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Thermal decomposition characteristics of ammonium hexachlorometallate(IV) complex salts of platinum metals

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Abstract

The thermal decomposition behaviour of ammonium hexachlororuthenate(IV), palladate(IV), osmate(IV), iridate(IV) and platinate(IV) was investigated in nitrogen atmosphere using TG and DTA techniques. X-ray powder diffractometry was used to identify the final solid decomposition products. The thermal decomposition of the complex salts yields the respective metals as the final residue. The thermal decomposition mechanism of these complex salts is suggested and the thermal stability in the solid state is discussed in terms of inorganic energetics, such as the ligand field stabilization energy and lattice energy. The sequence of thermal stability of the complex salts was found to be Os(IV) > Ir(IV) > Pt(IV) > Ru(IV) > Pd(IV).

Keywords: Complex salts; DTA; Hexachlorometallate(IV); Platinum metals; TG

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1. Introduction

The investigation of the thermal behaviour and stability of salts or complexes with the same composition but containing different metals often reveals the relationship between their composition, structure and the chemistry of their thermal decomposition. These types of studies are also of practical importance, as the thermal decomposition of compounds of the noble metals is often used to refine these metals.

In a previous work, we reported the thermal behaviour of double ammonium sulphate hexahydrate salts of the first-series divalent transition metals [1]. This paper describes the thermal decomposition of ammonium hexachlororuthenate(IV), pallad-

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ate(IV), osmate(IV), iridate(IV) and platinate(IV) in terms of the stability and energy correlations in the solid state.

2. Experimental

Analytical grade ammonium hexachlororuthenate(IV), palladate(IV), osmate(IV), iridate(IV) and platinate(IV) were purchased from Aldrich Chemical Company and used without further purification. In the experimental design of the study, the Rh(IV) complex was also intended to be investigated, but only the Rh(III) form was available and it was therefore excluded from this work.

TG, DTG and DTA data were obtained simultaneously by using a Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser. The measurements were carried out in flowing nitrogen atmosphere within the temperature range 20–1000°C in a platinum crucible. The heating rate was 10 K min^{-1} and the sample masses were in the range of 5–10 mg. Highly sintered α-Al_2O_3 was used as the reference material.

To identify the final decomposition products, large amounts of the compounds were heated in a tube furnace in a flowing nitrogen atmosphere at predetermined temperatures. The solid products were determined using a Philips PW 1710 X-ray powder diffractometer with Cu Kα radiation.

A known amount of the complex salts was dissolved in water and the UV/VIS spectra were recorded on a Varian DMS 100 UV/VIS spectrophotometer. The ligand field splitting energies of the complex salts were determined from the UV/VIS spectra.

The lattice enthalpies of both the complex salts and their solid decomposition products were estimated using Kapustinskii equation [2]

$$U = \frac{nZ^+Z^-}{r^+ + r^-}\left(1 - \frac{0.345\text{Å}}{r^+ + r^-}\right) 1210\,\text{kJ Å mol}^{-1}$$

where n is the number of ions in each formula unit, r^+, r^- are the ionic radii as Å, and Z^+, Z^- are the ion charge numbers.

3. Results and discussion

3.1. Thermal behaviour

All the complex salts were subjected to TG and DTA analysis from ambient temperature to 1000°C in flowing nitrogen atmosphere. The TG, DTG and DTA curves are illustrated in Figs. 1–5; the temperature ranges, experimental and calculated weight losses and final decomposition products are given in Table 1.

Although some of the physical properties, such as the empirical chemical formula $[(NH_4)_2MCl_6]$, geometry, etc., are the same, it was observed that these compounds do not have the same thermal behaviour. They have several endothermic decomposition

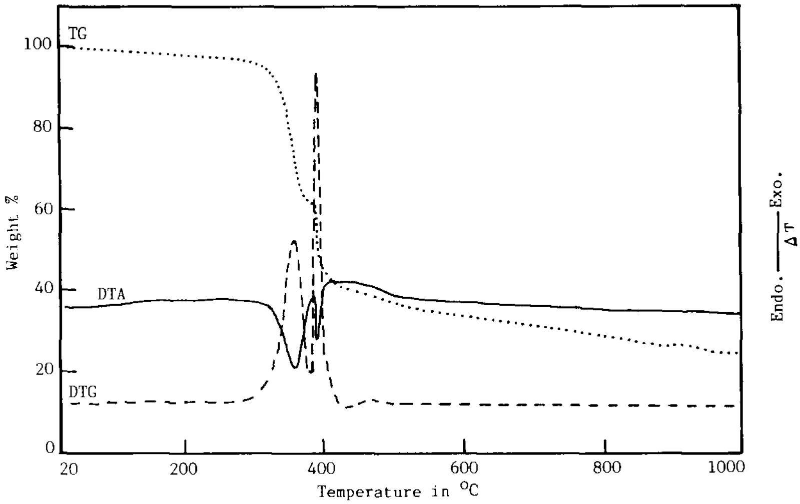

Fig. 1. DTA, TG and DTG curves of $(NH_4)_2RuCl_6$.

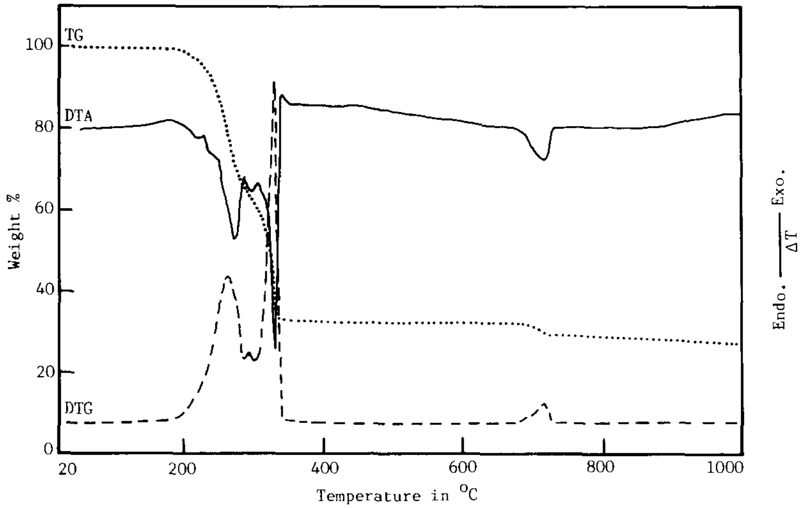

Fig. 2. DTA, TG and DTG curves of $(NH_4)_2PdCl_6$.

stages and the temperature ranges change significantly from one compound to another. For example, the Ru(IV) and Pt(IV) complex salts decompose in two stages, whereas the decomposition of the Pd(IV) complex takes place in three stages; the Rh(IV) and Ir(IV) complexes decompose in four stages. The volatile groups present in these compounds leave the salts on heating. All the salts decompose without melting. The

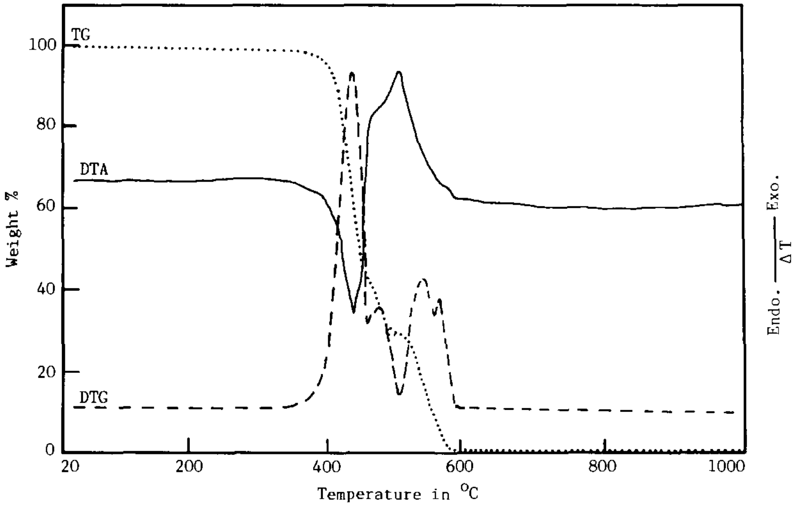

Fig. 3. DTA, TG and DTG curves of $(NH_4)_2OsCl_6$.

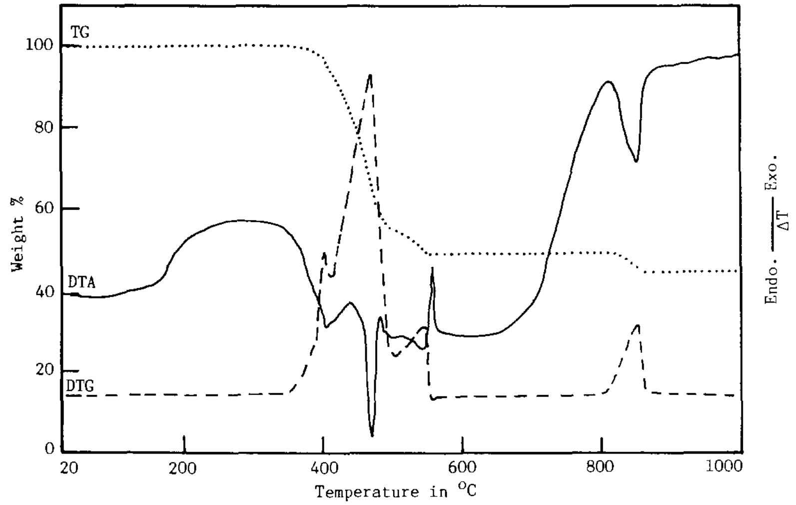

Fig. 4. DTA, TG and DTG curves of $(NH_4)_2IrCl_6$.

X-ray powder diffraction analysis showed that the final products formed at the end of the decompositions were only the respective metals. But, in the thermal decomposition of the Os(IV) complex, a semi-stable or volatile intermediate forms and this product decomposes and vaporizes above approx. 500°C leaving an empty crucible (Fig. 3). The experimental total weight loss values are in very good agreement with the calculated values as given in Table 1.

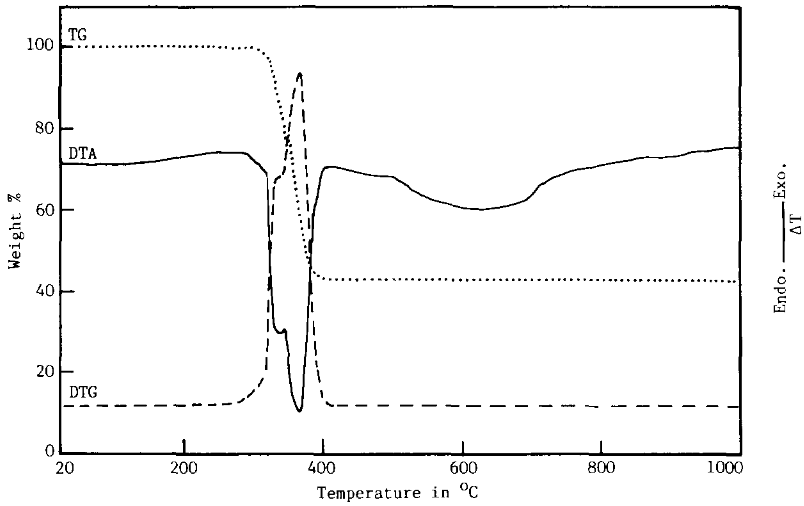

Fig. 5. DTA, TG and DTG curves of $(NH_4)_2PtCl_6$.

Table 1
Thermoanalytical results (TG, DTG, DTA) for the complex salts

Complex	Stage	Temp. range/°C	DTG_{max}/°C	Weight loss/%	Total weight loss/%		Final decomp. product
					Exp.	Calcd.	
$(NH_4)_2RuCl_6$	1	272–383	360	38.05			
	2	384–525	390	30.28	68.33	71.10	Ru
$(NH_4)_2PdCl_6$	1	190–295	263	36.37			
	2	296–354	330	29.50			
	3	675–735	714	3.05	68.92	70.04	Pd
$(NH_4)_2OsCl_6$	1	370–457	434	54.88			
	2	458–505	474	14.36			
	3	506–554	537	20.32			
	4	555–590	562	9.48	99.04	100.0	[a]
$(NH_4)_2IrCl_6$	1	335–415	402	7.85			
	2	416–505	469	37.71			
	3	508–565	543	5.45			
	4	803–880	854	4.78	55.79	56.41	Ir
$(NH_4)_2PtCl_6$	1	279–345	332	23.88			
	2	345–410	364	32.38	56.26	56.04	Pt

[a] Sublimation of the solid intermediate occurs.

Because of the complexity of the thermal decomposition process, it is difficult to give a detailed decomposition mechanism for each complex salt. However, simple weight loss calculations show that the thermal decompositions of these salts may be divided into two parts, each of which may consist of one or more decomposition stages. In the first part, the removal of ammonium chloride and the formation of the respective metal chlorides take place simultaneously. The decompositions of the metal chlorides occur in the second part. For example, the thermal decomposition of the Pt complex takes place in two stages. In the first stage (279–345°C), the evolution of two moles of NH_4Cl and the formation of $PtCl_4$ were observed. The second endothermic effect (345–410°C) is due to the thermal decomposition of $PtCl_4$ to give Pt. The decomposition sequence is

$$(NH_4)_2PtCl_{6(S)} \xrightarrow{279-345^{\circ}C} PtCl_{4(S)} + 2NH_4Cl_{(g)}$$

followed by

$$PtCl_{4(S)} \xrightarrow{345-410^{\circ}C} Pt_{(S)} + 2Cl_{2(g)}$$

Since it is quite difficult to distinguish these steps for each complex, general decomposition reactions can be written

I. $(NH_4)_2MCl_{6(S)} \longrightarrow MCl_{4(S)} + 2NH_4Cl_{(g)}$ for M is Ru, Pd, Os, Ir and Pt

II. $MCl_{4(S)} \longrightarrow M_{(S)} + 2Cl_{2(g)}$

3.2. Thermal stability

The ammonium hexachloro salts of platinum metals contain two kinds of ions: $[MCl_6]^{2-}$, the inner coordination sphere, and NH_4^+, the outer ionizable sphere. These complex salts have a chemical formula of $(NH_4)_2MCl_6$ with different metal ions and a cubic crystal structure. The complex ion, $[MCl_6]^{2-}$, is of low-spin type [3]. Because of this structural and chemical similarity, the interpretion of the thermal behaviour and stability of the salts is thought to be straightforward. However, examination of the present thermal data (Table 1) indicates that it is not so simple. Therefore, in order to discuss the stability of the complex salts in the solid state, we consider the initial decomposition temperature (T_i), the ligand field stabilization energy (LFSE) and the lattice enthalpy (U).

As the initial decomposition temperatures are taken as a parameter of thermal stability, the stability order is Os > Ir > Pt > Ru > Pd. This indicates that the thermal stability decreases steadily across each period. In the same group from Ru to Os or from Pd to Pt, the stability greatly increases. The increase in the groups seems to be a function of LFSE which increases down a group when the oxidation number (IV), the ligand type (Cl), the coordination geometry (octahedral) and the number of d electrons (Ru = Os = d^4 and Pd = Pt = d^6) are kept constant, as in this work. Although these complex salts are known to be low-spin types [3], because of the lack of pairing energy data, it is impossible to calculate the ligand field stabilization energy values. Nevertheless, a comparison of the spectroscopically determined ligand field splitting energy values (Δ_o) of the complexes with the same electronic configuration demonstrated that Δ_o or LFSE increases on descending a group due to expanding of the d-orbitals from 3d to 5d (Table 2). This is the most important metal trend to keep in mind. Therefore, the

Table 2
Initial decomposition temperatures (T_i), ligand field splitting energies (Δ_0) and lattice energies (U) of the complex salts

Complex	T_i/°C	Δ_0/kJ mol^{-1}	$U_{(NH_4)_2MCl_6}$/kJ mol^{-1}	U_{MCl_4}/kJ mol^{-1}	ΔU^a/kJ mol^{-1}
Ru	272	253	1431	8401	6970
Pd	190	290	1472	8458	6986
Os	370	289	1457	8344	6887
Ir	335	246	1426	8372	6946
Pt	279	335	1490	8458	6968

[a] $\Delta U = U_{MCl_4} - U_{(NH_4)_2MCl_6}$

increase in the thermal stability in the groups may be due to the contribution of LFSE.

The Δ_o or LFSE increases across the period from d^1 to d^6 for the low-spin complexes; this expected behaviour can also be seen in Table 2. However, the increase in LFSE across the periods does not result in the increase in the thermal stability of the complex salts: in contrast, it goes contrary to the thermal stability. This variation may be explained in terms of lattice enthalpy. The lattice energy values of the complex salts can readily be estimated by using either the conventional Born–Mayer equation or the Kapustinskii equation [2]. The latter is much more useful for crystals containing complex (i.e. polyatomic) ions and in the calculations it is also essential to have a set of thermochemical radii of the complex ions. An exhaustive compilation of calculated lattice energies of ionic salts and the thermochemistry of hexahalometallate(IV) complex salts (A_2MX_6) were reported by Jenkins and co-workers [4–6]. The thermochemical data listed in Table 2 were calculated using the Kapustinskii equation and the related ionic radii [2, 7, 8].

In a discussion of the thermal stability of ionic salts, Shriver et al. [9] demonstrated that the difference between the lattice energies of a salt and its solid decomposition product reflects the change in the stability

$$\Delta U = U_{MCl_4} - U_{(NH_4)_2MCl_6}$$

Since the lattice enthalpy of the chloride salt is greater than that of the respective complex salts, ΔU is positive and the decomposition becomes endothermic. The increases in ΔU result in the less endothermic decompositions. Hence, the greater the ΔU, the lower the decomposition temperature. Because of the lanthanide contraction, the lattice energies of both the complex salts and their decomposition products do not differ too much from each other. However, the ΔU differences between them were found to be meaningful in the assessment of the thermal stability of the complex salts and in the application of the rule explained above. The initial decomposition temperatures increase with decreasing ΔU values and they are very similar when the ΔU values are close to each other, as in the case of Ru(IV) and Pt(IV). This is also clearly shown on a plot of ΔU against T_i as illustrated in Fig. 6. The ΔU concept is a resonably good explanation for the variations in the stability of ionic salts containing complex ions, both across a period or down a group. For example, in the same period from Os to Pt

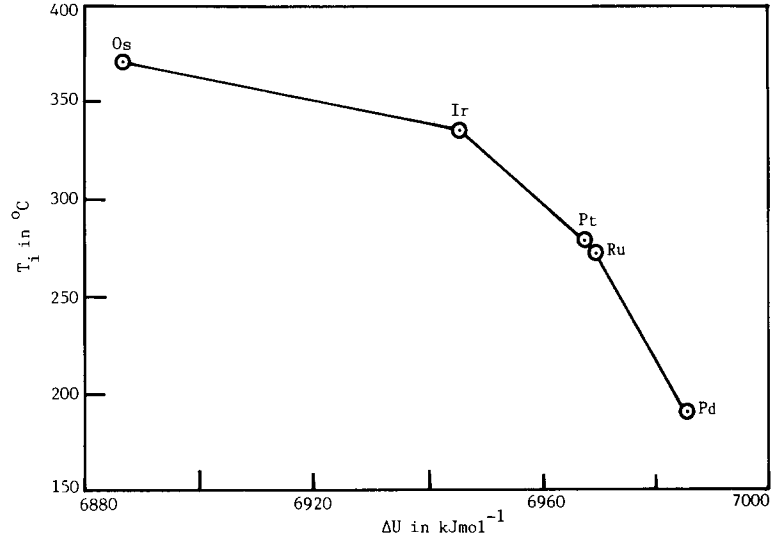

Fig. 6. Initial temperature of thermal decomposition of complex salts vs. ΔU.

and in the same group from Ru to Os or from Pd to Pt, the initial decomposition temperatures decrease, while the ΔU values increase.

The results of the present work indicate that the thermal stabilities of ionic solids depend on the differences in lattice enthalpy between the solid reactants and solid products for ionic solids containing transition metals, although a similar thermochemical and ionic radius greatly reduce these differences. Ligand field stabilization energies should also be taken into account although they are less significant.

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