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THERMODYNAMIC AND SPECTROPHOTOMETRIC STUDIES OF ACETOACETANILIDEHYDRAZONE COMPLEXES OF Cu(II), Ni(II) AND Co(II) METAL IONS

MOHAMED S. ABDEL MOEZ *, BASHEIR A. EL-SHETARY and MOHAMED F. EID
Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Cairo (Egypt)

FAROUK I. ZIDAN
Chemistry Department, Faculty of Science, Al-Azhar University, Cairo (Egypt)

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ABSTRACT

Complexes of *o*-carboxyphenylhydrazoneacetoacetanilide (*o*-CPHAA) with Cu(II), Ni(II) and Co(II) were studied in dioxane–water using the Irving and Rossotti method over the temperature range 10–40 ° C and at constant ionic strength (0.1 M). The acid dissociation constant $pK_{1,2}^{H}$ of the ligand and the stepwise stability constants (log K_1 and log K_2) of the complexes formed were computed at various temperatures. The values of the stepwise and overall changes in ΔG, ΔH and ΔS accompanying the neutralization of the ligand and complex formation were evaluated. This study reveals that the ionization of the ligand in the mixed solvent is an endothermic process, whereas the complex formation is an exothermic reaction. The optimum conditions for complex formation and the composition and stability constants (log K_1) of the complexes formed in solution between the ligand and Cu(II), Ni(II) and Co(II) were also determined (spectrophotometrically).

INTRODUCTION

Various studies have been carried out on the chelation of divalent metal ions with acetoacetanilide and other related ligands [1–3]. Relatively little attention has been paid to the complexation of transition metal ions with phenylhydrazoneacetoacetanilide (PHAA) and related compounds [4]. Although some information is available on the stability constants of acetoacetanilidehydrazone ligands [5,6], nothing on the thermodynamics of these ligands and their complexes with metals has been mentioned in the literature.

Therefore, in this investigation the acid dissociation constants of the *o*-CPHAA ligand and the stability constants of metal complexes (Cu(II),

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* Author to whom correspondence should be addressed.

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Ni(II) and Co(II)) were determined over the range 10–40 ° C. From this study, the thermodynamic parameters ΔG, ΔH and ΔS were evaluated. In addition the composition and stability constants of the complexes formed in solution were determined spectrophotometrically.

EXPERIMENTAL

Preparation of the o*-CPHAA ligand*

The diazonium salt of anthranilic acid was mixed with acetoacetanilide (AA) in sodium acetate medium as described previously [7]. The high purity of the ligand was checked by elemental analysis, melting point measurement and IR spectral analysis [5].

Reagents and materials

Standard solutions of metal ions were prepared by dissolving the required weights of AnalaR nitrate salts in bidistilled water. They were standardized following the recommended method [8]. Carbon dioxide free potassium hydroxide solution was prepared and standardized as described previously [8]. Freshly purified dioxane distillate [9] was used for the various studies. A 0.01 M *o*-CPHAA solution in dioxane was prepared and the desired concentrations were obtained by appropriate dilutions of stock solution. The pH readings were corrected in dioxane–water as described by Irving and Mahnat [10]. During the titrations, the desired temperature was maintained constant using a double-jacket cell as previously described [5]. Oxygen-free nitrogen gas was passed through the solution during the measurements.

Apparatus

The pH-metric titrations were carried out using a WTW digital pH-meter fitted with a combined electrode. The pH-meter was calibrated using standard BDH buffer solutions. A Perkin-Elmer 550 S recording spectrometer was used for the UV and visible spectra measurements. The IR spectrum was recorded in the solid state on a Perkin-Elmer model 437 spectrometer using the KBr technique.

RESULTS AND DISCUSSION

pH-metric study

The titration curves of the free ligand (*o*-CPHAA) and of mixtures of metal–ligand (ratio 1 : 2) are shown in Fig. 1. The titration curve of the free

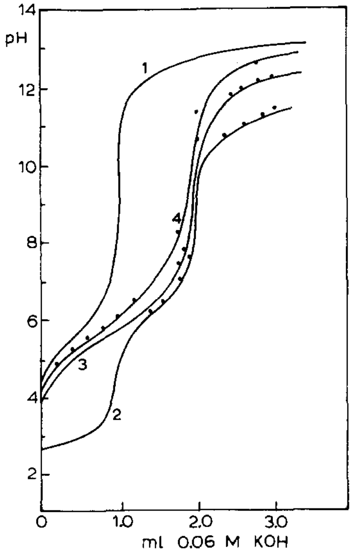

Fig. 1. Titration curves of M^{2+}–*o*-CPHAA complexes at 30 °C in 75% dioxane–water. 1, [*o*-CPHAA] = 2×10^{-3} M; 2, 1 + 1×10^{-3} M [Cu^{2+}]; 3, 1 + 1×10^{-3} M [Ni^{2+}]; 4, 1 + 1×10^{-3} M [Co^{2+}].

ligand shows two inflections corresponding to the deprotonation of carboxylic and hydrazone groups. The acid dissociation constants (pK_1^H and pK_2^H) were calculated using the method of Albert and Serjeant [11].

The pH readings were corrected in dioxane–water mixture as previously described [10]. Since the ionic product pK_w in 75% (v/v) dioxane–water is approximately 18.7 [12], the concentrations of H^+ and OH^- species are negligible in the region of proton dissociation. The dissociation constants pK_1^H and pK_2^H for the *o*-CPHAA ligand were calculated at various temperatures and the values obtained are given in Table 1. These values indicate that the neutralization reactions of the ligand studied are temperature dependent. From Arrhenius plots of log K_1^H and log K_2^H vs. $1/T$ the stepwise enthalpy changes ΔH_1 and ΔH_2 were deduced, and these are given in Table 1. The free energy changes ΔG_1 and ΔG_2 were also evaluated at various temperatures using the expression

$$-\Delta G^{\ominus} = 2.303RT \log K \quad (1)$$

where $pK_1^H = -\log K_1^H$ and $pK_2^H = -\log K_2^H$.

The mean values of ΔG_1 and ΔG_2 are listed in Table 1. Similarly the entropy changes ΔS_1 and ΔS_2 were evaluated using the following relationships

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (2)$$

$$-RT \ln K = \Delta H - T\Delta S \quad (3)$$

TABLE 1

Dissociation constants and thermodynamic parameters for the dissociation reaction of *o*-CPHAA in 75% (v/v) dioxane–water at 0.1 M ionic strength

Reaction	$pK_{1,2}^{H}$				$\Delta G^{\ominus}$ (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal K^{-1} mol^{-1})	
	10 °C	20 °C	30 °C	40 °C			method 1[a]	method 2[b]
$H_2L \rightleftharpoons H^+ + HL^-$	6.38	6.23	6.07	5.91	8.33	6.54	−6.01	−6.70
$HL^- \rightleftharpoons H^+ + L^{2-}$	13.15	12.89	12.65	12.36	17.28	11.44	−19.60	−21.16

[a] $\Delta S^{\ominus}$ calculated from eqn. (2). [b] $\Delta S^{\ominus}$ calculated from $T \log K$ vs. T plots.

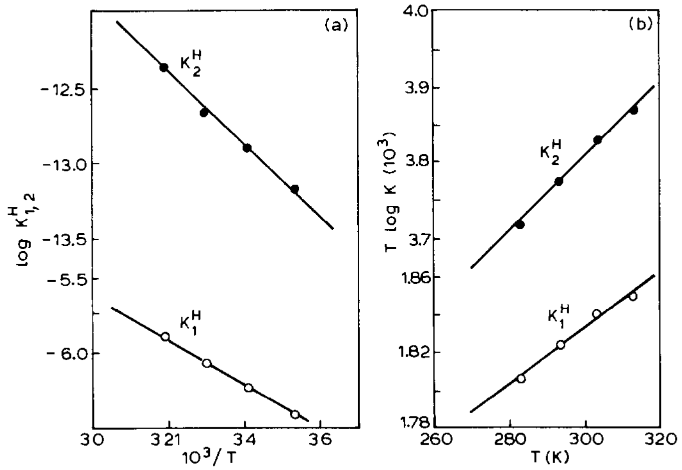

Fig. 2. a, log $K_{1,2}^{H}$ vs. $1/T$ plots of *o*-CPHAA; b, T log $K_{1,2}^{H}$ vs. T plots of *o*-CPHAA.

The stepwise entropy changes ΔS_1 and ΔS_2 for the ligand studied were evaluated either from eq. (2) or from the slope of Tlog K vs. T plots (Fig. 2). The values of ΔS_1 and ΔS_2 calculated by the two methods are in good agreement (Table 1).

The positive values of ΔH_1 and ΔH_2 indicate that the neutralization reactions of *o*-CPHAA are endothermic. The ionization of this ligand is enhanced with increasing temperature. It is evident from Table 1, that the heat of ionization required for the second dissociation reaction is much greater than that required for the first dissociation. The large positive values of ΔG_1 and ΔG_2 also indicate that the dissociation of *o*-CPHAA is not spontaneous and that a rise in temperature shifts the equilibrium to the right, i.e. it enhances the dissociation of the ligand.

The titration curves of *o*-CPHAA in the presence of Ni(II) and Co(II) ions at 30 °C show an inflection at $m = 4$ (where m = moles of base added per mole of metal ion) indicating the formation of ML_2 species (Fig. 1). This can be explained if the ligand under investigation behaves as a diprotic ligand. The formation of ML_2 species consumes 4 moles of base

$$2H_2L + M^{2+} + 4OH^- \rightleftharpoons ML_2 + 4H_2O$$

In contrast, the titration curve of the Cu(II) mixture (ligand : metal, 2 : 1) shows an inflection at $m = 2$ followed by a buffer zone and another inflection at $m = 4$. This accounts for the stepwise formation of ML and ML_2 species (Fig. 1). These results are in good agreement with the work of Taha and El-Inany [5] who showed that *o*-CPHAA and *o*-CPH-*p*-Cl-AA form ML_2 species with Ni(II) and Co(II), whereas a stepwise formation of ML and ML_2 species is observed for Cu(II).

The values of the stability constants (log K_1 and log K_2) of the chelates formed with Cu(II), Ni(II) and Co(II) obtained at various temperatures

TABLE 2

Stepwise formation constants and thermodynamic parameters of Cu(II)–*o*-CPHAA, Ni(II)–*o*-CPHAA and Co(II)–*o*-CPHAA chelates in 75% (v/v) dioxane–water at 0.1 M ionic strength

Metal ion	Temperature (°C)	log K_1	log K_2	$-\Delta G_1$ (kcal mol^{-1})	$-\Delta G_2$ (kcal mol^{-1})	$-\Delta H_1$ (kcal mol^{-1})	$-\Delta H_2$ (kcal mol^{-1})	ΔS_1 (cal mol^{-1})		ΔS_2 (cal mol^{-1})	
								Method 1[a]	Method 2[b]	Method 1[a]	Method 2[b]
Cu(II)	10	15.65	15.10	20.82	19.66	10.93	19.07	33.19	33.78	1.98	2.75
	20	15.14	14.55								
	30	15.20	14.16								
	40	14.86	13.71								
Ni(II)	10	11.74	10.64	15.55	14.19	9.15	8.80	21.74	21.79	18.09	19.61
	20	11.52	10.47								
	30	11.30	10.23								
	40	11.09	10.05								
Co(II)	10	11.60	10.16	15.06	13.28	14.30	11.73	2.55	2.75	5.19	6.64
	20	11.30	9.92								
	30	10.92	9.60								
	40	10.55	9.31								

[a] Calculated from eqn. (2). [b] Calculated from T log K vs. T plots.

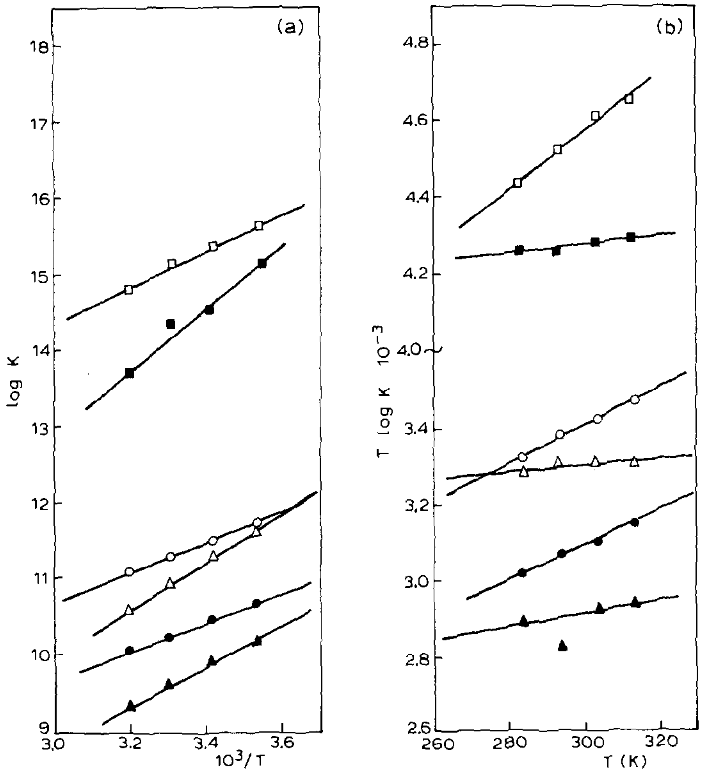

Fig. 3. a, log K vs. $1/T$ plots for Cu(II), Ni(II) and Co(II) complexes; b, T log K vs. T plots for Cu(II), Ni(II) and Co(II) complexes. Cu(II) complex: □, log K_1; ■, log K_2. Ni(II) complex: ○, log K_1; ●, log K_2. Co(II) complex: △, log K_1; ▲, log K_2.

using the method of Irving and Rossotti [13] are summarized in Table 2. The order of the stability of these chelate compounds follow the usual relative stabilities [14,15] for these metal ions, i.e. Cu(II) > Ni(II) > Co(II).

It is also clear from Table 2 that the stability of the complexes decreases with increasing temperature indicating that complex formation reactions are favourable at low temperature.

The stepwise thermodynamic parameters ΔG, ΔH and ΔS for the chelate compounds were calculated from the stepwise stability constants obtained at various temperatures as previously mentioned. The values of the thermodynamic parameters of the chelate compounds are summarized in Table 2. Arrhenius plots are presented in Fig. 3 to obtain ΔH and ΔH_2 values of the complexes formed. The large negative values of ΔG and ΔG_2 obtained in all cases indicate that the complex formation reactions proceed spontaneously. In addition, the values of ΔG_1 and ΔG_2 increase with an increase in temperature indicating that low temperature favours complexation [16]. These results are also confirmed by the negative ΔH values obtained in this study (Table 2). The positive entropy values observed for all metal chelates show that the stability of the complexes is mainly due to the ΔS values. It is well known that the enthalpy differences (ΔH) between chelated and non-chelated systems cannot in general, account for the chelate effect. The chelate effect is mainly an entropy effect [17]. Therefore, an increase in chelation corresponds to an increase in the positive values of S on complex formation. The results in Table 2 show that the magnitude of ΔS_1 for the Cu(II) complex (metal : ligand, 1 : 1) is positive and large. This confirms that the stability of this complex is mainly due to the ΔS_1 value and not to the ΔH_1 value [17]. Comparison of the entropy changes ΔS_1 and ΔS_2 for the Cu(II) chelates indicates that the formation of the 1 : 1 complex has a more favourable entropy change ($\Delta S_1 = 33$ cal K^{-1} mol^{-1}) compared with the 1 : 2 complex ($\Delta S_2 \approx 2.0$ cal K_2^{-1} mol^{-1}).

These results were confirmed by the spectrophotometric study of Cu(II) complex formation where the 1 : 1 complex was the only species formed in the solution.

The stepwise entropy changes ΔS_1 and ΔS_2 observed for the Ni(II) chelates were found to be of the same order of magnitude (Table 2). This indicates that both NiL and NiL$_2$ could be formed in solution. The similar values of ΔH_1 and ΔH_2 may also account for the above conclusion. The low entropy terms obtained for the Co(II) chelates (Table 2) could be explained on the basis that Co(II) complexes are less stable than both Cu(II) and Ni(II) chelates. It is also interesting to compare the stepwise entropy changes (ΔS_1 and ΔS_2) for the Co(II) complexes. The comparison shows that $\Delta S_1 > \Delta S_2$ indicating that the 1 : 2 complex is more stable than the 1 : 1 species. This result is further supported by the spectrophotometric study of Co(II) complex formation which indicates only the 1 : 2 species.

It is important to note that the exothermic values of the enthalpy changes ΔH_1 and ΔH_2 for the 1 : 1 and 1 : 2 metal chelates (Table 2) are fairly high and cannot be accounted for by the metal carboxylate bond only. This indicates the involvement of the nitrogen of the hydrazone group in chelation. These results are in good agreement with the work of Sharma et al. [18] who showed that the contribution of the carboxylate group to the total change in enthalpy is generally very small and is sometimes endothermic, e.g. in metal carboxylate complexes involving malonate and succinate.

Spectrophotometric study

The absorbance spectra of the mixtures of metal ions and ligand in 50% dioxane–water (v/v) medium were recorded in the region 300–600 nm against a blank of the ligand prepared under the same conditions. The following absorption bands were observed: Cu(II) complex, 440 and 400 nm; Ni(II) complex, 460 and 420 nm; Co(II) complex, 490, 430 and 320 nm.

The optimum pH values for complex formation were observed to be higher than pH 5.0 for Cu(II) complexes and higher than pH 6.5 for Co(II)

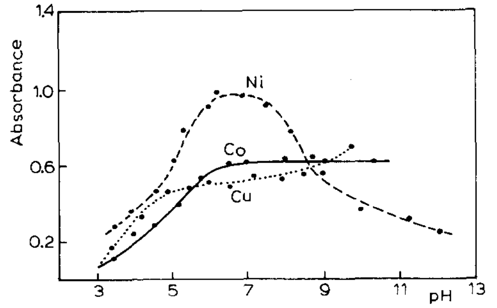

Fig. 4. Effect of pH on the absolute of metal(II)-*o*-CPHAA complexes ([M] = 5×10^{-5} M, [L] = 1×10^{-4} M) at $\lambda = 450$ nm. ······ Cu(II) complex; ------ Ni(II) complex; —— Co(II) complex.

complexes. For the formation of the Ni(II) complex the optimum pH range was between 6.0 and 8.0 (Fig. 4). The optimum reagent concentrations were 1×10^{-3}–2×10^{-3} M of ligand or metal ion. The complex system is stable for several hours.

The complexes of Cu(II) Ni(II) and Co(II) obeyed Beer's law from 1.0×10^{-5} to 4.0×10^{-4} M. The molar absorptivity calculated for the Cu(II), Ni(II) and Co(II) complexes were 5800, 4800 and 2500 mol^{-1} cm^{-1}, respectively at 450 nm.

Composition of the complexes

The compositions of the metal–ligand systems in solution for Cu(II), Ni(II) and Co(II) were determined by the method of continuous variation [21]. Equimolar solutions of ligand and metal ion (2×10^{-4} M) were mixed to a volume of 10 ml. The Cu(II) : ligand and Ni(II) : ligand ratios were found to be 1 : 1, while the Co(II) : ligand ratio was found to be 1 : 2 (Fig. 5). The compositions of the complexes were further confirmed by other techniques such as the molar ratio [22], the slope ratio [23] and the limiting logarithmic [24] methods. The results from the different methods of analysis agree very closely.

Spectrophotometric determination of stability constants of metal chelates

The stability constants of the chelates were obtained spectrophotometrically by measuring the absorbance of solutions of the ligand–metal mixture at a fixed concentration but at various pH values (Fig. 4). The spectra of the free ligand and the fully formed complexes were also obtained. The degree of formation of the complex was obtained from the relationship [23]

$$\bar{n} = \frac{O_{D_X} - O_{D_L}}{O_{D_{ML}} - O_{D_L}} \qquad (4)$$

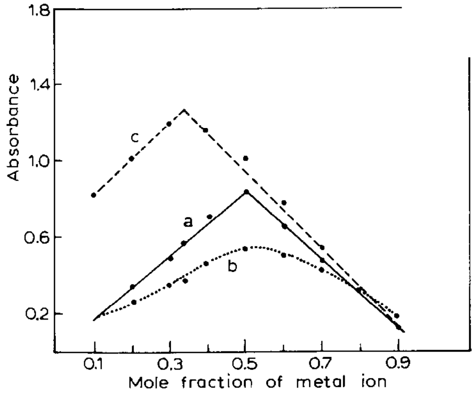

Fig. 5. Continuous variation method for metal(II)-*o*-CPHAA complexes ($[M] = [L] = 2\times10^{-4}$ M) at $\lambda = 450$ nm in 50% dioxane-water. a, Cu(II) complex; b, Ni(II) complex; c, Co(II) complex.

where O_{D_X}, O_{D_L} and $O_{D_{ML}}$ are the absorbances of the partially formed complex at a specific pH, the free ligand and the fully formed complex, respectively. The absorbance O_{D_L} of the ligand at measured wavelength has been cancelled, since the same concentration of the ligand solutions were used as blank during the measurements. The negative logarithm of the

TABLE 3

Stability constants for the metal complexes in 50% dioxane-water ($T_M = 5\times10^{-5}$ M, $T_L = 1\times10^{-4}$ M, $\lambda_{max} = 450$ nm, pK_1^H ligand = 6.06, pK_2^H ligand = 12.65 at 30 °C)

pH	O_{D_X}	$O_{D_{ML}}$	$\bar{n}$	pL	log K_1
Cu(II)-*o*-CPHAA complex					
3.40	0.115	0.80	0.144	15.94	15.16
4.10	0.210	0.80	0.390	14.74	14.54
4.80	0.430	0.80	0.538	13.38	13.45
					Mean = 14.383 ± 0.706
Ni(II)-*o*-CPHAA complex					
5.00	0.610	0.93	0.630	12.880	12.653
5.20	0.640	0.93	0.660	12.494	12.205
5.40	0.785	0.93	0.810	12.146	11.515
6.00	0.900	0.93	0.930	10.99	9.868
					Mean = 11.56 ± 1.057
Co(II)-*o*-CPHAA complex					
5.00	0.39	0.63	0.619	12.880	12.67
5.20	0.43	0.63	0.635	12.480	12.25
5.50	0.47	0.63	0.746	11.922	11.20
5.80	0.525	0.63	0.830	11.350	10.60
					Mean = 11.68 ± 0.822

concentration of the non-protonated ligand (pL) was obtained using eqn. (5) [24]

$$\mathrm{pL} = \log_{10}\left[\frac{B_0^{\mathrm{H}} + B_1^{\mathrm{H}}\mathrm{H}^+ + B_2^{\mathrm{H}}\mathrm{H}^{+2}}{(T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}})}\right] \tag{5}$$

where $B_0^{\mathrm{H}} = 1$, and B_1^{H} and B_2^{H} are the reciprocals of the acid dissociation constants of the ligand, i.e. $[\mathrm{LH}]/[\mathrm{L}][\mathrm{H}^+]$ and $[\mathrm{LH}_2]/[\mathrm{L}][\mathrm{H}^+]^2$ respectively. T_{L} and T_{M} are the stoichiometric concentrations of the ligand and metal ion. The equation of the formation curve is

$$\bar{n} + (\bar{n} - 1)K_1[\mathrm{L}] = 0 \tag{6}$$

where K_1 is the stability constant of the ML complex. The stability constants K_1 calculated using eqn. (6) at various pH values are shown in Table 3. The values of the stability constants (log K_1) determined using the spectrophotometric method were in good agreement with those obtained from the pH-metric study.

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