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Syntheses, chemical characterization, and thermochemistry of pyridinium salts of 1,2-dithiooxalato-*S,S'* complexes of Ni(II), Pd(II) and Pt(II)

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Abstract

Three complexes of formula $(HB)_2[M(dto)_2]$ where HB^+ is pyridinium, M is Ni(II), Pd(II) or Pt(II), and dto^{2-} is 1,2-dithiooxalato-*S,S'* (hereafter abbreviated as NIDTPY, PDDTPY and PTDTPY, respectively) have been synthesized and characterized by elemental analysis, IR and UV–vis spectroscopies and X-ray diffraction techniques. Thermal decompositions of compounds have been studied by thermogravimetry (TG and DTG) and differential thermal analysis (DTA) under argon–oxygen and argon atmospheres. The final decomposition products were identified by elemental analysis and the X-ray powder diffraction technique. Thermoanalytical data show that the surrounding atmosphere influences the course of the decomposition process, and the final products. In argon–oxygen atmosphere, the final residues were identified as a mixture of nickel sulphides, oxides and sulphate for the nickel compound, Pd(0) and PdO for the palladium compound, and platinum(0) for the platinum compound. Thermal decompositions in argon atmosphere yielded nickel(II) sulphide, a mixture of Pd/PdS, and metallic platinum, respectively.

INTRODUCTION

This work is an extension of our general research programme on aromatic organoammonium salts of dithiooxalate ligand complexes [1–4], the object of which is to carry out a more complete characterization of this type of complex and to reveal the influence of the surrounding atmosphere and nature of the metal on the thermal decomposition and the final residues.

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 [5–8]. One of these sulphur donor ligands is the 1,2-dithiooxalate dianion. However, these studies focus mainly on the structural properties and very little has

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been published to date about the decomposition of thiooxalate complexes in general and 1,2-dithiooxalate complexes in particular.

The oxidative thermal decompositions of various nickel, palladium 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 processes [9].

We describe herein the syntheses, chemical characterization and the thermal behaviour of three pyridinium 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), or Pt(II). In a previous paper we have reported the crystal structure and packing of the pyridinium salt of bis(1,2-dithiooxalato-*S,S′*)nickelate(II) anion [10].

EXPERIMENTAL

Synthesis of the complexes

The dithiooxalate ligand was used as purchased from Eastman Kodak. The potassium salts of the complex anions $[M(S_2C_2O_2)^2]^{2-}$ were prepared according to the Cox method [11].

The compounds were all prepared by direct reaction of aqueous solutions of the appropriate $K_2[M(S_2C_2O_2)_2]$ salts and pyridinium hydrochloride, in an approximately 1:2 molar ratio (Table 1). The resulting insoluble microcrystalline powders of the compounds were isolated by vacuum filtration, washed with EtOH and Et_2O and recrystallized from *N,N*-dimethylformamide.

Apparatus and measurements

Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer 240 carbon, hydrogen and nitrogen analyser. The concentra-

TABLE 1

Syntheses reagents, yield and elemental analysis of the complexes

Complex	Colour	Reagent/g (mmol)		Yield/%	Analysis, calc. (found)/%			
		(BH)Cl	$K_2[M(dto)_2]$		C	H	N	M
NIDTPY	Dark purple	0.31 (2.68)	0.50 (1.32)	86	36.62 (36.70)	2.63 (2.66)	6.10 (6.15)	12.78 (12.82)
PDDTPY	Yellow	0.25 (2.16)	0.43 (1.01)	83	33.17 (33.22)	2.39 (2.41)	5.53 (5.52)	20.99 (21.02)
PTDTPY	Yellow–red	0.05 (0.43)	0.10 (0.19)	80	28.23 (28.27)	2.03 (1.99)	4.70 (4.75)	32.75 (32.79)

tion of the metal ion was determined using a Perkin-Elmer 360 atomic absorption/flame emission spectrometer. Infrared absorption spectra were recorded on an IR Beckman 4240 spectrometer using KBr discs over the wavenumber range 4000–350 cm^{-1}. UV–vis spectra (650–220 nm) were measured in ethanol solutions (2×10^{-5} M) using a Bausch–Lomb Spectronic 2000 spectrophotometer and 1 cm silica cells. Density values were measured by flotation in a mixture of n-$C_6H_{14}/CHBr_3$. X-ray powder diffraction patterns of PDDTPY and PTDTPY and the final products from thermal decomposition of the the three compounds were recorded at room temperature with a Philips PW 1710 instrument equipped with a graphite monochromator, using Cu Kα radiation. Diffraction patterns of thermal decomposition residues were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards, JCPDS [12].

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.

RESULTS AND DISCUSSION

The crystal structure of NIDTPY was reported in a previous paper [10] and the cell parameters for the Pd and Pt complexes have been obtained by powder diffraction data; 2θ values were corrected using the GUINIER [13] program with an Si standard pattern. Accurate cell parameters were obtained by least-squares refinement using the LSUCRE [14] program. Table 2 summarizes the crystal data for the three complexes and shows that they are all isostructural.

The IR spectra certify the presence of pyridinium cations; evidence of this is the presence of bands at about 3000 cm^{-1} for the C–H groups and 2770 cm^{-1} for $N–H^+$ groups. The characteristic and very strong bands of pyridinium cations were obtained between 1650 and 600 cm^{-1}. IR assignments of the complex anions have been made in the 1600–350 cm^{-1} region and the slight discrepancies in the compounds are due to the different metal ions [1, 2, 15]. Table 3 shows the infrared bands for the complex anions with the corresponding assignments.

The UV–vis spectra of the compounds (Table 4) show a strong absorption band between 256 and 239 nm, attributable to the $\pi \rightarrow \pi^*$ transitions of the pyridinium cation [16] and the dithiooxalate ligand [17]. The rest of the bands, which do not appear in the cation spectra, are attributable to

TABLE 2

Crystal data for NIDTPY, PDDTPY and PTDTPY

	NIDTPY	PDDTPY	PTDTPY
Formula	$C_{14}H_{12}N_2NiO_4S_4$	$C_{14}H_{12}N_2O_4PdS_4$	$C_{14}H_{12}N_2O_4PtS_4$
Formula weight	459.19	506.92	595.58
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	5.793(3)	5.92(1)	5.89(1)
b/Å	14.280(5)	14.08(1)	14.08(1)
c/Å	11.222(3)	11.25(1)	11.23(1)
β/deg	97.29(4)	96.10(8)	96.44(6)
V/Å^3	920.8(9)	931(1)	926(1)
Z	2	2	2
D_x/g cm^{-3}	1.66	1.81	2.14
D_0/g cm^{-3}	1.65(1)	1.82(1)	2.14(2)

TABLE 3

IR bands for the $[M(dto)_2]^{2-}$ anions

NIDTPY	PDDTPY	PTDTPY	Assignment
1585(vs)	1575(vs)	1575(vs)	νC=O
1085(vs)	1080(vs)	1080(s)	νC=C + νC–S
940(s)	940(s)	945(m)	δC=O + ν_{as}C–S
580(m)	575(w)	580(w)	νC–S
410(w)	415(w)	420(w)	ν_{as}M–S
350(m)	350(w)		ν_sM–S

Key: vs, very strong; s, strong; m, medium; w, weak; ν, stretching tension; δ, deformation mode; s, symmetric; as, asymmetric.

TABLE 4

UV–vis spectra (EtOH, λ nm ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})) of the complexes

NIDTPY	PDDTPY	PTDTPY	Assignment
559.0 (2.8)		466.7 (5.4)	$M \rightarrow L(\pi^*)$
559.0 (2.8)		335.6 (4.2)	$d_{xy} \rightarrow d_{x^2-y^2}$
498.2 (2.3)		434.7 (6.9) 419.2 (6.4)	$M \rightarrow L(\pi^*)$
300.2 (4.3)	384.7 (7.4)		$L(\pi) \rightarrow M$
	276.7 (37.2)		$L(\sigma) \rightarrow M$
			$L(\pi) \rightarrow L(\pi^*)$
256.2 (4.8)	234.5 (21.1)	239.9 (2.4)	$\pi \rightarrow \pi^*$

TABLE 5

Thermal analysis data for NIDTPY, PDDTPY and PTDTPY 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/%
NIDTPY									
1	195	260	245(+)	79.35	1	185	260	235(−)	78.28
2^c	390	600	–	−6.85	2^c	260	600		1.79
				(72.50)					(80.07)
PDDTPY									
1	200	270	235(−)	62.80	1	185	305	260(−)	70.30
2^c	270	420		5.40	2^c	305	475		2.90
3	420	440	430(+)	3.92	3	775	900		5.68
4	440	465	450(+)	4.66				(78.80)	
				(76.78)					(78.80)
PTDTPY									
1	210	270	245(+)	50.15	1	185	275	250(−)	39.20
2^c	270	300		2.60	2^c	275	980		27.70
3	300	320	305(+)	6.90					(66.90)
4^c	320	425		7.25					
				(66.90)					

[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.

electronic transitions in the complex anions [17, 18] and the discrepancies are due to the existence of different M–S bonds. For the $[Pd(S_2C_2O_2)]^{2-}$ complex the $M \rightarrow L(\pi^*)$ and $d_{xy} \rightarrow d_{x^2-y^2}$ bands are probably overlapped with the very intense $L \rightarrow M$ bands at 276.7 nm [17].

Table 5 presents the steps, initial and final temperature, 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.

The TG–DTG–DTA curves for the compounds in the oxidative and inert atmospheres are shown in Figs. 1–3. The thermoanalytical result show that the thermal processes and the final residues are strongly influenced by the atmosphere involved and the starting compound. In both atmospheres, the thermogravimetric curves indicate that the decompositions are not simple, and stable intermediate products are not found during the processes owing to most of the stages being almost overlapped. Attempts to correlate the results with theoretical mass losses were not successful, except for the final solid products, which were identified by X-ray powder diffraction methods.

In the argon–oxygen atmosphere, the Ni(II) complex is stable up to 195°C, beyond which an abrupt mass loss takes place corresponding to a

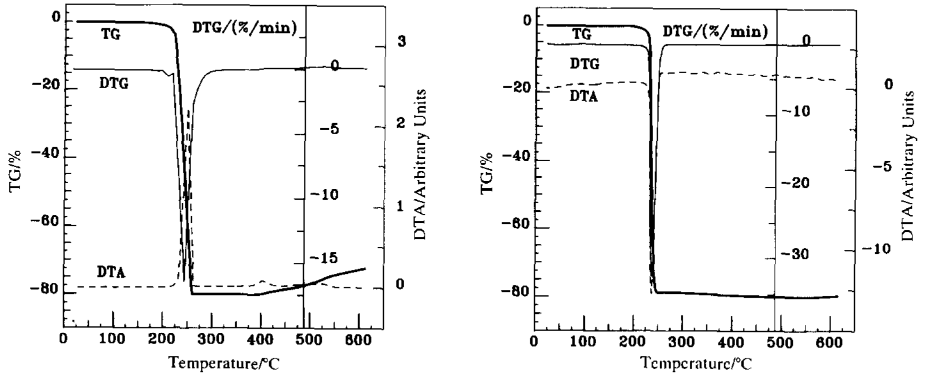

Fig. 1. TG-DTG-DTA curves for the thermal decomposition of NIDTPY in argon-oxygen (left) and argon (right) atmospheres.

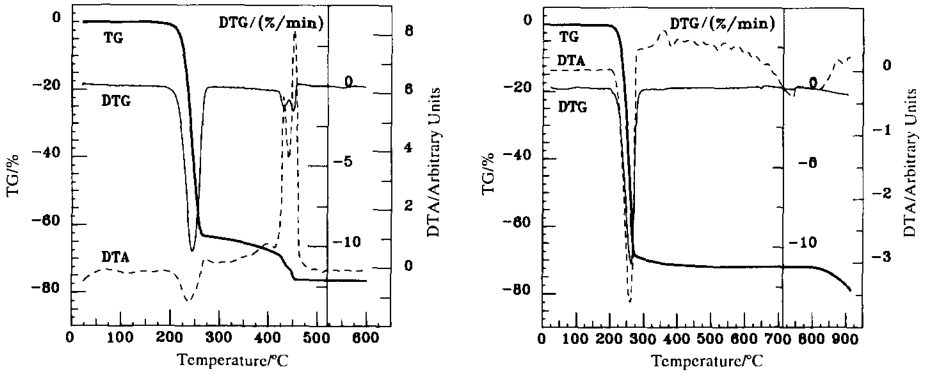

Fig. 2. Thermal decomposition of PDDTPY in argon-oxygen (left) and argon (right) atmospheres.

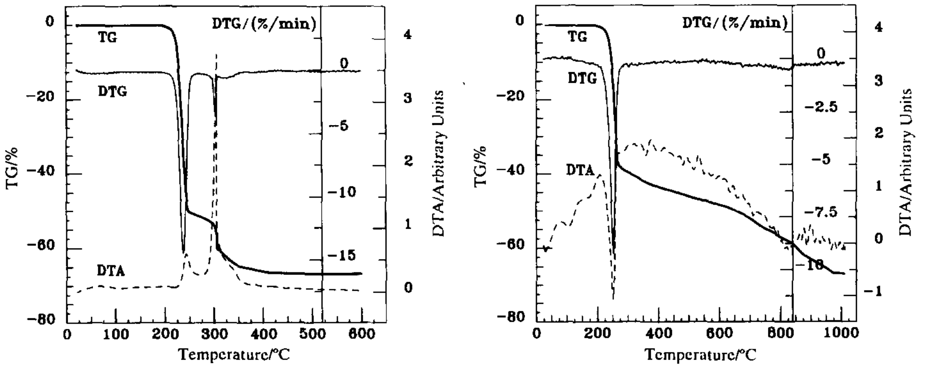

Fig. 3. TG-DTG-DTA curves for the thermal decomposition of PTDTPY in argon-oxygen (left) and argon (right) atmospheres.

strong exothermic peak in the DTA curve attributable to the complex pyrolysis. A plateau in the DTA–TG curves is observed in the range 260–390°C corresponding to the formation of NiS. Above 390°C a progressive mass gain takes places which corresponds to the oxidation of the nickel sulphide to yield nickel sulphate and non-stoichiometric nickel oxides [19].

In argon atmosphere, the complex is stable up to 185°C where an abrupt mass loss takes place corresponding to a strong endothermic peak in the DTA curve. This process is followed by a progressive mass loss which led to a flat TG curve until 600°C. An X-ray diffraction study of the final black residue, whose elemental analysis did not reveal the presence of carbon, exhibited peaks due to the stoichiometric NiS, in addition to others, not recorded in JCPDS files, which may be ascribed to non-stoichiometric sulphides; it is well known that this behaviour is shown by metallic sulphides when they are heated in an inert atmosphere [20].

The thermal decomposition of the Pd(II) compound under oxidative atmosphere starts at 200°C with an endothermic stage which is followed by a progressive mass loss and two strong exothermic peaks in the DTA curve up to 465°C. The final stable residue was identified as a mixture of palladium(0) [ASTM 5-0681] and palladium(II) oxide [ASTM 6-0515] in an approximate ratio of 1/3. In the inert atmosphere, the thermal degradation occurs in an endothermic step between 185 and 305°C followed by a mass loss up to 475°C. The chemical analysis of the residue gives no indication of carbon, nitrogen or hydrogen present in its composition, and it was identified as palladium(II) sulphide [ASTM 10-429]. This residue is stable up to 775°C, beyond which a mass loss takes place and a mixture of palladium(0) [ASTM 5-0681] and palladium(II) sulphide [ASTM 10-429] was found.

The TG curve of the Pt(II) complex in the oxidative atmosphere shows that the compound is stable up to 210°C, at which a first mass loss takes place corresponding to an exothermic peak centered at 245°C in the DTA curve. The decomposition finishes with a strong exothermic process below 320°C and a slight mass loss between 320 and 425°C which lead to platinum(0) [ASTM 4-802] as final product.

In the inert atmosphere this compound is stable up to 185°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 at approximately 980°C. The 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 take place before final products are formed. Only the final products could be identified by elemental analysis and the X-ray powder diffraction technique. The thermoanalytical results indicate that the compounds' decomposition processes and also the final products are influenced by the atmosphere involved and the starting material. In an excess of oxygen the decomposition steps for NIDTPY and PTDTPY are exothermic whereas for the PDDTPY one endothermic process followed by two exothermic processes are found. The final residues were identified as nickel sulphide, sulphate and nickel oxides for NIDTPY, palladium and palladium oxide for PDDTPY, and platinum(0) for PTDTPY. All decomposition steps in an inert atmosphere are endothermic, and the final residues were nickel(II) sulphide for NIDTPY, a mixture of Pd/PdS for PDDTY, and metallic platinum for PTDTPY.

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