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THERMAL DECOMPOSITION OF PALLADIUM–IMIDAZOLE COMPLEXES

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Two Pd–imidazole complexes have been synthesized following the reaction of $PdCl_2$ and imidazole at 1 : 2 and 1 : 4 metal : ligand ratios. Elemental and thermogravimetric analytical data obtained from these compounds illustrate that they have the formulae $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ and $Pd(IMDAH)_3Cl_2$ (IMDAH = imidazole), respectively. The mechanism of thermal decomposition for these complexes in air involves initial dissociation of H_2O and IMDAH ligands in the 120–340 °C range, subsequent dissociation of the chloride atoms to form PdO in the 530–570 °C range, and finally formation of Pd metal at 820–840 °C.

Heterocyclic ligands are used in several industrial and medical applications. For example, azoles have been used as corrosion inhibitors for metals and alloys [1] and complexes formed between azoles and Cu or Pd metals have been used to model biological structures and in anti-tumor drug therapy [2, 3]. The nature of chemical bonding in Cu-azole complexes has been studied by several techniques including X-ray photoelectron spectroscopy (XPS) [4, 5], Fourier transform infrared spectroscopy (FTIR) [6], and X-ray diffraction [7]. However, at this time relatively little work has appeared on Pd-azole compounds.

Pd-IMDAH (IMDAH = imidazole) complexes may be useful in industry as catalytic agents in epoxy curing reactions. For such applications the thermal stability of the complex could influence the curing mechanism of the resin and subsequently its physical properties. Previously, several Pd-IMDAH complexes have been prepared and characterized by FTIR spectroscopy [3]. This paper reports the synthesis and elemental characterization of two Pd-IMDAH complexes and describes their mechanism of thermal decomposition.

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Experimental

The Pd-IMDAH complexes were prepared by reacting $PdCl_2$ (1 mmol) and imidazole (either 2 or 4 mmol) in an acetone (50 ml)/dimethylformamide (2 ml) solution containing a few drops of HCl. In each case the reaction was immediate and resulted in the precipitation of orange (at the 1 : 2 metal/ligand ratio) or white (at the 1 : 4 metal/ligand ratio) powders. These products were filtered, washed with dry ether and then vacuum dried at 60° for 12 h.

Elemental (C, H, N) analyses were performed for both complexes by Desert Analytics Co. using combustion techniques. A DuPont Model 951 thermogravimetric analyzer coupled to the 990 data station was used to obtain thermal degradation profiles for the complexes and the free IMDAH ligand. The temperature was increased at the rate of 20 deg/min and a constant flow of air (250 cc/min) was admitted to the sample chamber. The sample size was approximately 5.0 mg and the errors on the experimental weights are ±0.5%.

Results and discussion

Figure 1 illustrates the thermal degradation profile recorded from the free IMDAH ligand. The onset of degradation is observed at 167° and initially the thermal degradation proceeds at a slow rate. This initial slow step is attributed to a loss of absorbed water. The thermal degradation then becomes much more rapid and the free ligand is completely volatilized at 209°.

Figure 2 depicts the thermal degradation profiles for both Pd-IMDAH compounds. The initial stages of decomposition are significantly different for the two compounds but the final degradation steps and weight percent residue are very

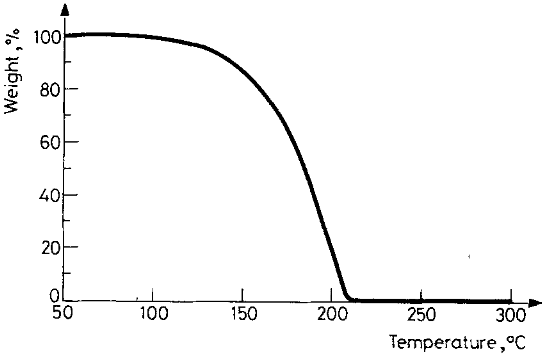

Fig. 1 TG profile for free imidazole (IMDAH) ligand recorded in air at a heating rate of 20 deg/min

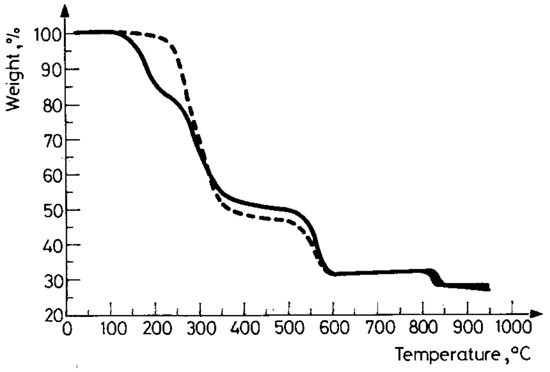

Fig. 2 TG profiles for (——) hydrated $Pd(IMDAH)_2Cl_2$ and (- - -) $Pd(IMDAH)_3Cl_2$ complexes recorded in air at a heating rate of 20 deg/min

similar for both species. The final weight percent residue is attributed to residual Pd metal only as $PdCl_2$ and PdO decompose at temperatures lower than 900° [8]. Thus, the TG data suggests that both complexes have approximately equal molecular weights. The molecular weight (M_{wt}) and final weight percent residue at 900° ($W\%_{900}$) may be related by

$$M_{wt} = 68.1X + 106.4Y + 70.9Y \tag{1}$$

$$W\%_{900} = 106.4Y/M_{wt} \tag{2}$$

where X and Y are the number of imidazole ligands and $PdCl_2$ molecules and the coefficients in Eq. (1) refer to the molecular weights of the imidazole ligands, Pd, and 2Cl, respectively. Combining equations 1 and 2 yields

$$X/Y = (1.56/W\%_{900}) - 2.60 \tag{3}$$

Solving Eq. (3) using the remaining weight percent obtained from Fig. 2 gives a ligand to metal ratio of three for either complex. This result is in agreement with the determined elemental analysis data (see Table 1) indicating that the white complex has the formula $Pd(IMDAH)_3Cl_2$. On the other hand, the elemental analysis data

Table 1 Elemental analysis of synthesized Pd-IMDAH complexes

Element	$Pd(IMDAH)_2Cl_2 \cdot 4H_2O$		$Pd(IMDAH)_3Cl_2$	
	obsd.	theory	obsd.	theory
C	19.5	18.7	30.6	28.3
H	2.5	2.1	3.3	3.1
N	14.9	14.5	23.3	22.0

of the orange complex do not support a ligand to metal ratio of three, and this discrepancy is attributed to hydration. Indeed, the TG profile of this complex exhibits a weight loss at temperatures lower than the degradation temperature of the free imidazole ligand consistent with a hydrated compound containing four H_2O molecules. Both TG and elemental analysis data are in accordance with the orange complex having the formula $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$.

The complete thermal decomposition mechanism of both complexes is now considered. The initial weight loss in the TG profile of the $Pd(IMDAH)_3Cl_2$ compound is attributed to the volatilization of the IMDAH ligands. The weight loss is about 52% which is in good agreement with the weight percent of ligand in this complex. The remaining weight corresponds to the weight percent of $PdCl_2$ which is thermally stable up to 500°. The weight loss at 530–565° (17%) is attributed to the formation of PdO and the remaining weight percent is in agreement at 32%. The final weight loss occurs at 825–840° and is attributed to the decomposition of PdO and formation of Pd metal. Again, the observed weight loss at this stage as well as the remaining weight percent (27%) are in agreement with the formation of Pd. The thermal decomposition mechanism for the white $Pd(IMDAH)_3Cl_2$ complex is summarized in equations (4–6).

$$Pd(IMDAH)_3Cl_2 \xrightarrow{240\text{–}330^\circ} PdCl_2 + 3IMDAH \tag{4}$$

$$PdCl_2 \xrightarrow[1/2\,O_2]{530\text{–}565^\circ} PdO + Cl_2 \tag{5}$$

$$PdO \xrightarrow{820\text{–}840^\circ} Pd + 1/2\,O_2 \tag{6}$$

As noted above, the initial stage of decomposition for the orange complex $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ corresponds to the dissociation of H_2O molecules. The weight loss (18%) is observed at 150–180° and is in agreement with the hypothesis that this complex is hydrated with four H_2O molecules. The weight loss (31%) observed at 190–340° corresponds to the dissociation of the imidazole ligands. It is noted that the remaining weight percent (51%) is higher than that expected for $PdCl_2$ (46%). This result may indicate some metal oxidation and could be related to the coordination geometry. The last two stages of thermal decomposition are similar to those observed for the white $Pd(IMDAH)_3Cl_2$ compound. The thermal decomposition steps of the orange $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ complex are summarized in equations (7–10).

$$Pd(IMDAH)_2Cl_2 \cdot 4H_2O \xrightarrow{120\text{–}180^\circ} Pd(IMDAH)_2Cl_2 + 4H_2O \tag{7}$$

$$Pd(IMDAH)_2Cl_2 \xrightarrow{190\text{–}340^\circ} PdCl_2 + 2IMDAH \tag{8}$$

$$PdCl_2 \xrightarrow[1/2\,O_2]{540\text{–}570^\circ} PdO + Cl_2 \tag{9}$$

$$PdO \xrightarrow{820\text{–}840^\circ} Pd + 1/2\,O_2 \tag{10}$$

In both complexes the IMDAH ligands are dissociated at temperatures above 240°, higher than the 209° volatilization of the free ligand. This result is an expected one due to the stabilization of the IMDAH ligands on coordination to the Pd metal center. Additionally, it may be noted that there appears to be a slight weight increase in both complexes at temperatures between 580 and 820°. This behaviour relates to the decomposition mechanism of PdO and may indicate that PdO_2 is formed in an intermediate step. It is noted that Pd-IMDAH complexes have been synthesized previously with reaction conditions similar to those in this study [3]. However, the products obtained previously do not have the same composition to those observed here. This indicates that several coordination forms may be possible for Pd-IMDAH complexes. Finally, in the course of this work it was found that the $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ complex reacts on contact with an In metal surface and forms InO. The catalytic activity of this complex on a metal surface is not presently well understood and is under further investigation.

Conclusion

Elemental analysis and TG data indicate that complexes with formulae $Pd(IMDAH)_3Cl_2$ and $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ have been formed during reaction of $PdCl_2$ with IMDAH ligands at 1 : 4 and 1 : 2 metal/ligand ratios, respectively. The TG profiles of these compounds in air illustrate a thermal decomposition mechanism where the ligands are initially removed and $PdCl_2$ is formed. The $PdCl_2$ then further degrades at higher temperatures to form PdO and subsequently Pd metal.

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Zusammenfassung — In einer Reaktion von $PdCl_2$ mit Imidazol wurde bei einem metall-Ligandenverhältnis von 1 : 2 bzw. 1 : 4 zwei Pd-Imidazolkomplexe dargestellt. Auf Grund der Ergebnisse von Elementaranalyse und Thermogravimetrieuntersuchungen besitzen die Verbindungen die Formeln $Pd(IMDAH)_2Cl_2 \cdot 4H_2O$ bzw. $Pd(IMDAH)_3Cl_2$ (IMDAH = Imidazol). Der Mechanismus der thermischen Zersetzung dieser Komplexe in Luft umschliesst eine anfängliche Dissoziation (Abgabe von Wasser und IMDAH-Liganden) im Temperaturbereich 120–340 °C, gefolgt von der Bildung von PdO unter Abspaltung der Chloratome bei 530–570 °C sowie die letztendliche Bildung von metallischem Pd bei 820–840 °C.

Резюме — Взаимодействием хлористого палладия и имидазола, взятых в соотношениях 1 : 2 и 1 : 4, получены имидазольные комплексы палладия. Элементный анализ и термогравиметрические аналитические данные для этих соединений показали, что они имеют состав $Pd(имидазол)_2Cl_2 \cdot 4H_2O$ и $Pd(имидазол)_3Cl_2$. Термическое разложение этих комплексов на воздухе сопровождается сначала выделением воды и имидазола в интервале температур 120–340°, а затем атомов хлора и образованием окиси палладия при температуре 530–570°. Конечным продуктом реакции является образование металлического палладия при 820–840°.