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Determination of thermodynamic parameters of some complexes of 2-methylindole-3-carboxaldehyde 4-phenyl-3-thiosemicarbazone

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Abstract

Cobalt(II), Ni(II), Cu(II) and Hg(II) form 1:2 (metal–ligand) complexes with 2-methylindole-3-carboxaldehyde 4-phenyl-3-thiosemicarbazone. The stability constants of these complexes in 60% (v/v) aqueous DMF were determined at different ionic strengths (0.10, 0.20 and 0.40 M KNO_3) and of 25, 30, 35 and 40°C (± 0.1°C) using a spectrophotometric method. From these constants, the thermodynamic stability constants and thermodynamic parameters $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ were calculated.

Keywords: Ligand; Spectrophotometry; Stability constant; Thermodynamics; Thiosemicarbazone

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1. Introduction

Thiosemicarbazones have found extensive applications in analytical chemistry for the determination of some transition metals [1–5], and in most metal–thiosemicarbazone complexes they behave as bidentate ligands [6].

Thermodynamic studies on the complexes of 4′-morpholinoacetophenone thiosemicarbazone [7], 2-methylindole-3-carboxaldehyde thiosemicarbazone [8] and 4′-morpholinoacetophenone 4-phenyl-3-thiosemicarbazone [9] with some transition metal ions have recently been reported. In this study, 2-methylindole-3-carboxal-

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dehyde 4-phenyl-3-thiosemicarbazone (MICP) has been synthesized for the first time. The thermodynamic stability constants and thermodynamic parameters of the complexes of this ligand with Co(II), Ni(II), Cu(II) and Hg(II) have been evaluated using a spectrophotometric method.

2. Experimental

2.1. Apparatus

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

2.2. Synthesis of MICP

In a 250 ml flask were placed 0.8 g of 2-methylindole-3-carboxaldehyde (Aldrich) and 20 ml of ethanol. The mixture was heated until dissolution of the reagent was complete. To this mixture were added 70 ml of hot water, 1.4 g of sodium acetate, 1.2 ml of glacial acetic acid and 0.8 g of 4-phenyl-3-thiosemicarbazide (Merck). The mixture was refluxed for 8 h and then cooled to room temperature. Yellow crystals of MICP were formed. The precipitate was washed with ethanol and hot water, then dried at 120°C (m.p. 210–211°C, yield 75%). Found: 66.66% C, 5.19% H, 18.14% N; calculated for $C_{17}H_{16}N_4S$: 66.20% C, 5.23% H, 18.17% N. MICP does not dissolve in ethanol, carbon disulphide, chloroform, carbon tetrachloride, benzene or hot water, but dissolves in *N,N*-dimethylformamide (DMF), dimethyl sulphoxide and hot ethanol.

2.3. Reagents

All reagents and solvents were of analytical grade. Solutions of cobalt(II) nitrate, nickel(II) sulphate, copper(II) sulphate and mercury(II) nitrate were prepared in distilled water. The copper(II) solution was standardized iodometrically and solutions of the other metals were standardized gravimetrically. A stock metal solution (0.002 M) was prepared from each standardized solution. A buffer solution of sodium carbonate–sodium bicarbonate ($C_T = 0.55$ M; pH 9.3) and potassium nitrate solution (2 M) were prepared in distilled water. A 0.1% (w/v) solution of MICP in DMF was used.

2.4. Procedures

2.4.1. Determination of molar absorption coefficients

Into a 10 ml volumetric flask were introduced 2 ml of buffer solution ($C_T = 0.55$ M; pH 9.3), 2 ml of 2 M potassium nitrate solution and X ml of MICP solution ($X = 0.6$ ml for Co and Ni; $X = 0.5$ ml for Cu and Hg. The X values are volumes

Table 1
Spectrophotometric characteristics of the complexes

Complex	λ_{max}/nm	ε/(dm^3 mol^{-1} cm^{-1})			Optimum pH range
	$I = 0.1$	$I = 0.2$	$I = 0.4$		
Co–MICP	388	35250	35800	37000	9.0–9.6
Ni–MICP	390	19200	19540	19900	9.0–9.6
Cu–MICP	385	25300	26400	28600	7.0–9.6
Hg–MICP	390	15200	15750	16850	7.0–9.6

sufficient to give the optimum ligand concentrations). This mixture was diluted with DMF to 10 ml, and mixed thoroughly, then 3 ml of the mixture was transferred to a stoppered quartz cell. The cell was warmed for 15 min at 25 ± 0.1°C, then 10–30 µl of the stock metal solution kept under the same conditions was added to the stoppered cell with a micropipette and the mixture was shaken (ionic strength $I = 0.4$). Five mixtures with differing metal concentrations were prepared for each metal. The changes in absorbance at the wavelength of maximum absorption were recorded against a similar solution containing no metal ion until the reaction was complete (Table 1).

2.4.2. *Determination of stability constants of the complexes*

In a 10 ml volumetric flask were placed 2 ml of buffer solution, 2 ml of 2 M potassium nitrate solution and 0.03–0.07 ml of stock MICP solution. This mixture was diluted with DMF to 10 ml and mixed thoroughly; five mixtures with differing MICP concentrations were prepared thus. A 3 ml portion of each mixture was transferred to a stoppered quartz cell. The cells were warmed for 15 min at (25 ± 0.1)°C in the circulating bath. Keeping the ligand/metal mole ratio at ≈ 2, the reaction was initiated by adding the stock metal solution, kept under the same conditions, to each mixture ($I = 0.4$). The changes in absorbance at the maximum wavelength were recorded in the same way as for the determination of the molar absorption coefficients. Each experiment was repeated three times.

At $I = 0.4$, the experiments performed for the determination of the molar absorption coefficients and stability constants were repeated at 30, 35 and 40 (±0.1)°C by preparing the mixtures afresh.

The experiments were also performed at ionic strengths of 0.2 and 0.1 at each of the temperatures mentioned above.

3. Results and discussion

The complexes of Co(II), Ni(II), Cu(II) and Hg(II) with MICP are yellow. The maximum absorption wavelengths λ_{max}, molar absorption coefficients ε various ionic strengths (0.1, 0.2 and 0.4 mol dm^{-3}) and optimum pH values of these complexes are given in Table 1.

Table 2
Stability constants (ln K) at different temperatures and ionic strengths I (in mol dm^{-3}) and thermodynamic parameters

Temp./°C	ln K			ln $K^{\ominus}$	$-\Delta G^{\ominus}$/(kJ mol^{-1})	$-\Delta H^{\ominus}$/(kJ mol^{-1})	$+\Delta S^{\ominus}$/(J mol^{-1} K^{-1})
	$I = 0.4$	$I = 0.2$	$I = 0.1$				
Co–MICP							
25	22.34	22.32	22.31	22.31	55.30	21.21	114.04
30	22.23	22.20	22.18	22.17	55.88		
35	22.12	22.09	22.05	22.03	56.44		
40	22.02	21.96	21.93	21.90	57.02		
Ni–MICP							
25	22.01	21.90	21.85	21.80	54.01	37.40	55.93
30	21.78	21.70	21.66	21.61	54.47		
35	21.49	21.40	21.37	21.35	54.70		
40	21.14	21.11	21.09	21.08	54.88		
Cu–MICP							
25	27.45	26.68	26.29	25.90	64.20	53.73	35.11
30	26.90	26.22	25.88	25.54	64.37		
35	26.38	25.79	25.49	25.19	64.54		
40	25.86	25.36	25.11	24.86	64.72		
Hg–MICP							
25	25.22	25.06	24.98	24.90	61.72	46.44	51.22
30	24.91	24.75	24.67	24.59	61.98		
35	24.61	24.45	24.37	24.29	62.23		
40	24.32	24.16	24.08	24.00	62.48		

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, as described elsewhere [7–9]. Formation of the Cu(II) and Hg(II) complexes is rapid, but that of Co(II) and Ni(II) is very slow at pH 7.0. As the precipitate is formed at pH ≥ 10, these experiments were carried out at pH 9.3. At this pH, for the complete formation of Co(II) and Ni(II) complexes, 1.5 h is necessary for the determination of stability constants, but in the determination of the molar absorption coefficients 20 min is sufficient.

For all complexes, the metal/ligand mole ratio was found to be 1:2 using the Job method. This result shows that MICP is a bidentate ligand. The stability constants (ln K), thermodynamic stability constants (ln $K^{\ominus}$) and thermodynamic parameters of the complexes were calculated from the measured absorbances as described elsewhere [7]. Sufficiently large negative values of $\Delta G^{\ominus}$ indicated spontaneous formation of the complexes (Table 2). Spontaneity increases with temperature. Negative values of $\Delta H^{\ominus}$ predicted the exothermic nature of the metal–ligand interaction. The values of $\Delta G^{\ominus}$ follow the order Cu > Hg > Co > Ni.

Plots of thermodynamic stability constants at zero ionic strength (ln $K^{\ominus}$ vs. T^{-1}) gave linear curves, which indicate a temperature independent heat of association of the reaction and zero values of $\Delta C_p^{\ominus}$. The spontaneous formation of the complexes was further confirmed by positive values of $\Delta S^{\ominus}$.

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.

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