

## Thermal Stability of Coordination Polymers

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### Synopsis

Polymers formed between three ligands and selected metal ions were prepared and their thermal stability in air was investigated. 1,5-Dihydroxynaphthalene-2,6-dicarboxylic acid (1,5-N-2,6) formed coordination polymers with Zn, Ni, Al, and Fe<sup>+3</sup>. Zn-1,5-N-2,6 was more stable than the corresponding Fe and Ni polymers. Pyromellitic acid (PMA) formed coordination polymers of high molecular weight with Th and U<sup>+4</sup>. The Th-PMA was stable up to 405°C., while the corresponding uranium compound decomposed below 400°C. The coordination polymer of 2,3,6,7-naphthalenetetracarboxylic acid (NT) with Th was less stable (decomposition temperature: 360°C.) than the corresponding pyromellitic polymer because the coordination of Th in Th-NT was partially accomplished by water molecules rather than carboxylic oxygens as in the Th-PMA polymer. The thermal stability of these polymers was a function of the metal involved in coordination. Higher thermal stability resulted when Zn or Th were used than if metals capable of changing their ionic valency were involved in polymer formation.

Prerequisites for the thermal stability of coordination polymers can be compiled from the published literature.<sup>1-3</sup> All the polymers which were found to be stable at 300°C. or higher met one or several of the following criteria: (1) use of thermally stable starting materials; (2) use of aromatic rather than aliphatic ligands; (3) use of ligands capable of forming five-, six-, or seven-membered rings with a metal, resulting in chelates of high thermodynamic stability; (4) the satisfaction of all ionic valencies of the metal by the ligand; (5) high molecular weight of the resulting polymer. Rarely, however, did any one of the published coordination polymers fulfill more than two or three of the above cited prerequisites.

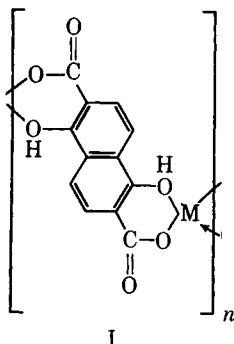
The role of the metal in coordination polymers has also been discussed extensively, and the hypothesis was advanced that use of metal ions with only one ionic valency results in formation of more stable coordination polymers than the use of metals which possess several oxidation states.<sup>4,5</sup> This hypothesis, however, does not seem to be applicable to all ligands.<sup>6,7</sup>

It was the aim of this investigation to synthesize polymers which would fulfill all or most of the listed prerequisites, and in particular, to study the influence of the metal on the thermal stability of the resulting polymers.

### RESULTS AND DISCUSSION

The presumed thermal stability of 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid (1,5-N-2,6) (m.p. 300°C.) and its two  $\pi$  systems made this

ligand a good choice for the formation of coordination polymers with divalent (and trivalent) metal ions with which this ligand could form electrically neutral six-membered chelate rings (I). Unexpectedly, the ligand



showed appreciable thermal degradation below its melting point (Fig. 1). The preparation of coordination polymers was carried out in spite of this shortcoming with the aim to study the influence of metals on the thermal stability of the resulting coordination polymers.

In order to study the influence of the metal ion on the thermal stability of the resulting polymer, the following metal ions were selected: Zn(II), Ni(II), Al(III), Fe(III), Th(IV), U(IV), U(VI). These ions constitute pairs of di-, tri-, and tetravalent metals. One in each of these pairs (e.g., Zn, Al, Th) has constant, the other variable valency (e.g., Ni, Fe, U). Four of these ions form  $d^2sp^3$  hybrids (e.g. Zn, Ni, Al, Fe) (although formation of  $sp^3$  hybrids with Zn and of  $dsp^2$  hybrids with Ni is possible). The tetravalent metals are octacoordinate and constitute a group of their own.

It should now be possible to compare the thermal stability of coordination polymers formed from: (1) different ligands with the same metal as a function of the ligand; (2) the same ligand with metals of the same initial valency and the same hybridization as a function of the metal (constant vs. variable valency for either di-, tri-, or tetravalent metals); (3) the same ligand with metals of different initial valencies (di- as well as trivalent) and the same hybridization again as function of the ability of the metal to change its valency.

The elemental analysis of the coordination polymer of 1,5-N-2,6 with zinc, as well as the thermogram (Fig. 1) showed that it contained 1 mole of water per mer of the polymer. This would require pentacoordinated Zn or, more likely,  $d^2sp^3$  hybridization with four coordination positions taken by two ligands, the fifth by water, and the sixth probably by a carbonyl oxygen of a neighboring mer of the coordination polymer. The weight loss between 150 and 220°C. (Fig. 1) corresponded to the loss of 1 mole of water. After a small plateau, more rapid decomposition set in at 220°C., which resulted in complete combustion of the organic material. ZnO was the residue at temperatures above 400°C.

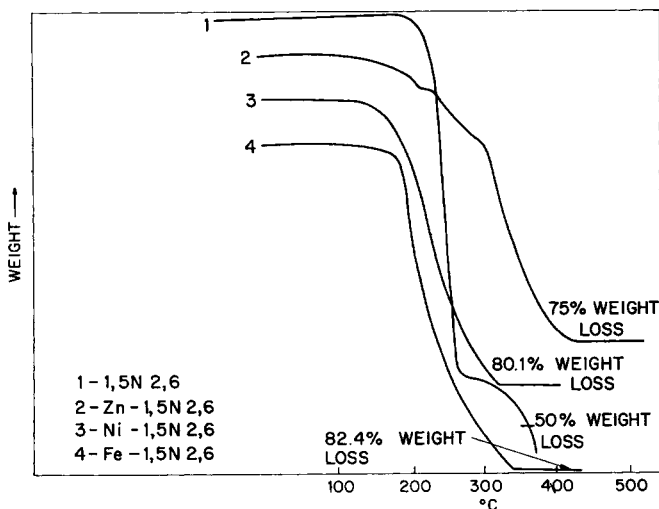


Fig. 1. Thermal stability of 1,5-dihydroxy-2,6-naphthalenedicarboxylic acid (1, -N-2,6) and its coordination polymers with zinc, nickel, and iron: (1) 1,5-N-2,6; (2) Zn-1,5-N-2,6; (3) Ni-1,5-N-2,6; (4) Fe-1,5-N-2,6.

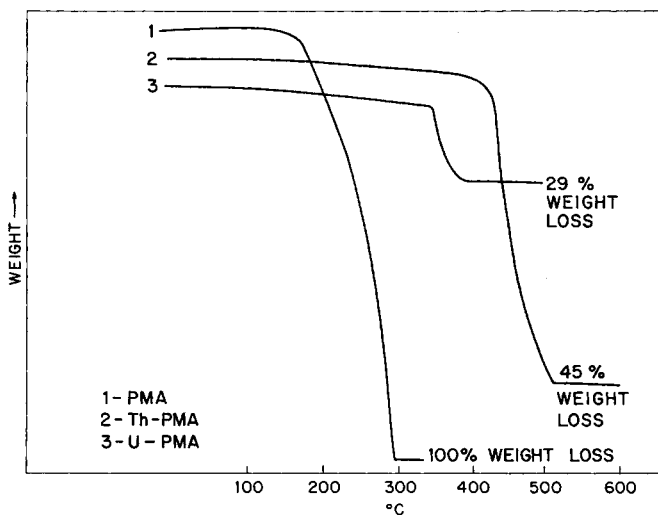
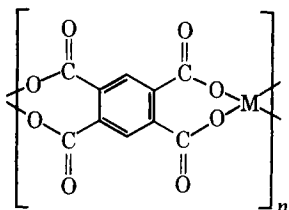


Fig. 2. Thermal stability of pyromellitic acid (PMA) and its coordination polymers with thorium and uranium (IV): (1) PMA; (2) Th-PMA; (3) U-PMA.

The nickel chelate contained 4 moles of water per mer which suggested hexacoordination of nickel, with two coordination positions taken by two ligands (carboxyl groups) and none by the phenolic OH groups. (The absence of the original  $\text{Cl}^-$  counterions was established). Unlike the zinc-coordination polymer, the decomposition of the nickel-containing polymer was not preceded by the loss of water (Fig. 1). Indeed, decomposition occurred in one step, sharply at approximately  $150^\circ\text{C}$ .

Polymers of 1,5-N-2,6 with Zn, Ni, and Fe contained water, yet decomposition of the nickel and iron polymers was spontaneous while the zinc polymer lost water first and then decomposed. In view of this, it can be assumed the decomposition of the nickel- and iron-containing polymers was catalyzed by these metals which were capable of redox reactions. The sharp break in the thermograms of these polymers seemed further to substantiate this point.<sup>8</sup>

Pyromellitic acid (PMA) is reported to be stable at its melting point (279°C.)<sup>9</sup> although it sublimes at 180°C. Its reaction with tetravalent metals should produce two seven-membered chelate ring systems, interlinking the aromatic rings (II). Such coordination polymers, if of high



II

molecular weight, would fulfill all the listed prerequisites for thermal stability. The decomposition of Th-PMA (Fig. 2) began at 405°C. and proceeded to the complete combustion of the organic material; ThO<sub>2</sub> is left as residue. The unstoichiometric uranium polymer began to decompose abruptly at approximately 350°C. It is interesting to note that in spite of the presence of an excess of ligand, the decomposition of the coordination polymer was not preceded by weight loss due to decarboxylation at incompletely reacted ligand molecules, which suggested again a catalytic influence of the metal capable of being oxidized (to UO<sub>2</sub><sup>+2</sup>).

The incorporation of another aromatic ring into the Th-PMA polymer, by going from benzene to naphthalene tetracarboxylic acid, was expected to result in a polymer even more stable than Th-PMA.

Figure 3 shows that the thermal decomposition of the starting material, 2,3,5,6-naphthalenetetracarboxylic acid (NT) proceeded in two steps. The weight loss between 125 and 180°C. corresponded to the loss of 2 moles of water per mole NT; the dianhydride was formed. Its decomposition began at approximately 260°C. and was completed at 485°C.

The coordination polymer of NT with Th, which contained according to elemental analysis 2 moles of water per mer, dehydrated between 100 and 250°C. (Fig. 3). Rapid decomposition of the anhydrous polymer began at 380°C.

The reason for the apparent discrepancy in thermal stability between Th-NT and Th-PMA may lie in the fact that, although neither of these ligands was octadendate and therefore could not complete the shell of the eight-coordinate thorium (IV) ion, coordination of Th(IV) in Th-PMA was accomplished without foreign molecules—perhaps by carbonyl groups of

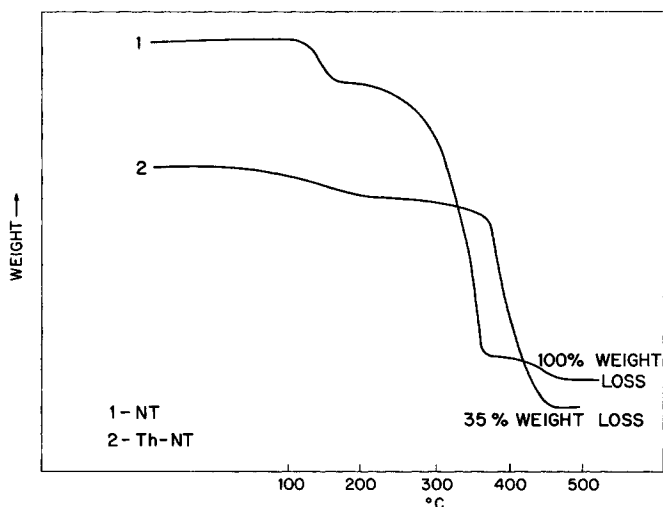
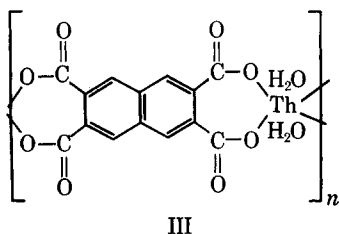


Fig. 3. Thermal stability of 2,3,6,7-naphthalenetetracarboxylic acid (NT) and its coordination polymer with thorium: (1) NT; (2) Th-NT.

neighboring chains. In the case of Th-PMA, however, two of the eight coordination positions of the Th(IV) ion were taken by water molecules (III). Upon their removal, a less favorable steric arrangement of the



ligand molecules remained which was more susceptible to thermal degradation than the Th-PMA.

## EXPERIMENTAL

### 1,5-Dihydroxynaphthalene-2,6-Dicarboxylic Acid (1,5-N-2,6)

The preparation of the starting material according to von Hemmelmayr<sup>10</sup> was modified somewhat: 25 g. of 1,5-naphthalenediol, 50 g. of KHCO<sub>3</sub> and 200 g. of 1,2,4-trichlorobenzene were heated at 230°C. for 3 hr. in a shaker tube. The mixture was then filtered and the residue washed with diethyl ether, dissolved in approximately 7 1/2 liters of distilled water, and filtered. HCl was added to the clear solution until a pH of 1.5 was attained. A yellow precipitate formed which was recrystallized from 50% ethanol-water. The yield was 32.2 g. (86% of theory).

ANAL. Calcd. for C<sub>12</sub>H<sub>8</sub>O<sub>6</sub>: C, 58.07%; H, 3.25%; equiv. wt. 124.09%. Found: C, 58.3%; H, 3.3%; equiv. wt. 125.

### Chelates

Several different approaches were tried for the preparation of each of the metal chelates. Best results were obtained according to the following procedures.

**Zn-1,5-N-2,6.** 1,5-N-2,6 (0.001 mole, 0.25 g.) was dissolved in 150 ml. of H<sub>2</sub>O. To this solution, the pH of which was 10, was added 6 ml. of approximately 1N KOH. Then, 1N HCl was added to attain a pH of 5.5. ZnCl<sub>2</sub>·6H<sub>2</sub>O (0.003 mole, 0.4 g.) was dissolved in 50 ml. of H<sub>2</sub>O under the addition of a few drops of 1N HCl and the solutions were combined; the pH was 5.5. A precipitate formed which was filtered, washed first with ethanol, then with diethyl ether and dried overnight at 100°C. *in vacuo*.

ANAL. Calcd. for (C<sub>12</sub>H<sub>6</sub>O<sub>6</sub>·Zn·1H<sub>2</sub>O)<sub>n</sub>: C, 43.73%; H, 2.44%; Zn, 19.83%. Found: C, 44.0%; H, 2.7%; Zn, 19.6%.

**Ni-1,5-N-2,6.** The procedure outlined for the zinc compound was followed. The amounts used were: 0.002 (0.5 g.). 1,5-N-2,6 dissolved in 150 ml. of H<sub>2</sub>O plus 12 ml. (7.1 g.) NiCl<sub>2</sub>·6H<sub>2</sub>O dissolved in 50 ml. of water, pH = 5.

ANAL. Calcd. for (1,5-N-2,6·Ni·4H<sub>2</sub>O)<sub>n</sub>: C, 38.23%; H, 3.74%; Ni, 15.57%. Found: C, 37.8%; H, 4.0%; Ni, 15.6%.

**Al-1,5-N-2,6.** The same procedure was followed. The amounts used were: 0.003 mole (0.75 g.), 1,5-N-2,6 dissolved in 100 ml. H<sub>2</sub>O plus 15 ml. of 1N KOH. The pH was adjusted with 1N HCl to 5.5. Then, 0.002 mole (0.48 g.) of AlCl<sub>3</sub>·6H<sub>2</sub>O dissolved in 53 ml. H<sub>2</sub>O, pH = 5, was added. The precipitate contained 12.5% aluminum. Calculated for (1,5-N-2,6·2/3 Al)<sub>n</sub>: 6.76% aluminum. All attempts to improve the composition of this compound failed.

**Fe-1,5-N-2,6.** The same procedure followed. The amounts used were 0.003 mole (0.75 g.) 1,5-N-2,6 dissolved in 100 ml. H<sub>2</sub>O plus 15 ml. of 1N NaOH. The pH was adjusted to 5.5 with 1N HCl, and of 0.002 mole (0.54 g.) FeCl<sub>3</sub>·6H<sub>2</sub>O dissolved in 50 ml. H<sub>2</sub>O was added.

ANAL. Calcd. for (1,5-N-2,6·2/3 Fe·H<sub>2</sub>O)<sub>n</sub>: C, 47.82%; H, 2.67%; Fe, 12.35%. Found: C, 47.4%; H, 3.0%; Fe, 12.3%.

All attempts to prepare stoichiometric uranium- and thorium-containing coordination polymers failed.

**Th-PMA.** Several procedures to prepare the thorium-pyromellitic acid (PMA) coordination polymer were tried. The best stoichiometry was obtained according to the following procedure. Pyromellitic acid (0.02 mole, 5.08 g.) (obtained in the purest form from the Eastern Laboratory of E. I. du Pont de Nemours & Company) was dissolved in 500 ml. H<sub>2</sub>O. The PMA solution was added dropwise from a dropping funnel to the stirred solution of ThCl<sub>4</sub> which was kept at 100°C. A white precipitate formed which was dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> for 48 hr.

ANAL. Calcd. for (C<sub>10</sub>H<sub>2</sub>O<sub>8</sub>·Th)<sub>n</sub>: C, 24.91%; H, 0.42%; Th, 48.14%. Found: C, 24.5%; H, 0.7%; Th, 47.5%.

**U-PMA.** Stoichiometric U-PMA compositions could not be isolated. Best results were obtained according to the procedure used for the preparation of Th-PMA. The quantities were 0.002 mole (0.508 g.) PMA dissolved in 50 ml. H<sub>2</sub>O plus 0.004 mole (3.2 g.) of UCl<sub>4</sub> dissolved in 100 ml. H<sub>2</sub>O. The precipitate contained 33% uranium (theory 38.75%).

**Th-NT.** Of 2,3,6,7-naphthalenetetracarboxylic acid (NT) (0.001 mole, 0.3 g.) (obtained in purest form from Eastern Laboratory, E. I. du Pont de Nemours & Company) was dissolved in 100 ml. of boiling water. This solution was added rapidly to a hot stirred solution of 0.0015 mole of ThCl<sub>4</sub> in 100 ml. of water. A white precipitate formed immediately. After centrifugation the clear, supernatant solution had a pH of 6. The precipitate was slurried and centrifuged several times until the supernatant solution failed to give a chloride reaction with AgNO<sub>3</sub>. The precipitate was dried at 100°C. *in vacuo*.

ANAL. Calcd. for (NT·Th·2H<sub>2</sub>O)<sub>n</sub>: C, 29.60%; H, 1.42%; Th, 40.8%. Found: C, 30.1%; H, 1.7%; Th, 40.6%.

Determinations of the thermal stability of all compounds described above were carried out on a thermogravimetric balance, system Chevenard, in an air atmosphere. The decomposition temperature was defined as the temperature at which the rate of weight loss became 3%/min. when the sample was heated at a rate of 5°C./min.

All polymers described above were insoluble in all conventional solvents, making a convenient determination of their molecular weights impossible.

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### Résumé

Les polymères formés entre trois ligandes et des ions métalliques choisis ont été préparés et leur stabilité thermique à l'air examinée. L'acide 1,5-dihydroxynaphtalène-2,6-dicarboxylique forme des polymères de coordination avec le Zn, Ni, Al, et Fe<sup>3+</sup>. Le polymère au zinc était plus stable que ceux au Fe et Ni. L'acide pyromellitique (PMA) forme des polymères de coordination de poids moléculaire élevé avec Th et U<sup>4+</sup>. Le Th-PMA est stable jusqu'à 405° tandis que celui à l'U décompose en-dessous de 400°. Le polymère de coordination de l'acide 2,3,6,7-naphtalène-tétracarboxylique (NT) avec Th est moins stable (décomposition à 360°) que le polymère pyromellitique correspondant, parce que la coordination du Th dans Th-NT est partiellement réalisée par des

molécules d'eau plutôt que par les oxygènes carboxyliques, comme c'est le cas dans le polymère Th-PMA. La stabilité thermique de ces polymères est une fonction du métal coordonné. Une stabilité thermique meilleure est obtenue avec le Zn ou le Th que si des métaux capables de changer de valence ionique participent à la formation de polymères.

### Zusammenfassung

Aus drei Liganden und ausgewählten Metallionen gebildete Polymere wurden dargestellt und ihre thermische Stabilität in Luft untersucht. 1,5-Dihydroxynaphthalin-2,6-dicarbonsäure (1,5-N-2,6) bildete Koordinationspolymere mit Zn, Ni, Al, und  $Fe^{+3}$ . Zn-1,5-N-2,6 war stabiler als die entsprechenden Fe- und Ni-Polymeren. Pyromellitsäure (PMA) bildete mit Th und  $U^{+4}$  hochmolekulare Koordinationspolymere. Th-PMA war bis zu  $405^\circ$  stabil, während sich die entsprechende Uranverbindung unterhalb  $400^\circ$  zersetzte. Das Koordinationspolymere aus 2,3,6,7-Naphthalintetracarbonsäure (NT) und Th war weniger stabil (Zersetzungstemperatur  $360^\circ C$ ) als das entsprechende Pyromellitsäurepolymere, da die Koordination von Th in Th-NT zum Teil durch Wassermoleküle erfolgte und nicht durch Carboxylsauerstoff, wie im Th-PMA-Polymeren. Die thermische Stabilität dieser Polymeren war eine Funktion des an der Koordination beteiligten Materials. Zn oder Th lieferten eine höhere thermische Stabilität als sie bei der Verwendung von Materialien, welche zur Änderung ihrer Ionenwertigkeit fähig sind, zur Polymerbildung erhalten wurde.

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