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Thermal decomposition of some salts of hexathiocyanato-platinic acid

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Abstract

Six salts of $H_2[Pt(SCN)_6]$ dibasic acid with metals and organic amines were obtained and characterized by chemical analysis. The thermal decomposition of these compounds was studied by derivatography. Some kinetic parameters of this process were calculated and discussed. The results are compared with those obtained earlier with the analogous chloro- and bromo-derivatives.

INTRODUCTION

The hexathiocyanato-platinate complex anion, $[Pt(SCN)_6]^{2-}$, can be obtained by a substitution reaction from $K_2[PtCl_6]$ and KCNS in aqueous solution [1]. The free acid can also be liberated from the lead salt $Pb[Pt(SCN)_6]$ with an excess of dilute sulphuric acid [2]. This strong dibasic acid produces CO_2 from alkaline carbonates and hydrogen by interaction with zinc. $H_2[Pt(SCN)_6]$ forms salts with various metals (Ag, Tl, Cu, Zn, Ni, etc.) [3], with metal(II)–amine $[M(amine)_n]^{2+}$ (Cu, Ni, Cd, Zn; amine NH_3, 1,2-diaminoethane (en), 1,2-diaminopropane (pn); $n = 4,6$) and with mixed metal(III)–amine salts (M(III) = Co, Cr, Rh) [4–6]. It has been observed that $[Pt(SCN)_6]^{2-}$ undergoes some substitution reactions, e.g. the interaction with NH_3 leads to reduction to Pt(II), followed by the formation of *cis*-$[Pt(NH_3)_2(SCN)_2]$ [7].

A series of ammonium salts of the type $(amine \cdot H)_2[Pt(SCN)_6]$ with some aliphatic, aromatic and, especially, with heterocyclic amines and alkaloids (nicotine, sparteine, codeine, etc.) were also obtained and characterized. The ammonium salts contain no crystallization water; they are generally sparingly soluble in water, more soluble in alcohol and insoluble in ether.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

The thermal behaviour of the hexathiocyanate-platinates was studied only briefly. The potassium salt burns in air with a blue flame. On thermal decomposition of this substance in the absence of air, Pt, KCNS and gaseous products are formed. The melting points and the decomposition temperature intervals of some ammonium salts were also determined. These temperatures are particularly influenced by the nature of the amine molecule (m.p. 50–200°C) [8,9].

In our earlier papers [10,11] the thermal decompositions of some $A_2[PtX_6]$-type complexes were studied where A is the cation of a monovalent metal or of an amine, and X is Cl or Br.

In the present paper, six metal and ammonium salts of $H_2[Pt(SCN)_6]$ acid were obtained and characterized by chemical analysis. Their thermal decomposition was followed by means of derivatography.

EXPERIMENTAL

The $K_2[Pt(SCN)_6] \cdot 2H_2O$ was prepared by evaporation of a mixture of 1 mol $K_2[PtCl_6]$ and 6 mol KCNS in aqueous solutions. The salt crystallizes in brilliant, thin plates, reddish yellow in colour. It is necessary to avoid boiling the mixture because this leads to the formation of an insoluble, resinous material.

For the ammonium and thallium salts, 10 mmol of the hydrochloride of the corresponding amine in 20–50 ml water (20 mmol thallium acetate) were treated with 3 mmol $K_2[Pt(SCN)_6]$ in 15–20 ml aqueous solution. After 1–2 h, the crystalline products formed were filtered off, washed with ice-cooled water and dried in air.

The thermal measurements were carried out with a derivatograph (MOM, Budapest) up to 1000°C, with a heating rate of 5°C min^{-1}, a sample weight of 200 mg, static air atmosphere, α-Al_2O_3 reference and with a platinum crucible sample holder.

RESULTS AND DISCUSSION

The complex salts obtained by means of double exchange reactions are presented and characterized in Table 1.

The thermal decomposition of the complexes studied depends on the nature of the external sphere cation and occurs in several stages.

In the case of metal cations, the decomposition of $A_2[PtX_6]$-type complexes begins with redox processes. If X is Cl or Br, these reactions occur without the participation of atmospheric air and may be described by the following equation [10,11]:

$$A_2[PtX_6] \rightarrow Pt + 2X_2 + 2AX$$

TABLE 1

$M_2[Pt(SCN)_6]$ and (amine·H)$_2$[Pt(SCN)$_6$] salts obtained

No.	Complex [a]	Mol. wt. calcd.	Appearance	Pt analysis (%)	
				Calcd.	Found
1	Tl_2A	952.2	Irregular, dark yellow crops	20.5	20.3
2	(*o*-Toluidine·H)$_2$A	759.6	Sparkling, reddish yellow dendrites	25.7	25.8
3	(*p*-Toluidine·H)$_2$A	759.6	Long, reddish yellow discs	25.7	25.9
4	(Pyridine·H)$_2$A	703.6	Golden-yellow dendrites	27.7	27.9
5	(2,6-Lutidine·H)$_2$A	759.6	Irregular, reddish brown plates	25.7	25.3
6	(3,4-Lutidine·H)$_2$A	759.6	Short, reddish prisms	25.7	26.1

[a] $A = [Pt(SCN)_6]^{2-}$.

This redox reaction is followed by the volatilization of AX and the final solid residue consists of metallic platinum.

If X is NCS and A is Tl(I), the TG and DTA curves shown in Fig. 1 are obtained. As can be seen, the decomposition begins with three successive

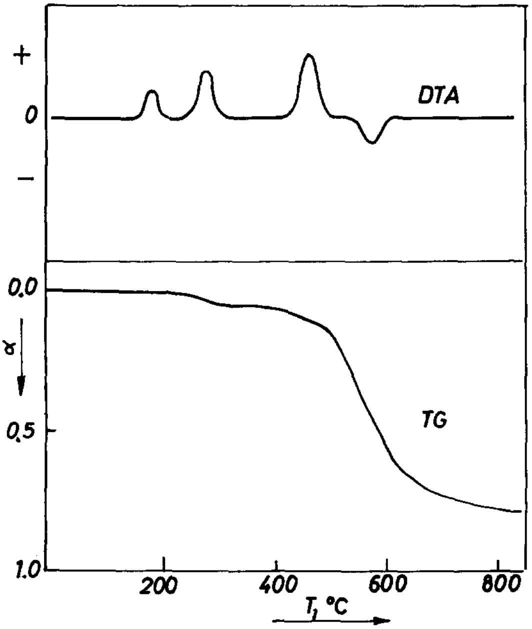

Fig. 1. DTA and TG curves of $Tl_2[Pt(SCN)_6]$.

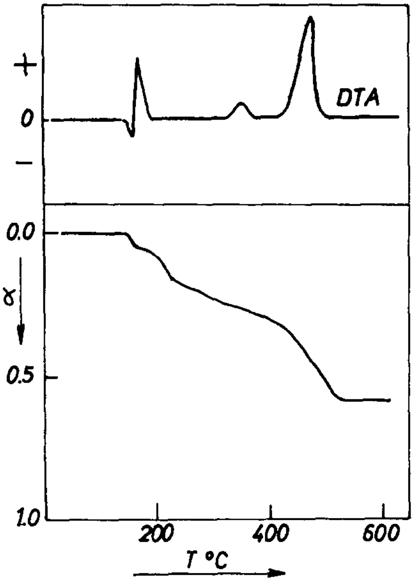

Fig. 2. DTA and TG curves of (*o*-toluidine·H)$_2$[Pt(SCN)$_6$].

exothermal stages leading to a weight loss of about 16%; this is followed by an endothermal stage, accompanied by a weight loss of about 63%. These results are consistent with the following exothermal redox reaction

$$Tl_2[Pt(SCN)_6] + 13O_2 = Pt + Tl_2SO_4 + 5SO_2 + 6CO_2 + 3N_2$$

followed by the endothermal volatilization of Tl_2SO_4. In this case also, metallic platinum is the only solid product.

If the external sphere cation contains an amine, the pyrolysis is completely different, with all the amines studied in this paper showing the same features. The first decomposition stage is endothermal at first, but rapidly becomes strongly exothermal as seen in Fig. 2. Presumably, the endothermal deamination process is overlapped by a strong redox reaction, occurring with the participation of atmospheric air. This stage is followed at higher temperatures by two more exothermal stages. The final product seems to be metallic platinum, but the weight of the residue up to 600°C remains a little high, indicating the presence of some additional Pt compounds.

The behaviour of the analogous chloro- and bromo-derivatives is quite different. The chloro-derivatives may sometimes contain crystallization water; in these cases the pyrolysis begins with an endothermal dehydration. Decomposition of the anhydrous amine salts begins with one or several endothermal deamination stages, frequently leading to the loss of one mole of amine · HX. The pyrolysis never becomes exothermal at temperatures lower than 280–300°C [10,11].

TABLE 2

Endothermal and exothermal DTA peak temperatures (°C)

Complex salt No.	Endothermal	Exothermal
1	570	175, 287, 472
2	156	160, 358, 475
3	155	160, 290, 450
4	151	162, 290, 530
5	140	178, 287, 490
6	120	165, 280, 480

The position of the endothermal and exothermal peaks on the DTA curves of the complexes studied is shown in Table 2. As can be seen, there is only a single endothermal peak in the case of the amine salts and the first sharp exothermal peak is always situated between 160 and 180°C.

Some portions of the TG curves allow us to perform a kinetic analysis and to derive the apparent kinetic parameters, reaction order (n), activation energy (E) and pre-exponential factor (Z). For this purpose our "nomogram method" [12,13] was used and the results obtained are presented in Table 3.

TABLE 3

Kinetic parameters derived from the TG curves

Complex no.	Stage [a]	n	E (kJ)	lg Z (s^{-1})	$\tau_{0.1}$
1	End.	0.96	105.9	3.69	1.286
2	End.	2.54	744.0	89.2	2.398
		2.54	415.1	50.0	2.458
	Exo. II	3.34	187.2	17.9	2.112
		1.32	161.4	15.2	2.142
	Exo. III	2.80	287.1	18.5	1.437
		2.61	415.8	29.5	1.472
3	End.	−0.54	52.0	3.61	2.523
	Exo. II	1.97	83.0	6.07	2.131
	Exo. III	2.97	617.4	43.1	1.417
4	Exo. II	2.05	162.6	12.6	1.839
		3.62	369.8	24.3	1.414
	Exo. III	1.15	184.9	9.92	1.365
		1.67	506.2	26.3	1.115
5	End.	1.75	162.0	15.4	2.167
	Exo. III	1.57	113.8	4.37	1.317
6	End.	2.57	198.8	19.3	2.146
	Exo. III	1.26	110.7	4.46	1.345

[a] End, endothermal; Exo, exothermal; I, II, III are first, second and third values in Table 2.

Table 3 also contains the $\tau_{0.1} = 10^3/T_{0.1}$ value, where $T_{0.1}$ is the absolute temperature at which the conversion α attains 0.1. In this table, stage "end" (except for complex No. 1) indicates where the first endothermal decomposition stage becomes strongly exothermal. In some cases for the same decomposition stage, two sets of kinetic parameters are indicated in Table 3. These values have been derived from different derivatograms, showing that the apparent kinetic parameters are rather sensitive to minor modifications in the working conditions.

One can see that the kinetic parameters vary over a wide interval: no correlation can be found, either with the nature of the reaction (stage of decomposition) or with the composition of the substance undergoing the pyrolysis reaction. Nevertheless, it is obvious that the lg Z values increase with increasing E value, i.e. a kinetic compensation effect is observed. Generally, kinetic compensation effects are believed to obey the linear kinetic compensation law

$$\lg Z = aE + b \tag{1}$$

Equation (1) is easily obtained from the Arrhenius equation

$$k = Z\ \mathrm{e}^{-E/RT} \tag{2}$$

by presuming that for a series of "similar" reactions there is an "isokinetic temperature" T_i at which all the reactions considered have the same "isokinetic" rate constant k_i [14–16]. From eqn. (2) one obtains

$$\lg Z = E/2.3RT_\mathrm{i} + \lg k_\mathrm{i} \tag{3}$$

Thus, $a = 1/2.3RT_\mathrm{i}$ and $b = \lg k_\mathrm{i}$.

Although eqn. (2) has been derived for homogeneous reactions, its use in heterogeneous kinetics seems to be justified as a first approach in many cases [16].

It is easy to understand that the existence of an isokinetic temperature may be expected in the case of thermal decomposition reactions which, under dynamic temperature conditions, begin to occur at a finite rate in a narrow temperature range [14].

Because the determination and even the definition of a "decomposition temperature" is rather difficult, we have proposed the use of the well-defined temperature $T_{0.1}$, and, as a first approach, to take it for T_i [17,18]. Thus, we can introduce a "theoretical" compensation parameter

$$a^* = 1/2.3RT_{0.1} = \tau_{0.1}/2.3R\,10^3 \tag{4}$$

The compensation parameters a and b can be obtained by means of linear regression from the kinetic parameters E and lg Z derived from the TG curves. One may expect that the larger the $T_{0.1}$ range, the further from linearity the lg Z against E plot [17,18].

TABLE 4

Kinetic compensation parameters

$T_{0.1}$ range (°C)	ρ	b	a (mol kJ^{-1})	a^* (mol kJ^{-1})	Δ (%)
123-624	0.9065	-4.614	0.0976	0.0932	+4.72
120-145	0.9998	-2.364	0.1238	0.1285	-3.67
185-205	0.9996	-3.330	0.1143	0.1118	+2.24
400-505	0.9990	-4.269	0.0780	0.0722	+8.04

All the kinetic parameters presented in Table 3 were processed by linear regression. The results are given in Table 4, which as well as giving the compensation parameters a and b, also lists the correlation coefficient ρ, the theoretical compensation parameter a^*, calculated by means of the arithmetical mean of the $\tau_{0.1}$ values of the corresponding decomposition stages, and the deviation Δ of a from a^*.

As seen from Table 4, by using narrow $T_{0.1}$ ranges, the linearity becomes excellent ($\rho > 0.999$), and a and a^* are very near to each other. The general picture is the same as observed earlier with the analogous chloro- and bromo-derivatives [10,11].

In order to confirm the importance of $T_{0.1}$, an attempt was made to determine all the kinetic parameters derived from the TG curves of $A_2[PtX_6] \cdot nH_2O$-type complexes, by taking $T_{0.1}$ ranges irrespective of the nature of the X ligand. The number of sets of kinetic parameters determined in each $T_{0.1}$ interval can be seen in Table 5.

The results obtained by means of linear regression are given in Table 6. One can see that the linearity is very good ($\rho > 0.996$) and the a and a^* values are very near to each other. This means that the kinetic compensation effect is merely a consequence of the application of the Arrhenius

TABLE 5

$T_{0.1}$ ranges and number of data processed

$T_{0.1}$ range (°C)	Number of $A_2[PtX_6] \cdot nH_2O$-type derivatives			
	X = Cl	X = Br	X = NCS	Overall
95-140	2	-	2	4
140-190	3	1	2	6
190-240	9	11	4	24
240-295	2	1	1	4
295-355	4	-	-	4
355-415	3	4	1	8
415-480	2	4	5	11
480-545	1	2	2	5
545-615	1	4	-	5

TABLE 6

Kinetic compensation parameters for decomposition stages of $A_2[PtX_6]$-type complexes with X = Cl, Br, NCS

$T_{0.1}$ range (°C)	ρ	b	a (mol kJ^{-1})	a^* (mol kJ^{-1})	Δ (%)
95–140	0.9968	−1.554	0.1272	0.1338	−4.93
140–190	0.9998	−4.293	0.1255	0.1187	+5.73
190–240	0.9980	−1.950	0.1050	0.1087	−3.40
240–295	0.9997	−3.858	0.1043	0.0996	+4.72
295–355	0.9999	−4.074	0.0941	0.0872	+7.91
355–415	0.9989	−3.305	0.0792	0.0790	+0.25
415–480	0.9996	−3.885	0.0761	0.0727	+4.68
480–545	0.9999	−3.293	0.0666	0.0669	−0.45
545–615	0.9993	−3.305	0.0619	0.0616	+0.49

equation and that the nature of the chemical process is not very important. Under the conditions of the TG analysis with constant heating rate, the rate constant is practically zero up to the decomposition temperature. Thus, if the decomposition temperatures are near to each other, irrespective of the nature of the process, there will be at the beginning of the decomposition, a temperature at which the k values do not differ very much from each other. According to the b values obtained, k_i is in the order of 10^{-3} s^{-1}. Such small rate constant values may be expected at the beginning of the thermal decomposition and one might presume that $T_i < T_{0.1}$. Therefore, $a > a^*$ can be expected, i.e. $\Delta > 0$. The results presented in Tables 4 and 6 are consistent with this conclusion because positive Δ values are much more frequent than negative ones.

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