

## Thermodynamic studies of some complexes of 4'-morpholinoacetophenone thiosemicarbazone

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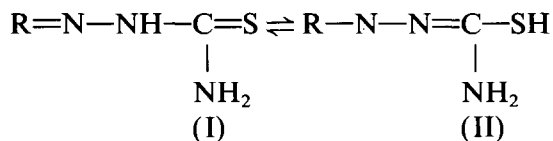
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### Abstract

Ni(II), Cu(II), Ag(I) and Hg(II) form 1:2 (metal–ligand) complexes with 4'-morpholinoacetophenone thiosemicarbazone. The stability constants of these complexes in 60% (v/v) aqueous DMF were determined at different ionic strengths (0.07, 0.13 and 0.20 M) and at different temperatures (25, 30, 35 and  $40 \pm 0.1^\circ\text{C}$ ) using a spectrophotometric method. From these constants, the thermodynamic stability constants and thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) were calculated.

### INTRODUCTION

In solution, thiosemicarbazones probably consist of an equilibrium mixture of the thion (I) and thiol (II) tautomers.



where R is the remaining group when the carbonyl oxygen atom has been removed from an aliphatic, aromatic, or heterocyclic aldehyde or ketone.

Investigations of metal–thiosemicarbazone complexes indicate that the ligand behaves mostly as the I form [1]. Thiosemicarbazones have found extensive applications in analytical chemistry because they have been used in the determination of some transition metals [2–6].

In most complexes, thiosemicarbazones behave as bidentate ligands because they can bond to metals through the sulphur and hydrazinic nitrogen atoms, although in a few cases they behave as unidentate ligands and bond through only the sulphur atom [1, 7, 8].

In this study, 4'-morpholinoacetophenone thiosemicarbazone (MAPT) was synthesized for the first time. The thermodynamic stability constants

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and thermodynamic parameters of the complexes of this ligand with Ni(II), Cu(II), Ag(I) and Hg(II) were evaluated using a spectrophotometric method.

## EXPERIMENTAL

### *Apparatus*

A Crison 2002 pH-ionmeter with a combined glass–calomel electrode, and a Shimadzu UV-160 spectrophotometer, with a 1.0-cm quartz cell, equipped with a Lauda MT 3 bath/circulation thermostat, were used.

### *Synthesis of MAPT*

In a 250 ml flask were placed 1.0 g of 4'-morpholinoacetophenone (Aldrich), 0.5 g of thiosemicarbazide (Merck) and 70 ml ethanol. To this was added 30 ml of acetate buffer solution (1.76 g of sodium acetate and 0.6 ml of glacial acetic acid). The mixture was refluxed for 3 h and then cooled to room temperature. Yellow crystals were formed. The precipitate was washed with ethanol and hot water, and then dried at 120°C (M.P. 244–245°C, yield 60%. Found: 56.6% C, 7.2% H, 21.9% N; calculated for C<sub>13</sub>H<sub>18</sub>ON<sub>4</sub>S: 56.1% C, 6.5% H, 20.1 N). MAPT does not dissolve in ethanol, carbon disulphide, chloroform, carbon tetrachloride or benzene but does dissolve in *N,N*-dimethylformamide (DMF) and dimethyl sulphoxide.

### *Reagents*

Solutions of nickel sulphate, copper(II) sulphate, silver nitrate, and mercury(II) nitrate were prepared in distilled water and standardized according to known methods. The stock metal solution (0.001 M) was prepared from each standardized solution. Buffer solutions of sodium acetate–acetic acid (0.50 M, pH 4.0) and sodium carbonate–sodium bicarbonate (0.30 M, pH 9.6) were also prepared. Two types of 1 M sodium nitrate solutions were prepared: one using acetate buffer and the other using carbonate buffer. The first solution (pH 4.0) was used for the Cu, Ag and Hg experiments, the second solution (pH 9.6) for the Ni experiments. MAPT solution of concentration 0.1% (w/v) was prepared in DMF. All reagents and solvents were of analytical grade.

### *Procedures*

#### *Determination of molar absorption coefficients*

To a 10 ml standard flask were added 3 ml of DMF, 0.2–0.8 ml of 0.001 M stock metal solution, 2 ml of 1 M sodium nitrate solution and an

appropriate volume of distilled water such that when 3 ml of 0.1% MAPT solution is finally added, the total volume will be 10.0 ml. Five mixtures of differing metal concentrations were prepared. The mixtures were warmed for 15 min at  $25 \pm 0.1^\circ\text{C}$  in the thermostatic bath. MAPT solution that was kept in the same thermostatic bath for the same time was added to each mixture, and then shaken (ionic strength,  $I = 0.20$ ), and one portion was transferred to the quartz cell thermostatted at the same temperature. The changes of absorbance at maximum wavelength were recorded against a similar solution containing no metal ion until the reaction was complete.

#### *Determination of stability constants of the complexes*

To a 10 ml standard flask were added 5.8–5.7 ml of DMF, 0.7–1.4 ml of 0.001 M stock metal solution, 2 ml of 1 M sodium nitrate solution and an appropriate volume of distilled water such that when MAPT solution is finally added, the total volume will be 10.0 ml. Five mixtures with differing metal concentrations were prepared. The mixtures were warmed for 15 min at  $25 \pm 0.1^\circ\text{C}$  in the thermostatic bath. Keeping ligand/metal mole ratio at about 2, the reaction was initiated by adding MAPT solution that was kept in the same thermostatic bath for the same time to each mixture ( $I = 0.20$ ). The absorbances were recorded in the same way as for the determination of the molar absorption coefficients.

Each experiment was repeated three times.

At 0.20 ionic strength, the experiments performed for determinations of the molar absorption coefficients and stability constants were repeated at 30, 35 and  $40 \pm 0.1^\circ\text{C}$  by preparing the mixtures afresh.

The experiments were performed at ionic strengths of 0.20, 0.13 and 0.07 at each of these temperatures.

## RESULTS AND DISCUSSION

The complexes of Ni(II), Cu(II), Ag(I) and Hg(II) with MAPT are a yellow-green colour. The maximum absorption wavelengths  $\lambda_{\text{max}}$ , molar

TABLE I  
The spectrophotometric characteristics of the complexes

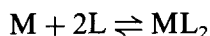
Complex	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$			Optimum pH
		$I = 0.20$	0.13	0.07	
Cu–MAPT	380	6750	6500	6350	4.0
Hg–MAPT	380	3500	3250	3000	4.0
Ag–MAPT	383	3900	3750	3650	4.0
Ni–MAPT	391	7400	6800	6300	9.6

absorption coefficients  $\epsilon$  at various ionic strengths ( $I/\text{mol dm}^{-3}$ ) and optimum pH values of these complexes are given in Table 1.

Changes in temperature do not appreciably modify the molar absorption coefficients of the complexes, but the absorbances increase slightly with ionic strength and are pH dependent. The Cu(II), Ag(I) and Hg(II) complexes have a maximum absorption at pH values close to 4.0, and these complexes are formed practically at once. The formation of the Ni(II) complex is very slow at pH 4.0. To increase the formation rate of this complex, pH values were increased. As nickel hydroxide is precipitated at  $\text{pH} \geq 10$ , nickel experiments were carried out at pH 9.6. Even at this pH, the formation rate of this complex is slow. For the complete formation of Ni–MAPT 1 h is necessary for the determination of the stability constants, but in the determination of the molar absorption coefficients 10 min was sufficient.

For the four complexes, the metal/ligand mole ratio was found to be 1:2 using the Job method. This result shows that MAPT is a bidentate ligand.

M, L and  $\text{ML}_2$  represent, respectively, the metal, the ligand and the complex.



If the L/M ratio is very large, the equilibrium shifts completely to the right, and one can write

$$C_M \approx [\text{ML}_2]$$

where  $C_M$  is the analytical concentrations of metal. Using measured absorbances of the mixtures, the molar absorption coefficients are determined from Beer's law. Because the measured absorbances pertain only to the  $\text{ML}_2$  complex [9], the following equation can be written for the stability constant of the complex

$$K = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2} = \frac{[\text{ML}_2]}{(C_M - [\text{ML}_2])(C_L - 2[\text{ML}_2])^2}$$

In this equation, if  $A/\epsilon$  is substituted for  $[\text{ML}_2]$ , the equation becomes

$$K = \frac{A/\epsilon}{(C_M - A/\epsilon)(C_L - 2A/\epsilon)^2}$$

where  $A$  is the measured absorbance and  $\epsilon$  the molar absorption coefficient.  $K$  is calculated from this equation [10]. The values of  $K$  were obtained by a program written in BASIC.

For each temperature, the average values of  $\ln K$  were then plotted against ionic strength for each metal–ligand system, and the curves were extrapolated to zero ionic strength to give the thermodynamic stability constants,  $\ln K^\circ$  (Table 2).

TABLE 2

The stability constants ( $\ln K$ ) at different temperatures and ionic strengths ( $I$ , mol dm<sup>-3</sup>), and the thermodynamic parameters

System	Temp/ °C	$\ln K$			$\ln K^\circ$	$-\Delta G^\circ/kJ mol^{-1}$	$+\Delta H^\circ/kJ mol^{-1}$	$+\Delta S^\circ/J mol^{-1} K^{-1}$
		$I = 0.20$	0.13	0.07				
Cu–MAPT	25	19.24	19.21	19.19	19.16	47.49	–31.66	53.2
	30	19.03	19.01	18.88	18.96	47.79		
	35	18.82	18.80	18.58	18.76	48.07		
	40	18.88	18.74	18.58	18.54	48.29		
Hg–MAPT	25	24.12	23.99	23.88	23.72	58.81	+39.06	328.1
	30	24.32	24.21	24.11	23.97	60.42		
	35	24.52	24.43	24.35	24.23	62.09		
	40	24.73	24.65	24.58	24.48	63.74		
Ag–MAPT	25	22.21	21.85	21.54	21.18	52.53	+56.39	359.2
	30	22.70	22.28	21.82	21.52	54.25		
	35	23.30	22.78	22.40	21.92	56.17		
	40	23.47	23.05	22.69	22.27	57.99		
Ni–MAPT	25	15.56	15.53	15.51	15.48	38.38	+20.11	195.6
	30	15.65	15.61	15.60	15.57	39.25		
	35	15.79	15.76	15.75	15.71	40.25		
	40	15.95	15.91	15.89	15.86	41.29		

For each metal–ligand system, values of  $\ln K^\circ$  were plotted against  $1/T$ . A straight line was obtained, showing that  $\Delta H^\circ$  and  $\Delta S^\circ$  are essentially independent of temperature over the temperature range considered. The slope of the line is  $-\Delta H^\circ/R$ , and the intercept at  $1/T = 0$  is  $\Delta S^\circ/R$ . The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  may be calculated, respectively, from the slope and the intercept of the plot. Using the equation  $\Delta G^\circ = -RT \ln K^\circ$ , the values of  $\Delta G^\circ$  for each metal–ligand were calculated [11, 12].

It was found that the average values of the stability constants ( $\ln K$ ) of the metal complexes are proportional to the ionic strength and inversely proportional to the temperature (Table 2). The negative and positive values of  $\Delta H^\circ$  indicated, respectively, the exothermic and endothermic nature of the metal–ligand interaction. Sufficiently large negative values of  $\Delta G^\circ$  indicated spontaneous formation of the complexes. Spontaneity increased with temperature. The values of  $\Delta G^\circ$  follow the order Hg > Ag > Cu > Ni for the complexes.

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