

Determination of Thermodynamic Parameters of some Complexes of 9-ethyl-3-carbazolecarboxaldehyde 4-phenyl-3-thiosemicarbazone (ECCAPT)

E. Güler AKGEMCİ, Tefrik ATALAY
*Department of Chemistry, Faculty of Education,
42099, Konya-TURKEY*

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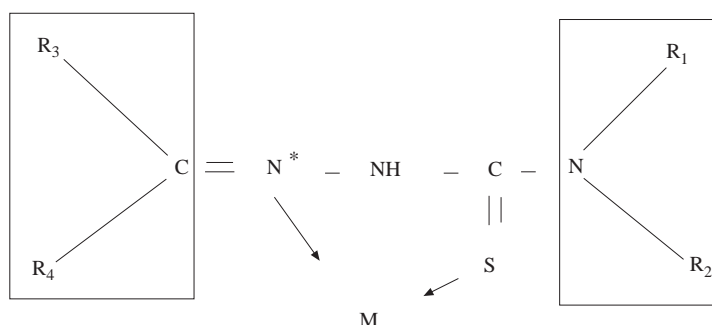
The complexes of Cu(II), Co(II), Zn(II), and Cd(II) with 9-ethyl-3-carbazolecarboxaldehyde 4-phenyl-3-thiosemicarbazone were synthesized and their stability constants were determined using a spectrophotometric method at different temperatures (25, 30, 35 and 40 ± 0.1 °C) and ionic strengths (0.05, 0.01 and 0.20 M KNO_3) in 50 % (v/v) aqueous DMF. From these constants, the thermodynamic stability constants and thermodynamic parameters (ΔG° , ΔH° and ΔS°) were calculated.

Key words: Spectrophotometry, thiosemicarbazone, thermodynamic, ligand, stability.

Introduction

Thiosemicarbazones (hydrazine carbothioamides) are prepared by condensation of thiosemicarbazide with an aldehyde or ketone in the presence of a few drops of glacial acetic acid¹. Sometimes hydrochloric acid must be present in the preparation of thiosemicarbazones².

The structure of active grouping for chelation is shown below:



Thiosemicarbazones act as chelating agents for metal ions by bonding through the sulphur or oxygen atom and the hydrazinic nitrogen atom, marked with an asterisk. The ligand may be monodentate, bidentate or tridentate³.

Since the discovery of the antitubercular activity of thiosemicarbazones (TSC) by Domagk, studies on their pharmacology have received a great deal of interest⁴. These compounds have revealed a broad

spectrum of therapeutic activity especially as antiviral, antimalarial, antibacterial, hypoglycaemic, hypcholesteroleamic, antihypertensive, antiulcer, antinociceptive, anticancer, CNS active and immunomodulating agents⁵. The activity of TSC is thought to be due to their power of chelation with traces of metal ions present in biological systems.

In the earlier thermodynamic studies of some metal complexes, potentiometric methods were used⁶⁻¹⁴. Thermodynamic studies on the transition metal ion complexes of some thiosemicarbazones using a spectrophotometric method have been reported¹⁵⁻¹⁸. The thermodynamic stability constants and thermodynamic parameters of the complexes of 2-benzoyl pyridine 4-phenyl-3-thiosemicarbazone with some transition metal ions have been recently evaluated¹⁹.

In this study, ECCAPT has been synthesized for the first time. The thermodynamic stability constants and thermodynamic parameters of the complexes of this ligand with Cu(II), Co(II), Zn(II) and Cd(II) have been evaluated by spectrophotometry.

Experimental

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 thermostatic bath, were used.

Synthesis of ECCAPT

In a 250 ml flask were placed 1 g of 9-ethyl-3-carbazolecarboxaldehyde (Aldrich) and 30 ml ethanol. The mixture was heated until dissolution of the reagent was complete. To this mixture were added 50 ml of hot water, 1.36 g of sodium acetate, 1.7 ml of glacial acetic acid and 0.8 g 4-phenyl-3-thiosemicarbazide (Merck). The mixture was refluxed for 1.5 h and then cooled to room temperature. Yellow crystals of ECCAPT were formed. The precipitate was washed with ethanol and hot water, then dried at 120°C. (m.p 198-200 °C, yield 85 %). ECCAPT does dissolve in N,N-dimethylformamide (DMF), acetone and hot ethanol. The structure of ECCAPT was identified by IR and ¹H NMR spectroscopy, elemental analysis (R₁, R₃ = H; R₂ = Ph; R₄=9-Et. Carbazoly). The following were found: 70.37 % C, 5.42 % H, 14.87 % N, 8.38 % S, calculated for C₂₂H₂₀N₄S: 70.97 % C, 5.38 %H, 15.05 % N, 8.60 % S. IR (ν cm⁻¹, KBr): 3240, 3150 (NH), 1525 (C=N), 740, 1305 (C=S). ¹H NMR (CDCl₃, ppm): 9.73 (NH), 9.15 (NH), 1.48 (CH₃), 4.40 (CH₂), 8.10 (CH), 7.28-8.37 (Ph).

Reagents

All reagents and solvents were of analytical grade. Solutions of Copper (II) sulphate, Cobalt (II) nitrate, Zinc (II) sulphate and Cadmium (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 (0.001 M) was prepared from each standardized solution. A buffer solution of tris-HCl (C_T=0.05; pH 8.8) and potassium nitrate solution (1 M) were prepared in distilled water. A 0.1 % (w/v) solution of ECCAPT in DMF was used.

Procedures

Determination of molar absorption coefficients

Into a 10 ml volumetric flask were introduced 2 ml of buffer solution ($C_T=0.05$ M; pH 8.8), 2 ml of 1 M potassium nitrate solution and X ml of ECCAPT solution (X=1.2 ml for Co, 1.5 ml for Cu, Zn and Cd. The X values are volumes with optimum ligand concentrations). This mixture was diluted with DMF to 10 ml and mixed thoroughly, and then 3 ml of mixture was transferred to a stoppered quartz cell. The cell was warmed for 15 min at 25 ± 0.1 °C, then 40-80 μ l of the stock metal solution kept under the same conditions was added to the stoppered cell with a micropipette and the mixture was shaken (I=0.2). 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).

Table 1. Spectrophotometric characteristics of the complexes

Complex	λ_{\max} (nm)	$\varepsilon/(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$			optimum pH
		I=0.05	I=0.10	I=0.20	
Cu-ECCAPT	400	41670	41800	41950	8.8
Co-ECCAPT	400	43790	44060	44430	8.8
Cd-ECCAPT	401	36230	36305	36455	8.8
Zn-ECCAPT	410	26205	26525	27155	8.8

Determination of stability constants of the complexes

Into a 10 ml volumetric flask were placed 2 ml of buffer solution, 2 ml of 1 M potassium nitrate solution and 0.04-0.08 ml of stock ECCAPT solution. This mixture was diluted with DMF to 10 ml and mixed thoroughly; five mixtures with differing ECCAPT 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 $\simeq 2$, the reaction was initiated by adding the stock metal solution, kept under the same conditions, to each mixture (I=0.2). 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=0.2, 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 0.1 and 0.05 at each of the temperatures mentioned above.

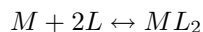
Results and Discussion

The complex of Cu(II), Co(II), Zn(II) and Cd(II) with ECCAPT are yellow in colour. The maximum absorption wavelength (λ_{max}), molar absorption coefficients (ε) at various ionic strengths and optimum pH values of the complexes are given in Table 1.

Changes in temperature did not modify appreciably the molar absorption coefficients of the complexes, but the absorbances increased slightly with ionic strength. Cu (II) and Cd (II) complexes are formed practically at once in the pH range 7.0-9.0, but the formation of the Co (II) and Zn (II) complexes is rapid at pH 9. For this reason experiments were carried out at pH 8.8.

For all complexes, the metal/ligand mole ratio was found to be 1:2 using Job's method²⁰. These results show that ECCAPT is a bidentate ligand.

M, L and ML₂ represent, respectively, the metal ion, ligand and the complex.



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

$$C_M \approx [ML_2],$$

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 ML₂ complex²¹, the following equation can be written for the stability constant of the complex:

$$K = \frac{[ML_2]}{[M][L]^2} = \frac{[ML_2]}{(C_M - [ML_2])(C_L - 2[ML_2])^2}$$

In this equation, if A/ε is substituted for [ML₂], the equation becomes

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

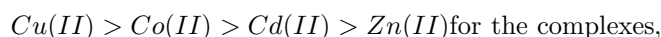
where A is the measured absorbance and ε the molar absorption coefficient. K is calculated from this equation²².

For each temperature, the average values of lnK were plotted against ionic strength for each metal-ligand system. Straight lines were obtained and they were extrapolated to zero ionic strength to yield the thermodynamic stability constant (lnK°). The values of ln K° were plotted against T⁻¹. A straight line was obtained, showing that ΔH° and ΔS° may be calculated, respectively, from the slope and intercept of plot. Using the equation ΔG° = -RT ln K°, the values of ΔG° for each metal-ligand were calculated.

The average values of the stability constants (lnK) of the metal complexes were found to be proportional to the ionic strength and inversely proportional to the temperature (Table 2).

The negative and positive values of ΔH° indicated, respectively, the exothermic and endothermic nature of the metal-ligand interaction. ΔS° is mainly responsible for the formation of the Co (II) complex, while ΔH° is responsible for the formation of the Cd (II) complex.

Sufficiently large negative values of ΔG° showed spontaneous formation of the complexes. Spontaneity increased with temperature, except in the Cd (II) complex. The values of ΔG° follow the order.



In our study, the results showed that Cu-ECCAPT is the most stable metal complex of ECCAPT. Copper (II) is a biologically active, essential ion, and its chelating ability and positive redox potential allow participation in biological transport reactions. Cu (II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and antiinflammatory agents²³. The various thiosemicarbazones have been used as analytical reagents. Thiosemicarbazones are rather selective and sensitive to copper¹. We think that the stable complexes of this thiosemicarbazone, synthesized for the first time, will also find the practical applications in the analytical and medical fields.

Table 2. Stability constants (lnK) at different temperatures and ionic strengths (I, mol dm⁻³) and the thermodynamic parameters.

System	Temp (°C)	lnK			lnK°	$-\Delta G^\circ$ (kJ mol ⁻¹)	$-\Delta H^\circ$ (kJ mol ⁻¹)	$+\Delta S^\circ$ (J mol ⁻¹ K ⁻¹)
		I=0.20	I=0.10	I=0.05				
Cu-ECCAPT	25	24.41	24.32	24.22	24.18	59.94	10.98	164.23
	30	24.34	24.25	24.15	24.11	60.77		
	35	24.26	24.18	24.08	24.04	61.59		
	40	24.19	24.11	24.01	23.97	62.41		
Co-ECCAPT	25	20.93	20.90	20.84	20.82	51.61	+12.53	215.12
	30	21.01	20.98	20.92	20.91	52.70		
	35	21.08	21.06	21.01	20.97	53.72		
	40	21.16	21.14	21.08	21.07	54.86		
Zn-ECCAPT	25	19.65	19.60	19.50	19.47	48.26	15.68	109.30
	30	19.55	19.50	19.40	19.37	42.82		
	35	19.45	19.39	19.30	19.27	49.37		
	40	19.35	19.30	19.20	19.17	49.91		
Cd-ECCAPT	25	21.21	21.15	21.14	21.10	52.30	97.26	-150.55
	30	20.61	20.55	20.52	20.49	51.64		
	35	20.02	19.94	19.89	19.85	50.85		
	40	19.41	19.35	19.28	19.25	50.12		

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