Thermodynamic and Electrical Studies of Co(II), Ni(II), and Cu(II) Complexes with Thiosemicarbazide and Aminoguanidine

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(For the memory of the late Prof. Fatma H. Mahmoud 1951-1999)

Summary. The stability constants of binary metal complexes of thiosemicarbazide and aminoguanidine with Co(II), Ni(II), and Cu(II) have been evaluated at 25°, 35°, 40° and 50° C. The formation of complexes reveals an exothermic behavior. Thermodynamic parameters for their formation were calculated. The structure of complexes was elucidated with the help of conductometric and infrared measurements. The electrical behavior of prepared complexes was followed. Semiconducting nature was emphasized. The coordination process improves the electrical properties of free ligands studied.

Introduction

An increased interest in thiosemicarbazide and aminoguanidine chemistry is mainly attributed to their wide range of biological applications[1,2]. These compounds and their derivatives exhibit enhanced biological activity when administered in the form of metal complexes[3-5].

From the coordination point of view, organic compounds containing sulphur and / or nitrogen donor atoms are good chelating agents[6-9]. Consequently, many metal complexes of thiosemicarbazide, aminoguanidine and their derivatives were synthesized and characterized on the basis of conductance, spectral, X-rays and thermal studies[10-12]. Some ligands coordinate in bidentate, tridentate or bridging tetradentate manner. M:L and M:2L complexes can be formed. Square planar and square pyramidal structures are observed.

In the course of our systematic study on the physical properties of organic complexes[13,14], the present investigation describes the thermodynamic and electrical properties of some thiosemicarbazide, TSC, and aminoguanidine, AG, metal complexes.

Experimental

All the chemicals used were of A.R. grade. pH measurements were made with a Cole-Parmer 5800-05 pH meter using a combined glass calomel electrode. To determine the proton-ligand, pK, and metal-ligand constants, log K, the free acid (HCl), free acid plus ligand (TSC or AG), and a mixture of a metal chloride with acid and ligand were titrated against sodium hydroxide at 25°, 35°, 40° and 50° C. Ionic strength of all solutions were maintained constant, I = 0.1 mol dm^{-3}, by adding required amounts of KCl.

To show the probable general stoichiometric ratio of complexes, a conductometric titration between 10^{-3} M metal ion solution and 10^{-2} M ligand solution was followed at room temperature. The conductograms were obtained using a digital conductivity-meter 5800-05 solution analyzer.

A series of solid complexes having the molar ratio 1:1 were prepared by mixing hot aqueous solutions containing the calculated amount of TSC ($S=C(NH_2)NHNH_2$) or AG ($NH=C(NH_2)NHNH_2$) with the corresponding metal chloride with stirring for 3 hours. Resulting precipitates were filtered, washed repeatedly with hot water then ethanol and finally dried over anhydrous calcium chloride. The structure of formed complexes was identified using IR- 500 spectrophotometer, Buck Scientific.

The ac electrical conductivity was measured as a function of temperature using an automatic Wayne Kerr bridge model 900 B at a constant frequency of 300 Hz. The sample temperature was measured using a copper-chrome-aluminum thermocouple. The samples were pressed under a pressure of 7 ton/cm^2 giving discs of 13 mm diameter and 0.5 – 0.7 mm thickness.

Results and Discussion

In order to elucidate the nature of the interaction between TSC or AG with Co(II), Ni(II) and Cu(II), the pK values of the free ligands and the log K values of binary complexes were computed according to the procedure of Irving and Rossotti using the three pH-titration curves[15]. The complexing processes have been studied at different temperatures in the range 298-323 K.

The values of the average number of ligands attached per metal ion, 0.2-1.0, indicate the formation of 1:1 complex. The calculated data are summarized in Table 1. It is evident that the complexes of thiosemicarbazide are fairly stable compared to the

corresponding aminoguanidine complexes. This may be attributed to the presence of strong potential donor site, C=S, in TSC compared to that C=NH in AG ligand. On the other hand, the stability constants of complexes fall in the Irving=Williams order, i.e., Co < Ni < Cu. With the increase in temperature, the stability values decrease exhibiting an exothermic behavior of complexation reactions.

Table 1. Stability constant values of complexes at different temperatures

Compounds	25^0C	35^0C	40^0C	50^0C
TSC	10.40	10.19	9.91	9.45
Co complex	6.95	6.65	6.36	5.68
Ni complex	7.88	7.68	7.45	7.05
Cu complex	9.05	8.75	8.48	8.00
AG	7.52	7.59	7.64	7.75
Co complex	4.75	4.34	4.13	3.70
Ni complex	5.25	4.81	4.65	4.20
Cu complex	5.67	5.20	5.00	4.55

To obtain further information about the complexing process of both ligands, the thermodynamic functions ΔG^o, ΔH^o and ΔS^o were determined using :

$$\Delta G^o = -RT \ln K = \Delta H^o - T \Delta S^o$$

The computed results are given in Table 2. It is clear that the free energy of complex formation becomes less negative with the increase in temperature showing that the complexing process is spontaneous and the spontaneity decreases with the rising of temperature. Expectedly, the enthalpy change values have been found to be negative due to the covalent interaction of metal ions with the lone pair electrons of both sulphur and nitrogen atoms of ligands. This means that the formation of all complexes occurs with evolution of heat. The entropy changes accompanying the formation of complexes are negative and thus the complexing process is strongly driven by enthalpic forces. The decrease in entropy values demonstrates higher order in complexed molecules.

It is interesting to illustrate the nature of bonding of complexed molecules through the analysis of the conventional thermodynamic data into two terms, electrostatic and non-electrostatic[16,13] :

$$\Delta G^{\circ} = \Delta G^{\circ}_{el} + \Delta G^{\circ}_{non} = nRT \ln M + RC (a + e^{T/\vartheta})$$

$$\Delta H^{\circ} = \Delta H^{\circ}_{el} + \Delta H^{\circ}_{non} = RC [a + (1 - T/\vartheta) e^{T/\vartheta}]$$

$$\Delta S^{\circ} = \Delta S^{\circ}_{el} + \Delta S^{\circ}_{non} = - nR \ln M - (RC/\vartheta) e^{T/\vartheta}$$

where ϑ is the characteristic temperature of solvent and M is its molality. Comparison of the electrostatic and non-electrostatic parts of thermodynamic parameters shows that ΔG°_{non} values are negative whereas ΔG°_{el} values are positive suggesting that non-electrostatic (covalent) forces are stronger than electrostatic (ionic) forces. The ratio of electrostatic and non- electrostatic decreases in the sequence : Co(II) > Ni(II) > Cu(II), i.e., the ionic character of the complexed molecules decreases in the same trend. Thus, it may be suggested that the ionic character of complexes increases with the increase in the number of unpaired electrons. The enthalpy data support the above contention, i.e., the covalency nature of the complexed molecules.

Table 2. Thermodynamic data of complexes at 298 K

Compounds	$-\Delta G^{\circ}$	$-\Delta H^{\circ}$	$-\Delta S^{\circ}$	ΔG°_{el}	$-\Delta G^{\circ}_{non}$	$-\Delta H^{\circ}_{el}$	$-\Delta H^{\circ}_{non}$
TSC							
Co complex	9.48	28.60	64.17	11.90	21.38	4.84	23.76
Ni complex	10.75	20.80	33.74	5.46	16.21	2.22	18.58
Cu complex	12.34	22.88	35.37	5.80	18.14	2.36	20.52
AG							
Co complex	6.48	23.80	58.13	10.63	17.11	4.32	19.48
Ni complex	7.16	19.22	40.47	6.89	14.05	2.80	16.42
Cu complex	7.74	20.59	43.13	7.45	15.19	3.03	17.56

ΔG^{0} , ΔH^{0} in K cal. mol^{-1} and ΔS^{0} in cal.K^{-1} mol^{-1}

In order to ascertain the possible stoichiometric ratio of complexes, conductometry titration was employed[17]. It is known that the conductance of any solution depends on the mobility of ions present and their concentrations. The addition of a solution to another one will affect the conductance according to whether ionic or not ionic

reactions occur. Therefore, the addition of ligand solution to the solutions of different cations will be accompanied by a change in conductance due to the formation of complexes. A common behavior of the conductograms (the relation between the conductance of cations solutions and ml added of ligands) is the continuous decrease with each successive addition of any ligand. The experimental titration curve consists of two straight lines intersecting at the equivalent point, i.e., the required stoichiometric ratio of complex, see Fig 1. It is observed that stable complexes are formed when one mole of TSC or AG interacts with one mole of transition metal cation as obtained from the potentiometric data.
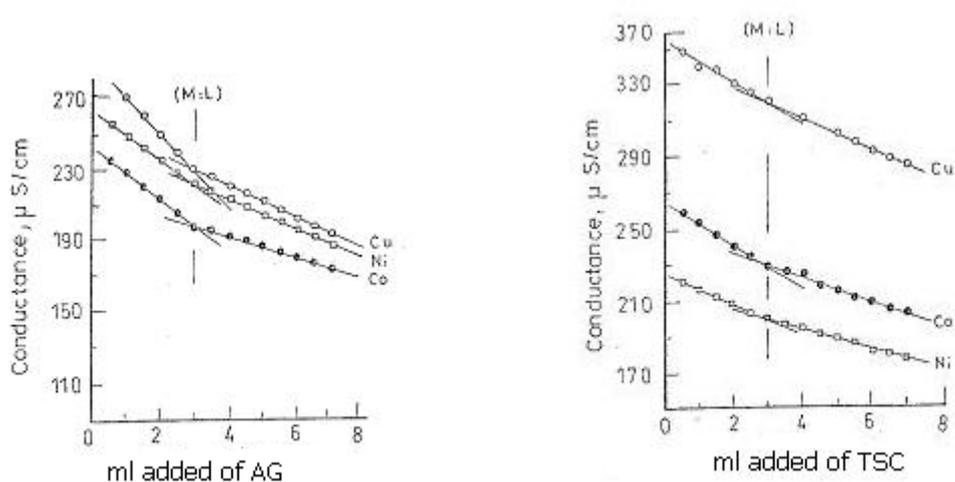

Fig. 1: Conductometric titration

The conductometric titration technique was not only used to predict the composition of complexes but also used to determine their stability constants using the relation[18]

$$K_n = \frac{1}{[L]^n} \frac{\Lambda_{exp} - \Lambda_M}{\Lambda_{ML} - \Lambda_{exp}}$$

where $\Lambda_{exp}, \Lambda_M, \Lambda_{ML}$ are the conductance values of solution, uncomplexed and complexed metal ions, respectively. n is the coordination number of ligand L. The calculated values are approximately equal to those obtained potentiometrically at 25°C.

Good information referring to the involvement of coordination sites of TSC or AG with the cations can be obtained by comparing the IR spectra of free ligands with those of their complexed molecules. The ligands show IR band at ~ 3355 cm^{-1} due to NH$_2$

group remaining unchanged in complexed molecules which indicates the presence of free NH_2 group[6]. The bands in the region 3260-3180 cm^{-1} are attributed to inter-molecularly hydrogen bond NH stretch[19]. In the metal complexes, the NH bands almost still unaltered suggesting the non-participation of NH group in bonding with the metal ion. The band of aminoguanidine at 1590 cm^{-1} ($\nu_{C=N}$) exhibits a negative shift by 30 cm^{-1} after complexation indicating the coordination of metal through azomethine nitrogen. The shift in the characteristic bands of C=S (1160 and 800 cm^{-1}) of thiosemicarbazide to lower frequency (1125 and 760 cm^{-1}) after the complexing process is a result of coordination through sulphur of thiocarbonyl group. The bending band of NH_2 group is observed at 1630 cm^{-1} and a lowering in frequency by 12-16 cm^{-1} with varying intensity of this band on complex formation supports the coordination through the terminal amino nitrogen of both ligands. Accordingly, the thiosemicarbazide molecule coordinates through N and S atoms[20], while the aminoguanidine molecule coordinates through N and N atoms.

Considerable attention has been paid on the study of the electrical properties of organic compounds and their complexes[21-25]. The electrical behavior is associated with the presence of π electrons of conjugated system which are not localized on definite carbon atoms, but capable of moving over the entire molecule. Incorporation of metal ions between organic molecules, i.e., formation of metal complexes, plays an important role for improving the electrical properties.

Therefore, the variation of logarithmic conductivity values of studied ligands and their copper complexes as a function of reciprocal temperature was followed in the temperature range 298-370 K. The linearity obtained shows the validity of the relation:

$$\sigma = \sigma^{o} \exp(-E/kT)$$

where E is the activation energy for releasing the free charge carriers, σ^{o} is pre-exponential factor and k is Boltzmann constant. The rate of increasing the conductivity values at low temperatures is slow but at high temperatures is considerably fast, as shown in Fig.2. This behavior can be attributed to the fact that at low temperature the charge carriers are firmly bound and the conduction is low, while as the temperature is increased, some bound charges are released to become free carriers and the conductivities is raised.

The values of electrical conductivity at 300 K are reported as: 1.78×10^{-10}, 4.35×10^{-9}, 3.98×10^{-8} and 7.57×10^{-8} ohm^{-1}cm^{-1}, for thiosemicarbazide, aminoguanidine and their copper complexes. It is clear that the conductivity is increased after formation of complexes, i.e., the metal ion may facilitate the flow of charge carriers throughout the ligand molecules.
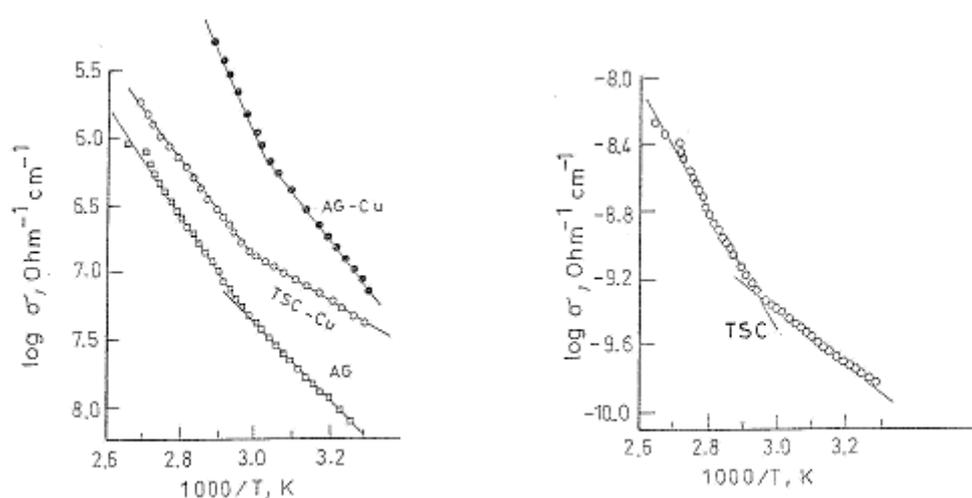

Fig 2: Electrical Conductivity of TSC, AG and their copper complexes

The evaluated activation energy in the low temperature region was found to be: 0.33, 0.61, 0.43 and 0.69 eV, for the four samples, respectively. However, the calculated mobility values of charge carriers using the relation: $\sigma = ne\mu$, give 1.57×10^{-11}, 1.96×10^{-5}, 1.69×10^{-7} and 7.55×10^{-3} cm^2 V^{-1} s^{-1} suggesting that the conduction takes place according to the hopping model, in which the charge carrier can move from one molecule to another by jumping over the barrier via an excited state.

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