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Thermal features and behaviour of 4-aminopyridinium salts of planar inorganic metal(II) 1,2-dithiooxalato-*S*,*S*′ complexes, with formula $(HC_5H_6N_2)_2[M(S_2C_2O_2)_2] \cdot 2H_2O$ (where M is Ni^{II}, Pd^{II} and Pt^{II})

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Abstract

Thermal decompositions of three 4-aminopyridinium salts of square-planar inorganic metal(II) 1,2-dithiooxalato-*S*,*S*′ complexes, $(HC_5H_6N_2)_2[M(S_2C_2O_2)_2] \cdot 2H_2O$ where M is Ni(II), Pd(II) and Pt(II) (hereafter abbreviated as NIDT4AP, PDDT4AP and PTDT4AP, respectively) have been studied by thermogravimetry (TG and DTG) and differential thermal analysis (DTA) under argon–oxygen and argon atmospheres. Thermoanalytical data show that the surrounding atmosphere influences the thermal decomposition processes as well as the final products. In argon–oxygen atmosphere, the final residues were identified as a mixture of nickel sulphides and oxides for NIDT4AP, metallic palladium and palladium oxide for PDDT4AP, and platinum(0) for PTDT4AP. Thermal decompositions in an inert atmosphere yielded nickel(II) sulphide for NIDT4AP, a mixture of Pd/PdS for PDDT4AP, and metallic platinum for PTDT4AP. The final decomposition products were identified by elemental analysis and the X-ray powder diffraction technique. No other stable intermediate products, except the corresponding anhydrous compounds, were found during the thermal decomposition owing to the complexity and the overlap of the processes in oxidative and inert atmospheres.

INTRODUCTION

Interest in square-planar metal complexes involving sulphur donor ligands has received increasing attention in recent years because of their electronic properties, the applications of these compounds in analytical chemistry, catalysis and their relevance to bioinorganic systems [1–4]. One of these sulphur donor ligands is the 1,2-dithiooxalate dianion. However,

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these studies focus mainly on the structural properties and very little has been published to date about the decomposition of thio-oxalate complexes in general and 1,2-dithiooxalate complexes in particular.

However, oxidative thermal decompositions of various nickel, palladnium and platinum complexes are used for the production of metal and metal oxides which are extensively applied as catalysts in a variety of important chemical process [5].

As a continuation and extension of our general research programme on aromatic organoammonium salts of dithiooxalate ligand complexes [6, 7], we have studied the thermal properties and thermochemistry of some 4-aminopyridinium salts of square-planar inorganic metal(II) 1,2-dithiooxalato-*S,S′* anions, $[M(S_2C_2O_2)_2]^{2-}$ where M is Ni(II), Pd(II) and Pt(II). The purpose of this work is to reveal the influence of the surrounding atmosphere and metal nature on the thermal decomposition as well as to get different final products, which depend on the experimental conditions.

EXPERIMENTAL

The compounds under investigation were obtained by direct reaction of the potassium bis(dithiooxalato)metalate(II) salts, prepared according to the Cox–Wardlaw–Webster method [8], and 4-aminopyridine base in aqueous solution as described in a previous paper [9]. The chemical characterization of the three compounds was reported in the same reference, along with the crystal structure of the bis(4-aminopyridinium) bis(1,2-dithiooxalato-*S,S′*)palladate(II) dihydrate.

A Setaram TAG 24 S 16 simultaneous thermal analyzer was used to obtain the differential thermal analysis (DTA) and thermogravimetric (TG and DTG) curves, simultaneously, in argon–oxygen (4:1 v/v) and argon atmospheres at a heating rate of 5 deg min^{-1}. All thermal decompositions were recorded in a dynamic atmosphere with a flow rate of 50 cm^3 min^{-1}. An amount of sample (10–20 mg) was exactly weighed in the platinum crucible. The thermally inert reference was 15 mg of α-Al_2O_3 previously calcinated at 1300°C for 5 h. X-ray powder diffraction patterns of the final products were recorded at room temperature with a Philips PW 1710 instrument equipped with a graphite monochromator, using Cu Kα radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards, JCPDS [10].

RESULTS AND DISCUSSION

Table 1 lists the steps, initial and final temperature (in °C), partial and total mass losses, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decompositions of the three compounds in an argon–oxygen and argon atmospheres.

TABLE 1

Thermal analysis data for NIDT4AP, PDDT4AP and PTDT4AP in argon–oxygen and argon atmospheres

Ar + O_2					Ar				
Step	T_i/°C	T_f/°C	$T_m{}^a$/°C	Δm^b/%	Step	T_i/°C	T_f/°C	$T_m{}^a$/°C	Δm^b/%
NIDT4AP									
1	85	140	125(−)	6.84	1	80	140	120(−)	7.00
2	200	260	250(+)	52.60	2	215	330	270(−)	74.72
3[c]	260	400		8.10	3[c]	330	600		1.70
4	400	450	427(+)	7.33					(83.42)
5	450	510	495(+)	7.10					
				(81.97)					
PDDT4AP									
1	80	130	120(−)	6.22	1	90	125	115(−)	6.14
2	250	288	275(−)	39.98	2	245	325	290(−)	61.90
3	288	325	300(−)	20.74	3[c]	325	845		12.12
4	325	530	450(+)	13.64					(80.16)
				(80.58)					
PTDT4AP									
1	80	123	110(−)	5.77	1	80	130	110(−)	5.35
2	230	315	280(+)	46.23	2	230	320	290(−)	39.62
3	315	350	340(+)	18.81	3[c]	290	830		25.10
				(70.81)					(70.07)

[a] Endothermic (−) or exothermic (+) process. [b] Total mass losses are shown in parentheses. [c] Progressive mass loss without clear peaks in DTG and/or DTA curves.

The TG–DTG–DTA curves for the compounds in the oxidative and inert atmospheres are shown in Figs. 1–3. In both atmospheres, the thermogravimetric curves indicate that the decompositions are not simple, and stable intermediate products are not found during the processes owing

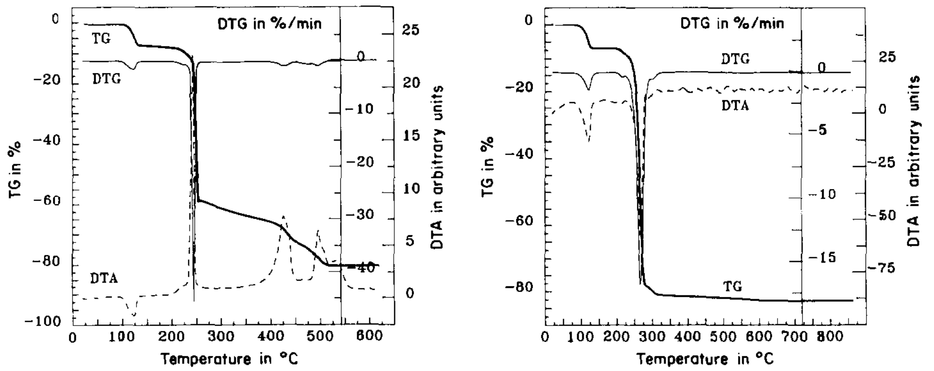

Fig. 1. TG–DTG–DTA curves for the thermal decomposition of NIDT4AP in argon–oxygen (left) and argon (right) atmospheres.

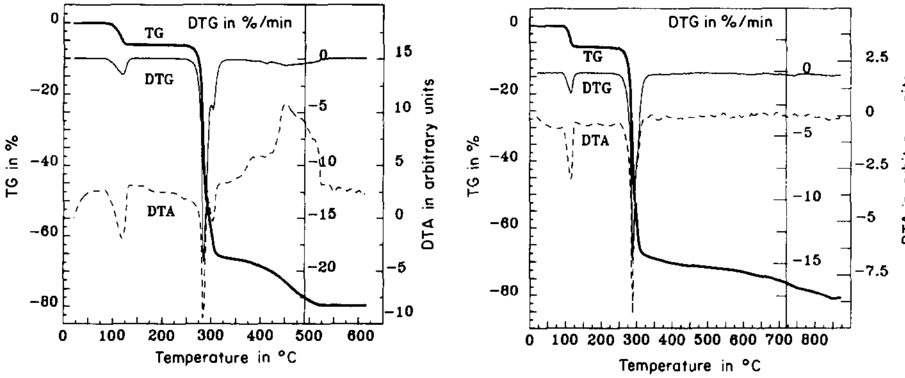

Fig. 2. Thermal decomposition of PDDT4AP in argon–oxygen (left) and argon (right) atmospheres.

to most of the stages being almost overlapped. Attempts to correlate the results with theoretical mass losses were not successful, except for the anhydrous complexes and the final solid products, which were identified by X-ray powder diffraction methods.

In both atmospheres, the compounds initially undergo an endothermic process with loss of the two water molecules between 80 and 140°C. The amount of lost water in the TG curves fits rather well with the composition established by structural work and chemical analyses. The dehydration temperature ranges are at the higher end of those previously observed for dehydration processes of non-coordinated water molecules in similar metallic complexes. The DTG peaks of the dehydration steps are symmetrical and the DTA curve peaks are not broad, indicating that the two water molecules are isoenergetically bound and are lost in a single step. This is in accordance with the X-ray structural studies [9] which show that the two water molecules are located in the crystal lattice in the same

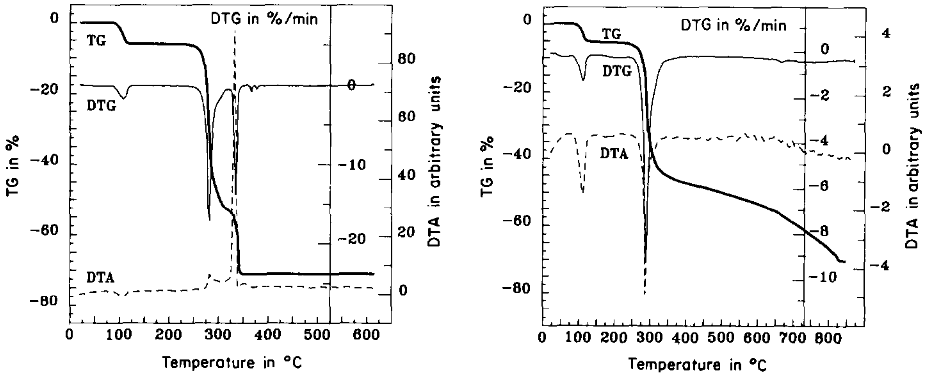

Fig. 3. TG–DTG–DTA curves for the thermal decomposition of PTDT4AP in argon–oxygen (left) and argon (right) atmospheres.

chemical environment and there is only an independent crystallographic water molecule. The three compounds are isostructural and have a laminar structure which is build up by parallel layers of ions stacked along the *a* axis, following a sequence ... acca ... (a means anion and c means cation). The ions are kept together in the same layer by means of electrostatic forced, $d_{z^2}-\pi$ and $\pi-\pi$ interactions, and strong hydrogen contacts between the hydrogen atoms of the pyridine ring nitrogen atom and two oxygen atoms of the dithiooxalate ligands. The water molecules are placed between the anion–cation layers and form an extensive network of hydrogen contacts with the aromatic cations ($N\ldots O_w$, 2.94 Å) and the complex anions ($O\ldots O_w$, 2.94 Å) which linked together the different ... acca ... layers. These strong H-bonding interactions involving water molecules mean that the loss of water of crystallization takes place at relatively high temperature. The important role of the water molecules in the crystal packing of these compounds is shown by the lowering of crystal stability of the corresponding anhydrous compounds which lose the crystalline condition during the dehydration process. However, they have been identified by elemental analysis and IR spectroscopy. It was not possible to compare the dehydration temperature ranges with those for other organoammonium salts of planar inorganic 1,2-dithiooxalato complexes because this type of compound form a very closed crystal structure and usually they do not have molecules of water of crystallization or other solvation molecules [1].

The thermal decomposition of anhydrous compounds is quite different in oxidative and inert atmospheres and the final residues from the thermal decompositions depend on the starting compound. In argon–oxygen atmosphere, the anhydrous nickel complex is stable up to approximately 200°C, beyond which a first abrupt mass loss takes place corresponding to a strong exothermic peak in the DTA curve, attributable to the pyrolysis of organic cations and the breakdown of the dithiooxalato ligands. The decomposition is followed by a progressive mass loss without clear peaks in the DTA and DTG curves and three exothermic processes, corresponding to the reordering of inorganic residues. The great diversity of possible products precludes exhaustive interpretations of these degradation processes. The chemical analysis of the solid stable final residue, obtained above 510°C, gives no indication of carbon, nitrogen or hydrogen present in the composition and it was mainly identified as NiS by comparing its X-ray powder diffraction pattern with the Powder Diffraction File No. 2-1280; but its X-ray powder diffractogram also shows the presence of some diffraction maxima which could be identified according to different nickel oxides and sulphides (NiO, Ni_2O_3 and Ni_2S_3) presented in the JCPDS. In the inert atmosphere, plateaux corresponding to anhydrous nickel compounds extend over a temperature range of about 140–215°C, beyond which a strong mass loss takes place associated with an endothermic peak centred at 270°C. The decomposition is continued by a slight mass loss with poorly resolved peaks in the DTG curve, which led to a constant mass at 600°C. The black final residue, for which elemental analyses did not revealed the presence of carbon, was identified as nickel(II) sulphide. No peaks belonging to nickel or other nickel compounds were found in the X-ray powder diffraction pattern.

In the oxidative atmosphere, the anhydrous compound obtained from the PDDT4AP complex undergoes decomposition in two endothermic processes between 250 and 325°C followed by a progressive mass loss with broad exothermic peaks in the DTA curve. The final product obtained above 530°C was mainly identified as a mixture of palladium(0) [ASTM 5-0681] and palladium(II) oxide [ASTM 6-0515] in a ratio 2/1. No PdS or other palladium sulphide could be detected. In the inert atmosphere, the thermal decomposition of the anhydrous compound starts at 245°C with an endothermic process which is followed by a progressive mass loss with poorly resolved peaks in the DTA/DTG curves. The elemental analysis of the final residue above 840°C, give no indication of C, N or H present in its composition, and it was identified by its X-ray powder diffraction pattern as mixture of palladium(0) and palladium(II) sulphide [ASTM 10-429].

After the dehydration step, the thermal decomposition of the platinum complex in the oxidative atmosphere is followed above 230°C by a weak exothermic process and a strong exothermic step beyond which a solid stable is obtained. This final product was identified as platinum(0) [ASTM 4-802]. In the inert atmosphere, this anhydrous compound is stable up to approximately 230°C at which a first abrupt mass loss takes place corresponding to an endothermic peak in the DTA curve. This last decomposition step is followed by a progressive mass loss with poorly resolved peaks in the DTG curve and no clear peaks in the DTA curve. The thermal decomposition finishes above 830°C. X-ray powder diffractogram shows that the final residue is platinum(0).

CONCLUDING REMARKS

Thermal decompositions of the metallic complexes described in this paper are not simple and numerous intermediate steps takes place before final products are formed. In oxidative and inert atmospheres the first step, between 80 and 140°C, corresponds to the endothermic dehydration processes. These dehydration processes imply a lowering in the stability of the crystal structure since the anhydrous compounds lose the crystalline condition. The thermoanalytical results indicate that the anhydrous compounds decomposition processes as well as the final products are influenced by the atmosphere involved and the starting material. In an excess of oxygen the decomposition steps for anhydrous NIDT4AP and PTDT4AP are exothermic whereas for the anhydrous PDDT4AP two endothermic processes followed by one exothermic process are found. The final residues were identified as a mixture of nickel sulphides and oxides for NIDT4AP, palladium and palladium oxide for PDDT4AP, and platinum for PTDT4AP. All decomposition steps in an inert atmosphere are endothermic, and the final residues were nickel(II) sulphide for NIDT4AP, a mixture of Pd/PdS for PDDT4AP, and metallic platinum for PTDT4AP.

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