.33	43.22	30.70 (± 0.77)	40.57 (± 0.04)
318	7.16	43.59		

Error is given in parentheses.

Table 2. Stepwise Stability Constants for ML and ML_2 Complexes of NAMP in 40 vol. % Ethanol—Water and 0.1 M-KCl at Different Temperatures

M^{n+}	298 K				308 K				318 K			
	log K_1	log K_2	log K_β	log K_1/log K_2	log K_1	log K_2	log K_β	log K_1/log K_2	log K_1	log K_2	log K_β	log K_1/log K_2
Mn^{2+}	5.21	4.45	9.66	1.17	5.24	4.49	9.73	1.17	5.29	4.57	9.86	1.16
Co^{2+}	5.62	4.97	10.59	1.13	5.67	5.02	10.69	1.13	5.72	5.07	10.79	1.13
Ni^{2+}	6.08	5.19	11.27	1.17	6.04	5.13	11.17	1.18	6.02	5.06	11.08	1.19
Cu^{2+}	6.77	5.72	12.49	1.22	6.88	5.66	12.54	1.22	6.97	5.58	12.35	1.21
Zn^{2+}	6.54	5.32	11.86	1.23	6.47	5.28	11.75	1.23	6.40	5.25	11.65	1.22
La^{3+}	6.69	5.58	12.27	1.20	6.64	5.52	12.16	1.20	5.57	5.47	12.03	1.20
Ce^{3+}	7.20	6.14	13.34	1.17	7.16	6.11	13.27	1.17	7.12	6.07	13.20	1.17
UO_2^{2+}	7.32	6.25	13.57	1.17	7.28	6.19	13.47	1.18	7.27	6.13	13.40	1.19

Apparatus, general conditions, and methods of calculation were the same as in the previous works [10, 11]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.02 M-NaOH in 40 vol. % ethanol—water:

1—5 cm^3 0.01 M-HCl + 5 cm^3 1 M-KCl + 20 cm^3 EtOH
2—5 cm^3 0.01 M-HCl + 5 cm^3 1 M-KCl + 10 cm^3 EtOH + 10 cm^3 0.001 M-ligand
3—5 cm^3 0.01 M-HCl + 5 cm^3 1 M-KCl + 10 cm^3 EtOH + 10 cm^3 0.001 M-ligand + 10 cm^3 2×10^{-4} M-metal salt

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. A constant temperature was adjusted to ± 0.05 K using an ultrathermostat (Neslab 2, RTE-220). The pH-meter readings in 40 vol. % ethanol—water are corrected according to the *van Uitert* and *Hass* [12].

RESULTS AND DISCUSSION

The average number of protons associated with NAMP at different pH values, $\overline{N}_A$, was calculated from the titration curves of acid in the absence and presence of NAMP. Thus, the formation curves ($\overline{N}_A$ *vs.* pH) for the proton—ligand systems were constructed and found to extend between 0 and 1 in the $\overline{N}_A$ scale. This means that NAMP has one dissociable proton (the enolized hydrogen ion of the carbonyl oxygen in the pyrazolone moiety). Different computational methods [13] were applied to evaluate the stepwise dissociation constants. The average values obtained are listed in Table 1.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\overline{N}$) *vs.* the free ligand exponent (pL) according to *Irving* and *Rossotti* [14]. These curves were analyzed and the successive stability constants were determined using different computational methods [15, 16]. The values of stability constants (log K_1, log K_2, and log β) as well as the ratio log K_1/log K_2 are given in Table 2. The following general remarks can be pointed out:

– The maximum $\overline{N}$ values in all cases were found to be ≅ 2, revealing that both ML and ML_2 types of complexes are formed in solution.

– No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide is excluded.

– The order of stability constants of the metal complexes of NAMP was found to be

$$K(UO_2^{2+}) > K(Ce^{3+}) > K(La^{3+}) > K(Mn^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}) > K(Zn^{2+})$$

The sequence of stability $K(Mn^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}) > K(Zn^{2+})$ of the complexes of NAMP is in agreement with that found by *Irving* and *Williams* [17, 18]. The order reflects the changes in the heat of complex formation across the series and arises from a combination of the influence of both the

Table 3. Thermodynamics for ML and ML_2 Complexes of NAMP in 40 vol. % Ethanol—Water and 1 M-KCl

M^{n+}	T/K	ΔG/(kJ mol^{-1})			ΔH/(kJ mol^{-1})			ΔS/(J mol^{-1} K^{-1})		
		$-\{\Delta G_1\}$	$-\{\Delta G_2\}$	$-\{\Delta G_\beta\}$	$\{\Delta H_1\}$	$\{\Delta H_2\}$	$\{\Delta H_\beta\}$	$\{\Delta S_1\}$	$\{\Delta S_2\}$	$\{\Delta S_\beta\}$
Mn^{2+}	298	29.73	25.39	55.12	7.76	11.4	19.25	125.72	123.63	249.35
	308	30.90	26.52	57.42				(± 0.12)	(± 0.14)	(± 0.12)
	318	32.25	27.85	60.10						
Co^{2+}	298	32.07	28.38	60.45	9.07	8.20	17.27	138.05	122.7	260.83
	308	33.46	29.60	63.06				(± 0.01)	(± 0.01)	(± 0.01)
	318	34.83	30.83	65.66						
Ni^{2+}	298	34.69	29.64	64.33	−5.93	−12.18	−18.11	96.52	58.60	155.12
	308	35.65	30.25	65.90				(± 0.01)	(± 0.03)	(± 0.01)
	318	36.62	30.81	67.43						
Cu^{2+}	298	39.79	32.67	72.46	−18.73	−13.14	−31.87	70.78	65.58	136.36
	308	40.57	33.38	73.95				(± 0.09)	(± 0.08)	(± 0.09)
	318	41.22	33.98	75.19						
Zn^{2+}	298	37.32	30.35	67.67	−12.64	−6.11	−18.75	82.80	81.31	164.11
	308	38.15	31.14	69.29				(± 0.01)	(± 0.03)	(± 0.02)
	318	38.97	31.96	70.93						
La^{3+}	298	38.17	31.84	70.01	−10.89	−10.3	−21.23	91.61	72.16	163.77
	308	39.16	32.58	71.74				(± 0.10)	(± 0.03)	(± 0.10)
	318	40.00	33.27	73.27						
Ce^{3+}	298	41.08	35.03	76.11	−6.76	−6.38	−13.14	115.17	96.19	211.36
	308	42.25	36.03	78.28				(± 0.03)	(± 0.05)	(± 0.03)
	318	43.38	36.96	80.34						
UO_2^{2+}	298	41.76	35.66	77.42	−4.55	−11.35	−15.90	124.80	81.61	206.41
	308	42.93	36.53	79.46				(± 0.12)	(± 0.08)	(± 0.12)
	318	44.26	37.29	81.55						

Error is given in parentheses.

polarizing ability of the metal ion [18] and crystal-field stabilization energies [19]. The greater stability of Cu^{2+} complexes results from the well-known Jahn—Teller effect. The stability constant of the divalent oxygenized cation complex (UO_2^{2+}) has higher value than those of the other divalent cation complexes (Table 2). This may be attributed to the bonded oxygen atoms which may increase the electrostatic attraction between the metal ion and the coordinated ligands and overcome any steric hindrance offered by the oxygen of the oxygenized cation [20].

The dissociation constant (pK_1^H) for NAMP as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 1 and 2. The slope of the plot (pK_1^H or $\log K$ *vs.* $1/T$) was utilized to evaluate the enthalpy change for the dissociation or complexation process, respectively. From the free energy change ΔG and ΔH values one can deduce the entropy change ΔS using eqns (*1*) and (*2*)

$$\Delta G = -2.303RT \log K = 2.303RT \cdot pK \qquad (1)$$

$$T\Delta S = \Delta H - \Delta G \qquad (2)$$

All thermodynamic parameters of the dissociation process of NAMP are listed in Table 1. Inspection of these values reveals that:

– The pK_1^H value decreases with increasing temperature revealing that its acidity increases with increasing temperature [5].

– A positive value of ΔH indicates that its dissociation is accompanied by adsorption of heat and the process is endothermic.

– A large positive value of ΔG indicates that the dissociation process is not spontaneous.

– A negative value of ΔS is obtained due to the increased order as a result of solvation processes [4].

All the thermodynamic parameters of the stepwise stability constants of NAMP complexes are listed in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as a sum of two contributions, the release of H_2O molecules and metal—ligand bond formation.

It was suggested [21] that the ions in aqueous solution order the water molecules around them and during complex formation between oppositely charged ions (ligand L^- and M^{n+}) lead to the breakdown of metal—water arrangement resulting in positive entropy and enthalpy changes. Examination of these values shows that:

– The stepwise stability constants ($\log K_1$ and $\log K_2$) for NAMP complexes decrease with increasing temperature for Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{2+}, Ce^{2+},

Table 4. Spectral Data of NAMP in Different Organic Solvents[a]

Solvent	First band		Second band	
	$\{\lambda_{max}\}$	$\{\varepsilon_{max}\}$	$\{\lambda_{max}\}$	$\{\varepsilon_{max}\}$
C_2H_5OH	240	55826.09	404	9756.22
CCl_4	260	sh	400	sh
Cyclohexane	230	sh	392	sh
Isopropanol	240	35478.26	402	64695.65
n-Propanol	240	37826.09	402	67043.48
Chloroform	244	24521.74	397	60000.00
Methanol	240	42782.61	406	63652.17
Diethyl ether	240	57913.04	394	82956.52

a) $c = 2.5 \times 10^{-5}$ mol dm^{-3}.

and UO_2^{2+} whereas with Mn^{2+} and Co^{2+} the reverse happens, *i.e.* their stability constants increase with increasing the temperature [8].

– The negative values of ΔG for the complexation process of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{2+}, and UO_2^{2+} with NAMP suggest a spontaneous nature.

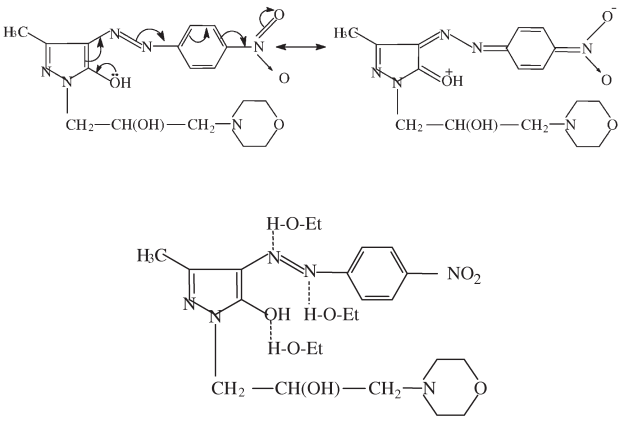
– The ΔH values are negative for Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} whereas in the case of Mn^{2+} and Co^{2+} they are positive. This means that these processes are exothermic and favourable at lower temperatures for Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} complexes, while in the case of Mn^{2+} and Co^{2+} complexes the process is endothermic and favourable at higher temperature.

– The positive values of ΔS for the complexation process of NAMP with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} confirm that the complex formation is entropically favourable. This may be due to the exposure of the polar oxygen, nitrogen, and metal ion of the chelate to solvent molecules [22].

The spectrum of NAMP was recorded in organic solvents of different polarities. The λ_{max} and ε_{max} values of the different bands obtained from the spectra are collected in Table 4. The electronic absorption spectra are composed of two sets of bands. The first one (A) in the interval 240—260 nm is due to the medium energy ($\pi \rightarrow \pi^*$) transition corresponding to the transition within the aromatic system and its conjugation [5]. The second one (B) in the interval 392—406 nm is mainly strong and high intense and can be assigned to the intramolecular charge transfer within the whole molecule. NAMP has a red shift of the charge transfer (CT) band and due to the presence of *p*-NO_2 (electron-accepting group) will enhance the electron density by its high positive mesomeric and positive inductive effects, respectively.

Also, the blue shift of CT band is due to the intermolecular hydrogen bonding formed between the solvent molecules and the *n*-electrons of OH and N═N groups.

The spectra of 5×10^{-5} M-NAMP in 30 vol. % ethanol—water within the pH range 2—12 and at



298 K were recorded. The spectra of NAMP in aqueous buffer solutions show regular changes with increasing pH of the medium, especially the CT band at 404 nm. Increasing the pH leads to an increase of the absorbance till it attains a constant value at 9.5. The CT band becomes broad and exhibits a red shift as a result of the ionization of the phenolic OH group.

The pK_1^H value of NAMP (Table 5) was obtained by applying different spectrophotometric methods, namely, the halfheight [23], modified limiting absorbance [24], and the modified Colleter method [25] at 298 K.

This study was carried out to determine the optimum pH at which NAMP forms a coloured complex with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+}. Thus, solutions containing 5×10^{-4} mol dm^{-3} of metal ion and 5×10^{-4} M-NAMP in Britton universal buffer of varying pH and in 30 vol. % ethanol—water were used. Measurements have shown that the pH at which the maximum complex formation occurs depends on the metal ion (Table 5). The sequence of addition metal—buffer—ligand or ligand—buffer—metal has no effect on the optimum pH values for the complexes. However, at pH values higher than these values the absorbance of the complexes decreases with increasing pH, which may be attributed to their decomposition.

It was found that the complexes are completely

Table 5. Stoichiometry of M^{n+}—NAMP Complexes in 20 vol. % Ethanol—Water by Mole Ratio (M. R.) and Continuous Variation (C. V.) Methods at 298 K

Complex	pH	λ_{max}/nm	Stoichiometry	
			M. R.	C. V.
Mn^{2+}—NAMP	7.0	480	1:1	1:1
			1:2	1:2
Co^{2+}—NAMP	7.5	480	1:1	1:1
			1:2	1:2
Ni^{2+}—NAMP	7.0	480	1:1	1:1
			1:2	1:2
Cu^{2+}—NAMP	8.5	488	1:1	1:1
			1:2	1:2
Zn^{2+}—NAMP	8.0	490	1:1	1 :1
			1:2	1:2
La^{3+}—NAMP	5.0	510	1:1	1:1
			1:2	1:2
Ce^{3+}—NAMP	4.0	500	1:1	1:1
			1:2	1:2
UO_2^{2+}—NAMP	4.5	505	1:1	1:1
			1:2	1:2

Table 6. Stoichiometry of M^{n+}—NAMP Complexes Using Conductometric Titration

M^{n+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	La^{3+}	Ce^{3+}	UO_2^{2+}
M^{n+}—NAMP	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2

developed spontaneously and remain constant for 48 h. It was also found that raising the temperature up to 333 K has no effect on the formation of the complexes, whereas boiling destroys the formed complexes.

Stoichiometries of the complexes result from measurements in the range 200—600 nm for the complex solution with NAMP at the optimum pH values with characteristic absorption maxima (Table 5). These studies were carried out to investigate the stoichiometries of the formed complexes from the mole ratio [26] and using continuous variation [27] methods. Both methods indicated the formation of n(metal):n(ligand) = 1:1 and 1:2 complexes with the metal under investigation (Table 5).

Stoichiometries of the complexes of NAMP with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, and UO_2^{2+} result from the conductometric measurements. These studies were carried out to investigate the stoichiometries of the formed complexes by breaks denoting the formation of n(metal):n(ligand) = 1:1 and 1:2 complexes (Table 6). Therefore, the reaction between the metal ions and NAMP occurs *via* the formation of a covalent linkage with the oxygen of the OH group (pyrazolone moiety) and the nitrogen of the azo group. The increase in conductance upon titrating metal ions by NAMP is probably due to the liberation of the hydrogen ions from the OH during the complex formation [5]. The decrease of the conductance value occurs due to i) the increase of the volume of the metal ion chelate formation which is accompanied by the decrease in the value of diffusion coefficient of the particle, ii) the lowering of the charge on the metal ion through covalent bond formation with NAMP.

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