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THERMODYNAMIC AND THERMAL INVESTIGATION OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH ADENINE

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Abstract

Complexes of adenine, AdH, with cobalt, nickel and copper chlorides were prepared and their thermodynamic functions were determined. The complexing processes are endothermic in nature. The thermal behaviour of complexes was followed up by using TG and DTA analyses. The stoichiometry of thermal decomposition of the investigated complexes was suggested.

Keywords: thermodynamic parameters, TG and DTA

Introduction

The chemistry of adenine and its metal complexes is of much current attention due to its contribution in many biological systems. Adenine show various probabilities of coordination with transition metal ions due to its potential donor sites. It coordinates with nickel, cobalt and palladium halides as a mono- or bidentate ligand and chloride bridging was found in the dehydrated complexes [1–3]. Binary and ternary complexes of Cu(II) with adenine and amino acids were prepared and characterized using spectral, thermal and magnetic measurements [4]. The electrical behaviour of adenine complexes was studied [5] which exhibited a semiconducting character.

Thermodynamic and thermal analyses play an important role in studying the structure and properties of metal complexes [6–13]. Consequently, in the present work, which has originated from our interest in studying the physical properties of metal complexes, the thermodynamic and thermal analyses of some adenine complexes have been investigated.

Experimental

All chemicals used were of pure laboratory grade. A digital pH-meter 5800-05 solution analyzer, Cole Parmer, was used for pH measurements. The method of Irving

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and Rossotti was used to determine the stability constants and related thermodynamic parameters of the complexes as described previously [14–16]. The measurements were repeated at 295, 305, 315 and 325 K.

The solid complexes were prepared in 50% (*v*/*v*) aqueous ethanol medium with a molar ratio of M:2L. In case of cobalt and nickel complexes 0.568 g of adenine dissolved in a small amount of bi-distilled water was mixed with a solution containing 0.5 g of $CoCl_2·6H_2O$ or $NiCl_2·6H_2O$, respectively. An equal volume of ethanol and water was added to the reacting mixture. The reaction mixtures were allowed to reflux for four days. For copper complex a solution of 0.793 g of adenine was mixed with a solution of 0.5 g $CuCl_2·2H_2O$ with continuous stirring. A blue precipitate was appeared at once. The prepared complexes were filtered, washed several times with water then ethanol and finally dried over anhydrous $CaCl_2$. The analytical data of the formed complexes are summarized in Table 1. Determination of chloride ions was carried out using Mohr's and Volhard's methods. Atomic absorption Perkin Elmer spectrophotometer A 100, was used for the determination of the metal ions.

Table 1 Analytical data of solid complexes

Compound (*MW*)	Analysis/%; found/(calc.)					Colour *m.p.*/°C
	C	H	N	*M*	Cl	
$[Co(AdH)_2Cl_2]\ H_2O$ (418.04)	28.6 (28.70)	3.20 (2.87)	35.80 (33.48)	14.01 (14.09)	15.90 (16.96)	violet 335
$[Ni(AdH)(Ad)Cl\ 3H_2O]\ H_2O$ (435.5)	28.50 (27.56)	4.40 (3.90)	30.80 (32.15)	13.87 (13.48)	9.71 (8.14)	green 300
$[Cu(AdH)_2Cl_2]\ 2H_2O$ (440.65)	26.50 (27.23)	3.20 (3.18)	30.40 (31.77)	14.80 (14.42)	16.40 (16.09)	blue 275

The thermal analysis of the complexes was performed using a Shimadzu DTA-TGA in the range 20–800°C with a uniform heating rate of 10°C min^{-1}. Platinum cell was used and mass of samples were ca. 3.5 mg. Nitrogen was used as a dynamic atmosphere (flow rate is 30 $cm^3\ min^{-1}$). Gravimetric analysis were carried out for solid complexes in a very clean, dried and carefully weighed platinum crucible. The samples were heated gradually from 20 to 800°C in an automatically controlled electric furnace for a period ranging from 3 to 4 h till constant mass at each temperature.

Results and discussion

The protonation and stability constants of adenine and its complexes were determined potentiometrically using the usual manner [14–16]. The calculated data are reported in Table 2. It is clear that the formation of the complexes takes place in two steps and the formation of M:L is more stable than M:2L. This finding may be attributed to the presence of pyrimidine ring and NH_2 group which showed electron – withdrawing and/or the electron – repelling character between adenine molecules.

The increase in temperature of heat treatment of the investigated complexes leads to an increase in the values of the stability constants suggesting an endothermic behaviour for the complexing process.

Table 2 Stability constants of adenine and its complexes

Compounds		Temperatures			
		195 K	305 K	315 K	325 K
Adenine	pK	9.50	8.90	8.85	9.40
Cobalt complex	$\log K_1$ $\log K_2$	3.20 2.95	3.60 3.30	4.20 3.80	4.50 4.00
Nickel complex	$\log K_1$ $\log K_2$	3.50 3.26	4.10 3.65	4.50 3.85	4.80 4.05
Copper complex	$\log K_1$ $\log K_2$	4.80 4.40	5.75 5.30	6.23 5.90	6.75 6.50

The thermodynamic functions, ΔG^0, ΔH^0 and $\Delta \mathrm{S}^0$, associated with the formation of complexes are computed using the well known relations:

$$\Delta G^0 = -2.303RT\lg K = \Delta H^0 - T\Delta S^0$$

and

$$\lg\frac{K_1}{K_2} = -\frac{\Delta H^0}{2.303R}\,\frac{T_2 - T_1}{T_1 T_2}$$

The results obtained are collected and given in Table 3. The positive values of the enthalpy changes demonstrate that the metal–adenine bonds are weak and the complexing process is endothermic in nature. However, the complexes are stabilized by relatively big increase in ΔS values, i.e., increase of the randomness of the complexes studied. At a given temperature, the more closely spaced the energy levels, the greater the number of levels that can be populated and consequently the greater the entropy, i.e., disorder. An increase in temperature provides energy for the population of even more energy levels and the accessibility of energy levels increases, therefore the disorder increases and higher stability values are obtained [17]. In other words, the big values of ΔS^0 means that the entropy is the main driving force for the formation of adenine complexes in aqueous medium.

Table 3 Thermodynamic data of adenine complexes at 295 K

Compounds	$-\Delta G^0$/kcal mol^{-1}	ΔH^0/kcal mol^{-1}	ΔS^0/cal mol^{-1} K^{-1}
Cobalt complex	4.32 3.98	19.76 14.18	81.62 61.57
Nickel complex	4.73 4.40	18.94 11.32	80.22 53.30
Copper complex	6.48 5.94	27.88 20.24	116.47 112.98

To clarify the nature of interaction between the metal ions and adenine molecule, covalent or ionic, the calculated thermodynamic data can be analyzed into electrostatic and non-electrostatic using the procedure suggested by Murakami and Yoshino [18].

$$\Delta G^0=\Delta G^0_{\mathrm{non}}+\Delta G^0_{\mathrm{el}}=nRT\ln M+RC(a+\underline{e}^{T/\theta})$$

$$\Delta H^0=\Delta H^0_{\mathrm{non}}+\Delta H^0_{\mathrm{el}}=RC[a+(1-T/\theta)e^{T/\theta}]$$

$$\Delta S^0=\Delta S^0_{\mathrm{non}}+\Delta S^0_{\mathrm{el}}=-nR\ln M-(RC/\theta)e^{T/\theta}$$

where θ is the characteristic temperature of the solvent and M is its molality. The terms C and a can be determined by solving the above equations. The obtained data are given in Table 4. It is obvious that the negative values of ΔG^0_{el} compared to those of $\Delta G^0_{\mathrm{non}}$ suggest that the electrostatic forces are stronger than non-electrostatic ones, i.e., the ionic character is more predominant. Whilst, $\Delta H^0_{\mathrm{non}}$ on and ΔH^0_{el} values are positive, however, the values of $\Delta H^0_{\mathrm{non}}$ are higher than those of ΔH^0_{el} indicating that the electrostatic nature of bond formation is predominant. The ratio of electrostatic values to non-electrostatic values are approximately constant for all complexes indicating that the complexing processes take place by a similar stoichiometry.

Table 4 Electrostatic and non-electrostatic components of thermodynamic parameters

Compounds	$\Delta G^0_{\mathrm{non}}$	$-\Delta G^0_{\mathrm{el}}$	$\Delta H^0_{\mathrm{non}}$	ΔH^0_{el}
Cobalt complex	14.67	18.99	12.31	7.45
	12.45	16.43	7.74	6.44
Nickel complex	13.96	18.69	11.61	7.33
	10.28	14.68	6.57	4.76
Copper complex	19.89	26.37	17.54	10.34
	23.50	29.44	12.53	7.70

The thermal decomposition of complexes was followed using TG and DTA techniques in the temperature range 20–800°C. The thermogrevimetric curves of adenine and its cobalt complex are given in Figs 1a and b. The thermal degradation of the complex shows three decomposition steps. The first peak at maximum temperature of 57°C which was not associated with any mass loss may be ascribed to the cleavage of hydrogen bonds or van der Waals bonds. The second stage occurs at maximum temperature of 120°C and associated with a mass loss of 4.065% corresponding to the loss of one uncoordinated water molecule (calc.=4.305%). The complete thermal decomposition of the complex occurred at 361.8°C with a mass loss of 76.423% (theoretically equals to 77.74%) giving tricobalt tetraoxide as a final product. Therefore, the stoichiometry of the thermal analysis can be represented as:

$$[\mathrm{Co(AdH)_2Cl_2}]\cdot\mathrm{H_2O}\xrightarrow{120^\circ\mathrm{C}}[\mathrm{Co(AdH)_2Cl_2}]+\mathrm{H_2O}$$

$$3[\mathrm{Co(AdH)_2Cl_2}]+2\mathrm{O_2}\xrightarrow{361.8^\circ\mathrm{C}}\mathrm{Co_3O_4}+\text{decomposition products}$$

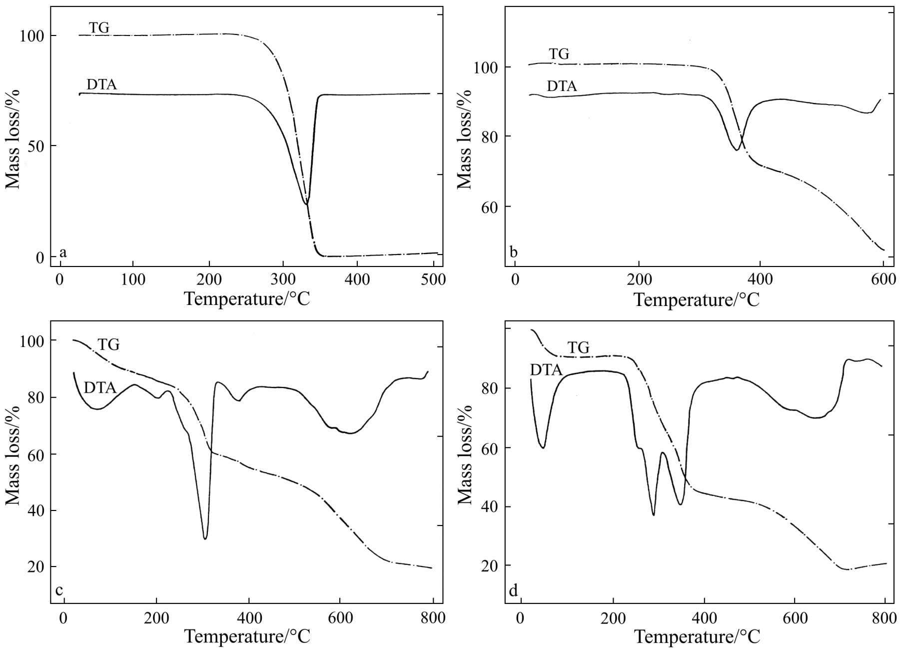

Fig. 1 TG and DTA curves of a – free adenine and its b – cobalt, c – nickel and d – copper complexes

To establish the proposed formula and structure of nickel complex, the thermal analysis was studied as shown in Fig. 1c. Four degradation steps were observed. The first decomposition step at 76.05°C has the same meaning as discussed earlier. The second step of degradation occurs at 120°C and is accompanied by a mass loss of 5.238% suggesting the loss of one uncoordinated water molecule (calc.=4.14%). The third step takes place at 208.2°C and is associated with the loss of three water molecules (obs.=12.11 and calc.=12.40%). The last degradation step was observed in the range 380–630°C with a mass loss of 66.67% corresponds to the loss of chloride and adenine molecules (neutral and anionic). Theoretically, the mass loss is 67.65%. In this step, the nickel ion will interact with the oxygen produced from the degradation of water molecules in the above steps yielding nickel oxide as a final product. Consequently, the proposed stoichiometry for the thermal decomposition of nickel–adenine complex may be written as:

$$[\mathrm{Ni(AdH)(Ad)Cl{\cdot}3H_2O]{\cdot}H_2O} \xrightarrow{120^\circ\mathrm{C}} [\mathrm{Ni(AdH)(Ad)Cl{\cdot}3H_2O]+H_2O}$$

$$[\mathrm{Ni(AdH)(Ad)Cl{\cdot}3H_2O}] \xrightarrow{208.2^\circ\mathrm{C}} [\mathrm{Ni(AdH)(Ad)Cl}]+3\mathrm{H_2O}$$

$$[\mathrm{Ni(AdH)(Ad)Cl}]+0.5\mathrm{O_2} \xrightarrow{380^\circ\mathrm{C}} \mathrm{NiO}+\text{decomposition products}$$

Finally, the stoichiometry of thermal decomposition of copper complex was studied and the thermogravimetric curves are demonstrated in Fig. 1d. The TG curves exhibit three main decomposition steps. The first step with no loss in mass was observed at 53.62°C. The second step appeared at 120°C and related to loss of two uncoordinated water molecules (obs.=8.695% and calc.=8.168%). The remaining part of ligands in the coordination sphere and chloride ions from the metal complex break in three steps at 262.5, 292.01 and 352°C. The total mass loss is 72.98% (cal.=74.81%) which was attributed to the loss of two chloride and two adenine molecules. The final decomposition product was found to be copper oxide. Accordingly, the stoichiometry of thermal decomposition can be suggested as:

$$[\mathrm{Cu(AdH)_2Cl_2}]\cdot 2\mathrm{H_2O} \xrightarrow{120°\mathrm{C}} [\mathrm{Cu(AdH)_2Cl_2}]+2\mathrm{H_2O}$$

$$[\mathrm{Cu(AdH)_2Cl_2}]+0.5\mathrm{O_2} \xrightarrow{352°\mathrm{C}} \mathrm{CuO}+\text{decomposition products}$$

The above findings were supported by the infrared spectra of the final thermal decomposition products. The spectra show the absence of all bands associated with the adenine molecule.

Conclusions

The formation of cobalt, nickel and copper adenine complexes is an endothermic process, i.e., the complexes are stable at elevated temperature. An electrostatic nature of the bond formation is observed. The thermal investigation of complexes illustrates that a complete decomposition occurred at nearly 360°C giving the metal oxide as a final product.

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