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# Evaluation of thermodynamic parameters and stability constants of Cu(II), Ag(I) and Hg(II) complexes of 2-methylindole-3-carboxaldehyde thiosemicarbazone

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## Abstract

The stability of Cu(II), Ag(I) and Hg(II) complexes of 2-methylindole-3-carboxaldehyde thiosemicarbazone have been determined using a spectrophotometric method in 50% (v/v) aqueous ethanol at different ionic strengths (0.12, 0.22 and 0.4 M) and at different temperatures (25, 30, 35 and $40 \pm 0.1$°C). For each metal–ligand system at each temperature, the thermodynamic stability constant ($\ln K^{\ominus}$) was obtained graphically at zero ionic strength from plots of $\ln K$ versus ionic strength. The thermodynamic parameters were evaluated from plots of $\ln K^{\ominus}$ versus $1/T$.

*Keywords:* Copper compound; Ligand; Mercury compound; Silver compound; Spectrophotometry; Stability; Stability constant; Thermodynamics; Thiosemicarbazone

## 1. Introduction

In the earlier thermodynamic studies of some metal complexes, potentiometric methods were used [1–5]. A thermodynamic study of the complexes of 4′-morpholinoacetophenone thiosemicarbazone with some metal ions using a spectrophoto-

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metric method has been recently reported [6]. In the present study, 2-methylindole-3-carboxaldehyde thiosemicarbazone (MICT) was synthesized for the first time. The thermodynamic stability constants and thermodynamic parameters of the complexes of this ligand with Cu(II), Ag(I) and Hg(II) were evaluated by a spectrophotometric method.

## 2. Experimental

### 2.1. Apparatus

A Crison 202 pH-ionmeter with a combined glass–calomel electrode, Shimadzu UV-160 spectrophotometer with a 1.0-cm quartz cells and equipped with a Lauda MT 3 circulating thermostatic bath were used.

### 2.2. Synthesis of MICT

2-Methylindole-3-carboxaldehyde (Aldrich) (0.5 g) and ethanol (30 ml) were placed in a 250 ml flask. The mixture was heated until dissolution of the reagent was complete. Then 70 ml of hot water, 1.36 g of sodium acetate, 0.6 ml of glacial acetic acid and 0.25 g of thiosemicarbazide (Merck) were added to this mixture. The mixture was refluxed for 5 h and then cooled at room temperature. Yellow crystals were formed. After filtering 500 ml of water was added to the precipitate, and the mixture was heated until dissolution of the precipitate was complete. Then the solution was cooled to room temperature. Yellow crystals were formed again. The precipitate was washed with water, then dried at 120°C: (m.p. 218–219°C, yield 65%. Found: 54.0% C, 5.0% H, 22.6% N; calculated for $C_{10}H_9N_4S$: 55.2% C, 4.2% H, 25.8% N). MICT is insoluble in cool water, carbon disulfide, chloroform, carbon tetrachloride and benzene but soluble in ethanol, dimethyl sulfoxide, dimethylformamide and hot water to 90–100°C.

### 2.3. Reagents

Solutions of copper(II) sulfate, silver nitrate and mercury(II) nitrate were prepared in distilled water and standardized according to known methods. Stock metal solutions of 0.001 M were prepared from each standardized solution. Potassium nitrate solution (2 M) and a buffer solution of sodium acetate–acetic acid (0.21 M, pH 5.7) were prepared in distilled water, and an MICT solution of concentration 0.1% (w/v) was prepared in ethanol. All reagents and solvents were of analytical-reagent grade.

### 2.4. Procedures

#### 2.4.1. Determination of molar absorption coefficients

To a 10 ml standard flask were added 0.9–0.65 ml of distilled water, $X$ ml of MICT solution ($X = 0.7$, 0.8 and 1 ml for Ag(I), Cu(II) and Hg(II) respectively), 2 ml of 2 M potassium nitrate solution, 2 ml of buffer solution (0.21 M, pH 5.7) and an appropriate volume of ethanol such that when 0.1–0.35 ml of stock metal solution was finally added, the total volume was 10 ml. Five mixtures containing different metal concentrations were prepared. The mixtures were warmed for 15 min at 25 ± 0.1°C in the thermostatic bath. Metal solution that had been kept in the same thermostatic bath for the same time was added to each mixture, then shaken ($I = 0.4$), and one portion was transferred to the quartz cell thermostated 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.

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

To a 10 ml standard flask were added 0.35–0.8 ml of distilled water, 2 ml of buffer solution, 2 ml of 2 M potassium nitrate solution, 0.05–0.25 ml of MICT solution and an appropriate volume of ethanol such that when stock metal solution was finally added, the total volume was 10 ml. Five mixtures with different ligand concentrations were prepared. The mixtures were warmed for 15 min at 25 ± 0.1°C in the thermostatic bath. Maintaining a ligand/metal mol ratio of 2, metal solution that had been kept in the same thermostatic bath for the same time was added to each mixture and the reaction was initiated ($I = 0.4$). The absorbances were recorded in the same way as in the determination of the molar absorption coefficients.

Each experiment was repeated three times.

At an ionic strength of 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 0.12 at each of these temperatures.

## 3. Results and discussion

The complexes of Cu(II), Ag(I) and Hg(II) with MICT are yellow. The maximum absorption wavelengths ($\lambda_{max}$), the molar absorption coefficients ($\varepsilon$) at various ionic strengths ($I$ in 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 absorbances increase slightly with ionic strength. Ag(I) and Hg(II) complexes are formed practically at once. The formation of Cu(II) complex is slow. For the complete formation of Cu–MICT, 40 min are necessary for the determination of stability constants, but in the determination of the molar absorption coefficients 8 min are sufficient.

For the three complexes, the metal/ligand mol ratio was found to be 1:2 by Job's method. This result shows that MICT behaves as a bidentate ligand.

Table 1
The spectrophotometric characteristics of the complexes

| Complex | $\lambda_{max}$ in nm | $\varepsilon$ in L mol$^{-1}$ cm$^{-1}$ | | | Optimum pH |
|---|---|---|---|---|---|
| | | $I = 0.12$ | $I = 0.2$ | $I = 0.4$ | |
| Cu–MICT | 370 | 23000 | 23350 | 24250 | 5.7 |
| Ag–MICT | 369 | 12700 | 13300 | 14960 | 5.7 |
| Hg–MICT | 369 | 26800 | 27050 | 27370 | 5.7 |

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

| Temp. in °C | ln $K$ | | | ln $K^\ominus$ | $-\Delta G^\ominus$ in kJ mol$^{-1}$ | $+\Delta H^\ominus$ in kJ mol$^{-1}$ | $+\Delta S^\ominus$ in J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | $I = 0.4$ | $I = 0.2$ | $I = 0.12$ | | | | |
| Cu–MICT | | | | | | | |
| 25 | 19.82 | 19.80 | 19.78 | 19.75 | 48.96 | 11.33 | 202.16 |
| 30 | 19.87 | 19.85 | 19.84 | 19.82 | 49.96 | | |
| 35 | 19.95 | 19.93 | 19.92 | 19.90 | 19.99 | | |
| 40 | 20.05 | 20.02 | 20.00 | 19.97 | 52.00 | | |
| Ag–MICT | | | | | | | |
| 25 | 24.83 | 24.52 | 24.37 | 24.13 | 59.82 | −47.26 | 42.28 |
| 30 | 24.59 | 24.21 | 24.05 | 23.82 | 60.05 | | |
| 35 | 24.36 | 24.04 | 23.80 | 23.56 | 60.37 | | |
| 40 | 24.08 | 24.63 | 23.40 | 23.19 | 60.39 | | |
| Hg–MICT | | | | | | | |
| 25 | 25.31 | 24.78 | 24.52 | 24.23 | 60.00 | −42.08 | 60.43 |
| 30 | 24.89 | 24.45 | 24.21 | 23.95 | 60.37 | | |
| 35 | 24.43 | 24.10 | 23.98 | 23.70 | 60.73 | | |
| 40 | 23.99 | 23.71 | 23.60 | 23.40 | 60.93 | | |

Thermodynamic stability constants (ln $K^\ominus$) and thermodynamic parameters of the complexes were determined as described elsewhere [6]. The values of the stability constants (ln $K$) were found to be proportional to the ionic strength and inversely proportional to the temperature in the Ag(I) and Hg(II) complexes (Table 2).

For each metal–ligand system, the values of (ln $K^\ominus$) were plotted against $1/T$. A straight line was obtained showing that $\Delta H^\ominus$ and $\Delta S^\ominus$ are essentially independent of temperature over the temperature range considered. The negative and positive values of $\Delta H^\ominus$ indicated, respectively, the exothermic and endothermic nature of the metal–ligand interaction. Sufficiently large negative values of $\Delta G^\ominus$ showed spontaneous formation of the complexes. Spontaneity increased with temperature (Table 2 ). The values of $\Delta G^\ominus$ follow the order Hg > Ag > Cu which is compatible with the findings of our earlier study [6]. The values of $\Delta S^\ominus$ are all positive, indicating that change in entropy favors complex formation. $\Delta S^{\ominus}$ is mainly responsible for the formation of Cu(II) complex, but $\Delta H^{\ominus}$ is responsible for the formation of the other complexes.

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