

THERMAL ANALYSIS OF NICKEL(II) COMPLEXES WITH SOME N-MONOSUBSTITUTED ETHYLENEDIAMINES

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The thermal analysis of complexes of N—R-ethylenediamine, where R = ethyl, propyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-hydroxypropyl, with the halides, thiocyanate and sulphate of nickel is reported. The procedural decomposition temperatures of the complexes are given and considered in relation to the structures of the compounds.

The thermal properties of some nickel(II)-ethylenediamine complexes in inert and oxidising atmospheres has been reported by George and Wendlandt [1]. They found that there was no general pattern of thermal dissociation which was applicable to all of the TG curves for the $[\text{Ni}(\text{en})_3]\text{X}_2$ complexes but that, under inert atmospheric conditions, all of the curves exhibited an inflection point which corresponded closely to the evolution of one mole of ethylenediamine per mole of complex. The mass-loss curves of $[\text{Ni}(\text{en})_3]\text{SO}_4$ and $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$, however, showed one-step decomposition reactions resulting in the formation of nickel oxide.

In this work we report the thermogravimetric and differential thermal analysis of complexes of N—R-ethylenediamine, where R = ethyl (et-en), propyl (pr-en), 2-hydroxyethyl (etol-en), 2-hydroxypropyl (iprol-en) and 3-hydroxypropyl (prol-en), with the halides, thiocyanate and sulphate of nickel. Attempts to study the pyrolysis of analogous complex salts formed by nickel nitrate and perchlorate were unsuccessful owing to the explosive nature of their decomposition. The procedural decomposition temperatures for thermal dissociation of the complexes are recorded.

The substitution of a hydrogen atom on the alkyl chain by a hydroxyl group has been shown [2] to provide a new centre for co-ordination in certain of the complexes and the thermal decomposition of these compounds, in which the ligand is tridentate, is described.

Experimental

A Stanton thermobalance modified as previously reported [3] was employed for the thermogravimetric study of the complexes. The following conditions were adopted in all the thermogravimetric work:

Heating rate: 4° per minute

Chart speed: 6" per hour

Furnace atmosphere: pyrolysis was carried out in each case using (1) a static air atmosphere and (2) a dynamic nitrogen atmosphere with a gas flow of 100 ml per minute.

Sample holder: a platinum crucible (diam. 1.0 cm, depth 0.8 cm, weight 1.0 g).

Sample: all samples were finely ground and only that portion which passed through a 120-mesh sieve was employed. The sample weight was 100 mg.

The preparation of the complexes and the isolation of stable intermediates has been described previously [2].

The thermogravimetric study of each compound was carried out in duplicate as a check on the reproducibility of the results; virtually identical pyrolysis curves were obtained in each case.

Differential thermal analysis of the complexes was carried out using a Stanton differential thermal analysis apparatus (Standata 6-25) under the following conditions:

Heating rate: 10° per minute

Chart speed: 12" per hour

Furnace atmosphere: conditions were identical to those used in the thermogravimetric work.

Sample and reference holders: a matched pair of platinum crucibles (diam. 0.5 cm, depth 0.8 cm, weight 0.5 g) was employed.

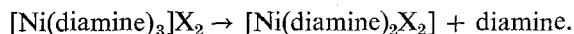
Sample and reference material: samples of the complexes were lightly ground (100 mesh) and the sample crucible packed using a "sandwich procedure" [4]. The reference material, α -alumina (20 mg), was weighed into the sample crucible followed by a layer of sample (20 mg) and the whole covered by a top layer of reference material (10 mg). This method was preferred to the dilution of the sample by mixing with the reference material, since this generally resulted in an aggregation of the particles of the two materials.

Results and discussion

The thermogravimetric (TG) curves obtained by pyrolysis of the *tris*-complexes in air did not indicate a general pattern of thermal decomposition applicable to all these complexes. The curves for $\text{Ni}(\text{et-en})_3\text{Br}_2$, $\text{Ni}(\text{et-en})_3\text{I}_2$, $\text{Ni}(\text{iprol-en})_3\text{SO}_4$ and $\text{Ni}(\text{pr-en})_3\text{I}_2$, however, gave horizontal weight levels corresponding to the loss of one mole of diamine per mole of complex; the *bis*-complexes $\text{Ni}(\text{et-en})_2\text{Br}_2$, $\text{Ni}(\text{pr-en})_2\text{I}_2$ and $\text{Ni}(\text{iprol-en})_2\text{SO}_4$ were isolated as stable intermediates and their physical properties have been reported [2]. The mode of decomposition of the *tris*-complexes under a nitrogen atmosphere was not found to differ markedly from that under air (Fig. 1).

A general feature of the DTA curves obtained by pyrolysis of the *tris*-complexes under air is that a relatively small endothermic peak is usually followed by two

large exothermic peaks (Fig. 1). With those *tris*-complexes which gave horizontal weight levels (TG curves) corresponding to the formation of *bis*-complexes, the endothermic peak clearly corresponds to the first stage of decomposition:



An exception to this general pattern is the DTA (air) curve for $\text{Ni}(\text{iprol-en})_3\text{SO}_4$ which only exhibits exothermic peaks.

The TG curves for the thermal decomposition of the *bis*-complexes in air and nitrogen were not characterised by well-marked horizontal weight-levels but points of inflection occurred which, however, did not correspond to the formation of stoichiometric compounds.

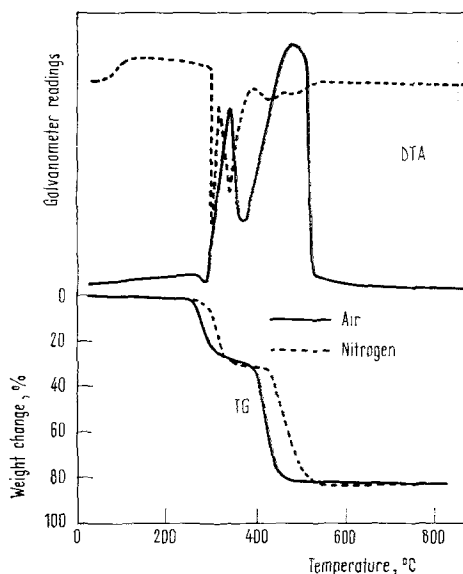


Fig. 1. TG and DTA curves of $\text{Ni}(\text{et-en})_3\text{Br}_2$

The thermal decomposition of those complexes in which the ligand is tridentate, with the exception of $\text{Ni}(\text{prol-en})_2\text{SO}_4$, follow a similar pattern which is illustrated by the TG and DTA curves of $\text{Ni}(\text{etol-en})_2\text{I}_2$ (Fig. 2). The TG curve shows that decomposition of the complex occurs in two stages; the first stage leads to the formation of an unstable intermediate containing less than one molecule of ligand per nickel(II) ion and this is followed by loss of the remaining ligand yielding nickel(II) oxide as the final product of pyrolysis. The small endothermic peak at 280° in the DTA (air) curve corresponds exactly to the melting point of the complex, while the two large exothermic peaks at 340° and 490° are associated with the two stages of decomposition. In the case of $\text{Ni}(\text{prol-en})_2\text{SO}_4$, thermal

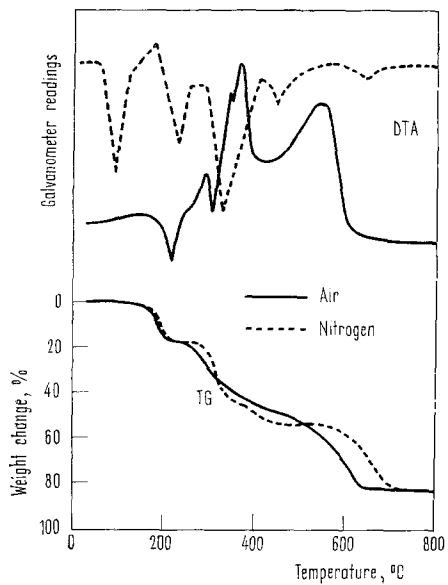


Fig. 2. TG and DTA curves of $\text{Ni}(\text{etol-en})_2\text{I}_2$

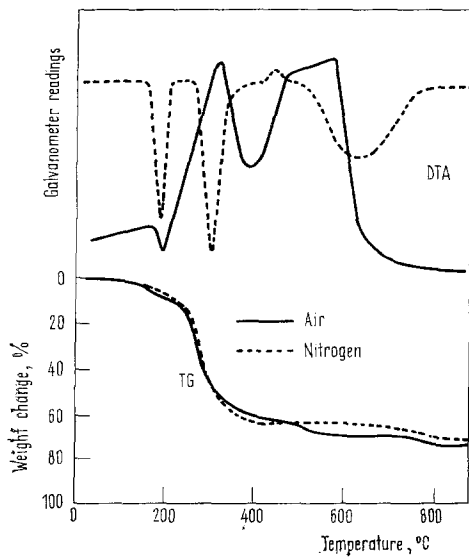


Fig. 3. TG and DTA curves of $\text{Ni}(\text{iprol-en})_2(\text{NCS})_2$

decomposition is more or less continuous with no well defined stages of decomposition.

It has been shown [2] that in the isothiocyanate complexes the diamine ligands are always bidentate and the NCS group is co-ordinated to nickel through the nitrogen atom. The TG curves for these complexes show thermal decomposition to be protracted over a wide temperature range and are difficult to interpret. The DTA (air) curves are, however, characterised by a small endothermic peak followed by two large exothermic peaks and it is suggested that decomposition occurs in three stages. The first stage corresponds to the formation of an unstable intermediate compound containing less than two molecules of ligand per nickel ion and is followed by loss of the remaining ligand and formation of nickel isothiocyanate. The end product of pyrolysis does not correspond to any stoichiometric compound. These features are illustrated by the TG and DTA curves of $\text{Ni}(\text{iprol-en})_2(\text{NCS})_2$ (Fig. 3).

The procedural decomposition temperatures [5] of the complexes under air and nitrogen are given in Table 1. For the *tris*-complexes, the temperatures tend to decrease with increasing molecular weight of the ligand in accord with the decreasing values of the stability constants of nickel complexes with these ligands as the size of the alkyl substituent is increased [6]. The procedural decomposition

Table 1
Procedural decomposition temperatures, °C

<i>Tris</i> -complexes	Air	Nitrogen	<i>Bis</i> -complexes	Air	Nitrogen
$\text{Ni}(\text{et-en})_3\text{Br}_2$	150	140	$\text{Ni}(\text{et-en})_2\text{Cl}_2$	225	240
$\text{Ni}(\text{et-en})_3\text{I}_2$	175	175	$\text{Ni}(\text{et-en})_2(\text{NCS})_2$	215	220
			$\text{Ni}(\text{et-en})_2\text{SO}_4$	55	75
$\text{Ni}(\text{etol-en})_3\text{Cl}_2$	140	150	$\text{Ni}(\text{etol-en})_2\text{I}_2^*$	240	250
$\text{Ni}(\text{etol-en})_3\text{Br}_2$	135	140	$\text{Ni}(\text{etol-en})_2(\text{NCS})_3$	220	220
			$\text{Ni}(\text{etol-en})_2\text{SO}_4$	235	200
$\text{Ni}(\text{pr-en})_3\text{I}_2$	120	120			
$\text{Ni}(\text{iprol-en})_3\text{Cl}_2$	80	80	$\text{Ni}(\text{pr-en})_2\text{Cl}_2$	240	240
$\text{Ni}(\text{iprol-en})_3\text{Br}_2$	40	90	$\text{Ni}(\text{pr-en})_2\text{Br}_2$	175	265
$\text{Ni}(\text{iprol-en})_3\text{I}_2$	100	100	$\text{Ni}(\text{pr-en})_2(\text{NCS})_2$	180	185
$\text{Ni}(\text{iprol-en})_3\text{SO}_4$	75	75	$\text{Ni}(\text{pr-en})_2\text{SO}_4$	80	140
			$\text{Ni}(\text{iprol-en})_2(\text{NCS})_2$	105	110
			$\text{Ni}(\text{prol-en})_2\text{Cl}_2^*$	245	270
			$\text{Ni}(\text{prol-en})_2\text{Br}_2^*$	240	265
			$\text{Ni}(\text{prol-en})_2\text{I}_2^*$	245	265
			$\text{Ni}(\text{prol-en})_2(\text{NCS})_2$	235	190
			$\text{Ni}(\text{prol-en})_2\text{SO}_4^*$	80	70

*Tridentate ligand.

temperatures for the *bis*-complexes do not exhibit any definite trend but a marked similarity is observed for those complexes in which the ligand is tridentate. A general feature of the compounds containing sulphate is their low procedural decomposition temperatures, although Ni(etol-en)₂SO₄ is anomalous in this respect. It has been shown [2] that, with the exception of Ni(prol-en)₂SO₄, the sulphate group in the *bis*-complexes has C_{2v} symmetry and is co-ordinated to the metal.

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RÉSUMÉ — On communique les résultats relatifs à l'analyse thermique des complexes formés par la N—R-éthylènediamine (R = éthyl, propyl, hydroxy-2 éthyl, hydroxy-2 propyl et hydroxy-3 propyl) avec les halogénures, le thiocyanate et le sulfate de nickel. On a cherché à établir une relation entre la température observée pour la décomposition et la structure des composés.

ZUSAMMENFASSUNG — Es wurde über die thermoanalytische Prüfung der Komplexe von N—R-äthylendiamin (R = Äthyl, Propyl, 2-Hydroxyäthyl, 2-Hydroxypropyl und 3-Hydroxypropyl) mit Nickelhalogenid, -sulfat und -rhodanid unter Angabe der entsprechenden Zersetzungstemperaturen in Zusammenhang mit den strukturalen Umwandlungen der Verbindungen berichtet.

Резюме — Описан термический анализ комплексов N—R-этилендиамина, где R = этил, пропи́л, 2-оксиэтил, 2-оксипропил и 3-оксипропил, с галогенидами, тиоцианатом и сульфатом никеля. Приведены температуры процесса разложения комплексов и рассмотрены в связи со структурой соединений.