

THERMAL ANALYSIS OF ETHYLENEDIAMINE COMPLEXES OF Ni(II) CHLORIDE

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Thermal analysis of mono-, bis- and tris-ethylenediamine (en) complexes of Ni(II) chloride was carried out using TG, DTG and DTA techniques. The kinetic parameters were estimated from dynamic TG studies using the Coats and Redfern equation. The thermal stability of the metal-ligand (Ni-N) bond in the complex was found to decrease with increasing Ni : en ratio. The DTA studies showed that the loss of en was initially endothermic but became increasingly exothermic with the progress of the decomposition. The final step in the case of all the three complexes was always composite in nature causing the loss of both Cl atoms with simultaneous oxidation of Ni to NiO. The dissociation of the Ni-en bonds appears to be regulated by the "nucleation and growth" mechanism. Kinetic parameters corresponding to various steps of decomposition of all the three complexes were evaluated.

It is well-known that Ni^{2+} forms three well-defined chelate complexes with ethylenediamine (en) with stoichiometries of $[\text{Ni}(\text{en})]^{2+}$, $[\text{Ni}(\text{en})_2]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$ in solution [1] with their relative stabilities decreasing in the order mono ($\log k \sim 7.5$) > bis ($\log k \sim 6.4$) > tris ($\log k \sim 4.3$). It is also known that in aqueous alcoholic medium these three complexes can be obtained in solid form [2] with distinct colours, viz. green (mono), blue (bis) and purple (tris). Measurements of electrical conductivity of the three en complexes of Ni(II) chloride in solid state at various temperatures exhibited a number of discontinuities indicating structural phase changes and/or decomposition of these complexes with rising temperatures. Although some information on thermogravimetric analysis of the bis- and tris-complexes and their differential thermal analysis over a restricted range of temperature (upto $\sim 450^\circ$) has been found in literature [3], detailed thermal analysis on all the three complexes including the related kinetic parameters has not been reported. Such information would be helpful in understanding the above-mentioned discontinuities in electrical conductivity and the mechanism of electrical conduction in such complexes. Therefore, as a part of our studies on coordination compounds, the work on thermogravimetric analysis (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) of the mono-, bis- and tris-en complexes of Ni(II) chloride was undertaken to determine their thermal stability, decomposition steps and related kinetic parameters over the temperature range up to $\sim 800^\circ$.

Experimental

The three complexes, Ni(en)Cl_2 , $\text{Ni(en)}_2\text{Cl}_2$ and $\text{Ni(en)}_3\text{Cl}_2$ were prepared by treating solutions of NiCl_2 and en in aqueous medium with appropriate stoichiometric ratios by following the procedure described in the literature [2]. The complexes were characterised by elemental microanalysis (C, H and N), estimation of nickel by volumetric method [4a] and chlorine by ion-exchange chromatography [4b] and also by infrared and electronic spectroscopy. The nickel chloride, methanol and ethylenediamine used in the preparation were all AR-grade reagents. Dynamic thermal analyses (TG/DTG/DTA) were carried out on a "Netzsch" Thermal analyzer in a platinum crucible in air atmosphere at a heating rate of 10 deg/min up to 800° (Fig. 1, Table 1).

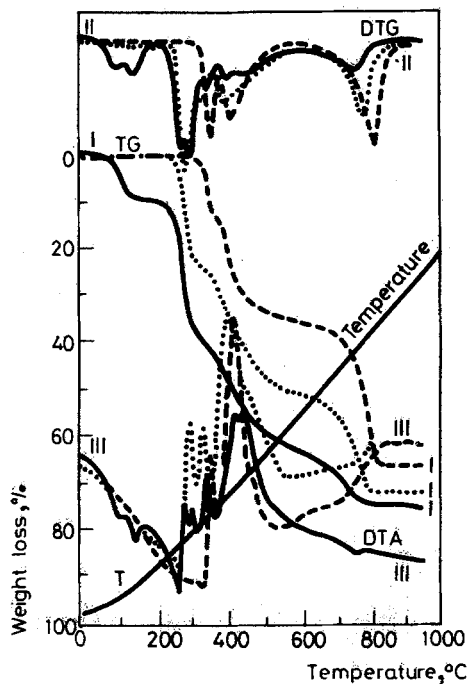


Fig. 1 TG (I), DTG (II) and DTA (III) curves for Ni(en)Cl_2 (---), $\text{Ni(en)}_2\text{Cl}_2$ (.....) and $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (—)

Table 1 Data on thermal decomposition and kinetic parameters of NiCl₂-ethylenediamine complexes

Complex	Step	Temp. range, °C	% mass loss observed (calc.)	Probable composition of		Order, <i>n</i>	Rate constant, <i>k</i> (<i>T</i> /K)	Activation energy <i>E_a</i> /kJ mol ⁻¹
				expelled group	residue			
Ni(en)Cl ₂	1	315-355	12.4 (10.5)	0.33 en	Ni(en) _{0.67} Cl ₂	1.75	0.83 (610)	273
	2	370-520	18.6 (16.8)	0.67 en	NiCl ₂	2.50	0.64 (690)	183
	3	560-800	37.68 (35.5)	Cl ₂	NiO	2.00	0.24 (1025)	293
Ni(en) ₂ Cl ₂	1	250-310	23.6 (24.2)	1 en	Ni(en) ₁ Cl ₂	1.75	0.69 (555)	188
	2	335-620	24.3 (24.0)	1 en	NiCl ₂	1.50	0.21 (695)	94
	3	635-775	22.7 (28.15)	Cl ₂	NiO	1.50	0.29 (1020)	276
Ni(en) ₃ Cl ₂ ·2H ₂ O	1	55-135	10.4 (9.7)	2 H ₂ O	Ni(en) ₃ Cl ₂	1.75	0.61 (365)	67
	2	145-300	31.54 (29.7)	1.5 en	Ni(en) _{1.5} Cl ₂	2.50	0.24 (540)	131
	3	310-495	21.35 (20.3)	1.5 en	NiCl ₂	2.5	0.27 (660)	131
	4	500-750	15.49 (15.91)	Cl ₂	NiO	0.66	0.11 (960)	56

Results and discussion

Elemental and spectral analysis

The results of elemental analysis indicate that the three complexes have molecular (empirical) formulas as Ni(en)Cl_2 , $\text{Ni(en)}_2\text{Cl}_2$ and $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$; the metal to ligand (Ni : en) ratios being the same as those for the respective species in solution [1]. The infrared spectra (nujol mulls) of all these complexes contain vibrational bands due to characteristic group frequencies corresponding to N—H stretching ($\sim 3140\text{--}3480\text{ cm}^{-1}$), NH_2 scissoring ($\sim 1570\text{--}1590\text{ cm}^{-1}$), NH_2 twisting ($\sim 970\text{--}995\text{ cm}^{-1}$), C—H stretching ($\sim 2860\text{--}3120\text{ cm}^{-1}$), CH_2 scissoring ($\sim 1450\text{--}1460\text{ cm}^{-1}$), CH_2 wagging ($\sim 1320\text{--}1340\text{ cm}^{-1}$), CH_2 twisting ($\sim 1270\text{--}1280\text{ cm}^{-1}$), Ni—N ($\sim 410\text{--}460\text{ cm}^{-1}$) and Ni—Cl ($510\text{--}530\text{ cm}^{-1}$) which are comparable with those reported in literature [5, 6] for similar compounds.

The electronic spectra in aqueous solutions for these three complexes contain 3 to 4 bands over the range $11,000\text{--}30,000\text{ cm}^{-1}$ characteristic of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ octahedral species in solution [7].

Thermal analysis

Of the three $\text{NiCl}_2\text{--en}$ complexes, it was found that the mono- and bis-complexes were anhydrous while the tris-complex was a dihydrate. The TG curve of Ni(en)Cl_2 showed loss of the chelated en over the temperature range of $315\text{--}520^\circ$ in two steps in a ratio of 1 : 2. The relative areas under the corresponding DTG peaks were consistent with this fractional loss of en. This observation suggests the possibility of a tri-nuclear framework of the complex. The loss of en was found to be exothermic from the DTA curves. This was followed by dissociation of NiCl_2 with loss of the two Cl's over the temperature range of $560\text{--}700^\circ$ with simultaneous oxidation of Ni, finally resulting in NiO at $\sim 800^\circ$ (Fig. 1).

The TG curve of $\text{Ni(en)}_2\text{Cl}_2$ showed a relatively sharp step over $250\text{--}310^\circ$ corresponding to the loss of one en followed by a somewhat broader step over $330\text{--}550^\circ$ indicating the slow loss of the second en. Both of these steps were again exothermic in nature. The third and final step occurred around 700° corresponding to the loss of both Cl atoms and simultaneous oxidation of Ni resulting in NiO as the ultimate residue as in the case of the mono-en complex.

The complex $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ exhibited a single and somewhat broad step over 60 to 130° in the TG curve corresponding to the loss of both water molecules. However, DTG and DTA curves clearly indicate it to be a composite step. The three en's were found to be lost in two steps of nearly equal magnitudes in the TG curves at $\sim 145^\circ$ and $\sim 310^\circ$, which is indicative of a transformation of the mononuclear tris-complex to some kind of binuclear complex after the first step. The loss of the

latter 1.5 en from the binuclear complex appears to take place at a slower rate than the first 1.5 en being lost from the initial mononuclear tris complex. The same behaviour was exhibited by the DTG trace corresponding to the two-step loss of the three en's. Again, the single step of the first fraction of the 1.5 en in the TG curve appeared to be actually a composite step from the DTG and DTA traces. From the DTA curve it is also apparent that the loss of crystal water is an endothermic process while the loss of the en exhibits exothermic peaks of progressively increasing magnitudes. The final step was dissociation of NiCl_2 with loss of both Cl atoms with simultaneous oxidation of Ni to NiO over a wide temperature range of ~ 500 to 750° similar as in the case of the mono- and bis complexes.

The kinetic parameters, viz. the order of reaction (n), activation energy ($E_a/\text{kJ mol}^{-1}$), the frequency factor (A) and rate constant (k) corresponding to each of the observed steps of decomposition in the TG curves discussed above were deduced by fitting the observed degree of decomposition (α) for each step to the Coats and Redfern equation [8].

The calculation of various kinetic parameters as explained above shows that, except for the last step in the case of the tris-complex, the order (n) for various steps ranges from 1.5 to 2.5 with the activation energies being of the order of 10^2 kJ/mol (Table 1). The crystal water in the tris-complex appears to be moderately strongly bound ($E_a \sim 67$ kJ/mol) which is not lost during the drying of the complex under vacuum. The loss of ligand molecules in mono-, bis- and tris-complexes occurring at progressively lower temperatures (~ 375 , 350 and 325° respectively) were also associated with progressively lower activation energies, viz., 230, 140 and 130 kJ/mol (averaged over the two step losses for en in each case). If the decomposition temperatures and activation energies are considered as the criteria of thermal stability then the thermal stability of metal-ligand bonds is found to decrease with increasing Ni:en ratio i.e. the stability decreases in the order mono > bis > tris (anhydrous). The deamination process for all the three complexes is found to be initially endothermic but further becomes progressively exothermic. Though the concept of order is not well defined for solid state thermal decomposition reactions, the number n deduced as above ranging over 1.5 to 2.5 can be considered to indicate the growth of nuclei to be two-dimensional and/or three dimensional in nature. The activation energies for the final steps in each case (viz., loss of chlorine together with atmospheric oxidation of Ni to NiO), were found to decrease with decreasing n though the related temperatures corresponding to the respective α max. values were quite comparable (~ 750 , 745 and 690° respectively).

The enthalpy changes for the bis- and tris-complexes in solution in presence of KCl are reported [1] to be ~ 75 and 120 kJ/mol respectively, both of which are smaller than the respective average activation energies (~ 140 and 130 kJ/mol) for

the loss of ligand molecules. Though the thermodynamic quantities for reactions in solution and solid state cannot be compared directly, the observation that $\Delta H < E_a$ can be taken to imply that the decomposition rate is regulated by the "nucleation and growth" mechanism [9].

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Zusammenfassung — Mittels TG-, DTG- und DTA-Verfahren wurde eine Thermounter suchung des mono-, bis- und tris-Äthylendiammin (en) komplexes von Ni(II)-chlorid durchgeführt. Unter Zuhilfenahme der Gleichung von Coats und Redfern wurden die kinetischen Parameter anhand der Daten aus dynamischen TG-Untersuchungen abgeschätzt. Es wurde gefunden, daß die thermische Stabilität der Metall-Ligand Bindung (Ni-N) der Komplexe mit anwachsendem Ni:en Verhältnis absinkt. Aufgrund der DTA Untersuchungen erwies sich die Abgabe von en anfänglich als endotherm, mit fortschreitender Zersetzung jedoch als zunehmend exotherm. Bei allen drei Komplexen war der letzte Schritt immer komplexer Natur und beinhaltete die Abgabe beider Chloratome verbunden mit einer gleichzeitigen Oxidation von Ni zu NiO. Die Dissoziation der Ni-en Bindung scheint durch einen „Keimbildungs- und wachstums“-mechanismus bestimmt zu werden. Die kinetischen Parameter für die einzelnen Zersetzungsschritte aller drei Komplexe wurden ermittelt.

Резюме — Методами ТГ, ДТГ и ДТА проведен термический анализ моно-, бис- и три-этилендиамминовых комплексов хлорида никеля. Исходя из данных динамической ТГ и используя уравнение Коутса-Редферна, были определены кинетические параметры. Найдено, что термоустойчивость связи металл-лиганд в комплексах уменьшается с увеличением соотношения никель:этилендиамин. ДТА исследования показали, что потеря лиганда носила первоначально эндотермический характер, но по мере дальнейшего разложения процесс становился все более экзотермическим. Конечная стадия разложения всех трех комплексов носила сложный характер, обусловленный потерей обоих атомов хлора и одновременным окислением никеля до его оксида. Разрыв связей никель-этилендиамин свидетельствует о механизме «образования и роста центров кристаллизации». Определены кинетические параметры различных стадий разложения всех трех комплексов.