



TETRAPHENYLPHOSPHONIUM 1,2-DITHIOOXALATO-S,S' COMPLEXES OF NICKEL(II), PALLADIUM(II) AND PLATINUM(II). SYNTHESIS, CHEMICAL CHARACTERIZATION, SPECTROSCOPIC AND X-RAY STUDIES, AND THERMOCHEMISTRY

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Abstract—Three salts of inorganic dithiooxalato complexes, $(\text{Ph}_4\text{P})_2[\text{Ni}(\text{dto})_2]$ (**1**), $(\text{Ph}_4\text{P})_2[\text{Pd}(\text{dto})_2]$ (**2**) and $(\text{Ph}_4\text{P})_2[\text{Pt}(\text{dto})_2]$ (**3**), where Ph_4P^+ is the tetraphenylphosphonium cation and dto^{2-} is the 1,2-dithiooxalato-S,S' ligand, were synthesized and characterized by elemental analysis, IR and UV-vis spectroscopies, thermal analysis (TG, DTG and DTA) and X-ray diffraction techniques. The IR and UV-vis spectra support the presence of the organic cation and the complex anions. The three compounds are isostructural and crystallize in the triclinic space group $P\bar{1}$. The thermal analytical data show that the starting compounds and the surrounding atmosphere significantly influence the course of the decomposition reactions, as well as the final products. They were examined by elemental analysis and X-ray powder diffractometry. In an argon-oxygen atmosphere, a mixture of nickel(II, III) oxides and nickel(II) sulphide for **1**, metallic palladium for **2** and platinum(0) for **3** were obtained, whereas under argon nickel sulphides, a mixture of Pd/PdS and metallic platinum were identified as the final products.

Interest in coordination chemistry of square planar d^8 metal complexes involving sulphur donor ligands has grown in recent years because of their electronic properties, the applications of these compounds in analytical chemistry and catalysis, and their relevance to bioinorganic systems.¹ One of these sulphur ligands is the 1,2-dithiooxalate dianion ($\text{dto}^{2-} = \text{S}_2\text{C}_2\text{O}_2^{2-}$), in which the presence of four donor atoms and the possibility of charge delocalization on its atoms results in a multifunctional ligand with unique coordination properties.²

Thermal decompositions of various nickel, palladium and platinum complexes are used for the production of metal and metal oxides which are

extensively used as catalysts in a variety of important chemical processes.³

We describe herein the chemical characterization and the thermal behaviour of three tetraphenylphosphonium salts of 1,2-dithiooxalato-S,S' metallate anions, $[\text{M}(\text{S}_2\text{C}_2\text{O}_2)_2]^{2-}$, where M is Ni^{II} , Pd^{II} or Pt^{II} . In a previous paper, we have reported the crystal structure and packing of bis(tetraphenylphosphonium) bis(1,2-dithiooxalato-S,S') nickelate(II).⁴

This work is an extension of our general research programme on organic salts of square planar inorganic metal(II) 1,2-dithiooxalato-S,S' anions, which is aimed at a more complete knowledge of this kind of complex and a deeper insight into the influence of the metal nature and the organic cation on the crystal packing,^{4,11} and the thermochemistry^{12,13} of these compounds.

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EXPERIMENTAL

General and instrumental

Elemental analysis, IR and UV-vis spectra, differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG) were recorded according to the procedure described in a previous paper.¹¹ Density values were measured by flotation in a mixture of $C_6H_6-CHBr_3$. X-ray powder diffraction patterns of microcrystalline powders of the complexes **2** and **3** and the final products of thermal decomposition were recorded at room temperature with a Philips PW 1710 instrument equipped with graphite-monochromated $Cu-K_\alpha$ 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.¹⁴

Synthesis of complexes

The dithiooxalate ligand was used as purchased from Eastman Kodak. The three potassium salts of the complex anions $[M(S_2C_2O_2)_2]^{2-}$ were prepared according to the literature method.¹⁵ The compounds were all prepared by room-temperature mixing of aqueous solutions of tetraphenylphosphonium chloride and the appropriate $K_2[M(S_2C_2O_2)_2]$ salt in an approximately 2:1 molar ratio. Immediately, insoluble microcrystalline powders of the compounds were obtained, which were recrystallized in *N,N*-dimethylformamide. After several weeks, crystals of the three compounds were collected by suction filtration, washed with H_2O and EtOH, and finally dried in air. All these complexes were characterized by elemental analyses and IR (Table 1) and UV-vis spectra (Table 2). The three compounds are soluble in organic solvents (EtOH, Et_2O , CH_3CN , CH_2Cl_2) and insoluble in H_2O .

RESULTS AND DISCUSSION

Spectroscopic characterization

There are only slight differences between the IR spectra of the three studied compounds, which are attributable to the nature of the metal. The IR spectra of complexes show two very strong absorptions at *ca* 1600 and 1580 cm^{-1} , characteristic of a C=O group. Three bands at near 1050, 915 and 615 cm^{-1} correspond to stretching and deformation modes of the C=C and C-S bonds. Finally, the

Table 1. Analytical and IR spectral data for complexes 1-3

Complex	Colour	Reagent/g (mmol)		Found (Calc.) (%)			IR (cm^{-1})				
		(Ph_4P)Cl	$K_2[M(dto)_2]$	C	H	M	$\nu(C=O)$	$\nu(C=C)$ $\nu(C-S)$	$\delta(C=O)$ $\nu_{as}(C-S)$	$\nu(C-S)$	$\nu(M-S)$
1	Black	1.50	0.50	63.8	4.2	6.1	1600vs	1055vs	915m	615w	420w
		(4.00)	(1.33)	(63.9)	(4.1)	(6.0)	1585s				370w
2	Yellow	1.00	0.50	60.8	4.0	10.3	1600vs	1050vs	910s	615w	395w
		(2.67)	(1.18)	(60.9)	(3.9)	(10.4)	1585vs				360w
3	Red	0.22	0.12	56.2	3.7	17.6	1600vs	1050vs	915m	615w	430w
		(0.59)	(0.23)	(56.1)	(3.6)	(17.5)	1580vs				400w

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

Table 2. UV-vis spectra [EtOH, λ nm ($\epsilon \times 10^{-3}$, $M^{-1} \text{ cm}^{-1}$)] of the complexes 1–3

1	2	3	Assignment
563.4 (2.39)		471.1 (2.3)	M \rightarrow L(π^*)
563.4 (2.39)			$d_{xy} \rightarrow d_{x^2-y^2}$
		430.5 (3.0)	M \rightarrow L(π^*)
509.1 (3.6)		413.5 (3.2)	
298.9 (23.1)	387.9 (7.4)	225.7 (79.2)	L(π) \rightarrow M
260.6 (22.9)			L(π) \rightarrow L(π^*)
226.0 (70.0)	275.3 (46.1)		L(σ) \rightarrow M
275.3 (22.1)	275.3 (46.1)	274.3 (14.7)	
266.7 (23.3)		267.5 (16.6)	cation
260.6 (22.9)		260.5 (14.9)	

two bands near 400 cm^{-1} were assigned to tension of the M—S bonds.^{7,11}

The bands at *ca* 3200 and 3000 cm^{-1} are assigned to the vibration of the C—H groups. The other characteristic bands of the cation were obtained between 1650 and 600 cm^{-1} .

Table 2 lists the maximum peaks of the UV-vis spectra of the three compounds. The spectra show absorptions at *ca* 260 , 265 and 275 nm , which may be due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the tetraphenylphosphonium cations and the $\pi \rightarrow \pi^*$ transitions of the complex anions. The remaining spectral bands correspond to electronic transitions in the complex anions.^{11,16,17}

X-ray diffraction structural study

The cell parameters of 2 and 3 were obtained by powder diffraction data; 2θ values were corrected using the GUINIER program¹⁸ with SiO_2 standard pattern. Accurate cell parameters were obtained by least-squares refinement using the LSUCRE program.¹⁹ The two compounds are isostructural with the bis(tetraphenylphosphonium) bis(1,2-dithiooxalato-*S,S'*)nickelate(II) (1) reported in a previous paper.⁴ Table 3 gives the crystal data for the three isostructural complexes. The density values of these compounds are lower than those found for similar complexes containing planar cations. This is due to the presence of π - π interactions involving the aromatic planar cations and the dithiooxalate group, where a significant degree of electronic delocalization is present, which produces a more effective crystal packing.^{8,11}

Thermal analysis

The purpose of this study is to reveal the influence of the surrounding atmosphere and the nature of the metal on the thermal decomposition, as well as to obtain different final products that may develop novel catalytic properties. Table 4 lists the steps, initial and final temperatures ($^{\circ}\text{C}$), partial and total weight losses (%), enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decompositions of the three compounds in argon-oxygen and argon atmospheres.

The TG-DTG-DTA curves for the three compounds under argon-oxygen and argon atmospheres are shown in Figs 1–3. The thermoanalytical

Table 3. Crystal data for compounds 1–3

Compound	1 ^a	2 ^b	3 ^b
Formula	$\text{C}_{52}\text{H}_{40}\text{NiO}_4\text{P}_2\text{S}_4$	$\text{C}_{52}\text{H}_{40}\text{O}_4\text{P}_2\text{PdS}_4$	$\text{C}_{52}\text{H}_{40}\text{O}_4\text{P}_2\text{PtS}_4$
Formula weight	977.76	1025.49	1114.15
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (\AA)	11.050(5)	11.02(1)	11.113(3)
<i>b</i> (\AA)	13.263(7)	13.357(4)	13.256(4)
<i>c</i> (\AA)	18.385(8)	18.464(7)	18.40(2)
α ($^{\circ}$)	111.97(5)	111.54(3)	111.72(4)
β ($^{\circ}$)	90.49(5)	90.54(5)	90.53(5)
γ ($^{\circ}$)	106.10(4)	106.26(5)	105.97(3)
<i>V</i> (\AA^3)	2382(2)	2407(2)	2402(2)
<i>Z</i>	2	2	2
<i>D_c</i> (g cm^{-3})	1.36	1.42	1.54
<i>D_o</i> (g cm^{-3})	1.37(1)	1.43(1)	1.55(1)

^a From Ref. 4.

^b X-ray powder diffraction data.

Table 4. Thermal analysis data for compounds 1–3 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 (%)
Compound 1									
1	245	305	285(+)	29.50	1	230	300	270(–)	33.50
2 ^c	305	350		26.70	2	300	380	335(–)	50.50
3 ^c	350	450		17.80	3 ^c	380	620		1.50
4	450	535	510(+)	14.20	4 ^c	620	850		6.00
5 ^c	535	600		1.60					(91.50)
				(89.80)					
Compound 2									
1	255	300	280(–)	39.75	1	245	300	280(–)	32.50
2	300	375	345(–)	44.50	2	300	375	330(–)	42.50
3	375	500	420(+)	5.00	3 ^c	375	950		12.00
				(89.25)					(87.00)
Compound 3									
1	270	325	290(–)	33.50	1	270	320	270(–)	27.50
2 ^c	325	395		27.50	2	320	430	340(–)	32.00
3	395	440	425(+)	4.00	3 ^c	430	590		8.50
4	440	500	450(+)	6.50	4 ^c	590	890		10.20
5 ^c	500	600		10.00	5 ^c	890	1000		3.30
				(81.50)					(81.50)

^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.

results show that the compounds are anhydrous and the thermal processes and the final residues are strongly influenced by the atmosphere and the starting compound. In both atmospheres, the thermogravimetric curves indicate that the decomposition processes are not simple, since most of the stages overlap. The final solid products were identified

by elemental analysis and X-ray powder diffraction methods.

In the oxidative atmosphere, **1** is stable up to 245°C, beyond which a mass loss takes place corresponding to an exothermic process centred at 285°C in the DTA curve, attributable to the pyrolysis of organic cation and the breakdown of the

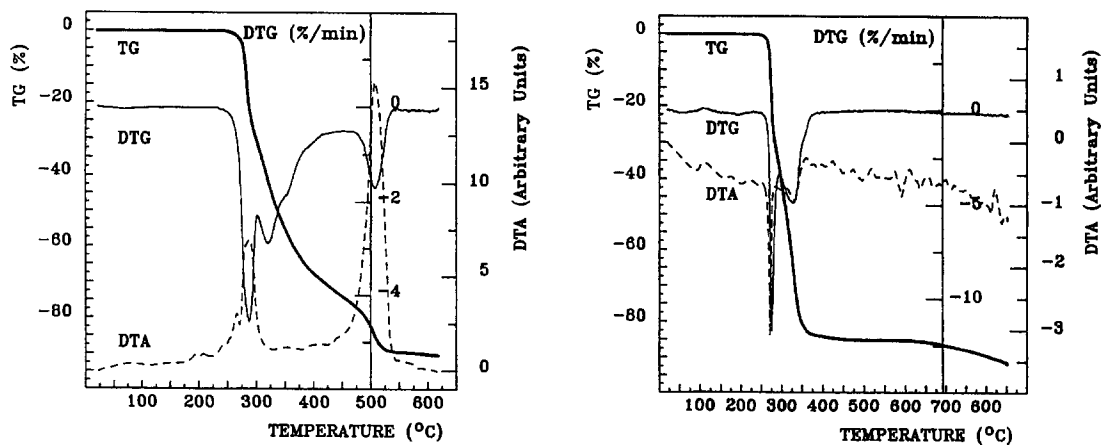


Fig. 1. TG–DTG–DTA curves for the thermal decomposition of compound **1** in argon–oxygen (left) and argon (right) atmospheres.

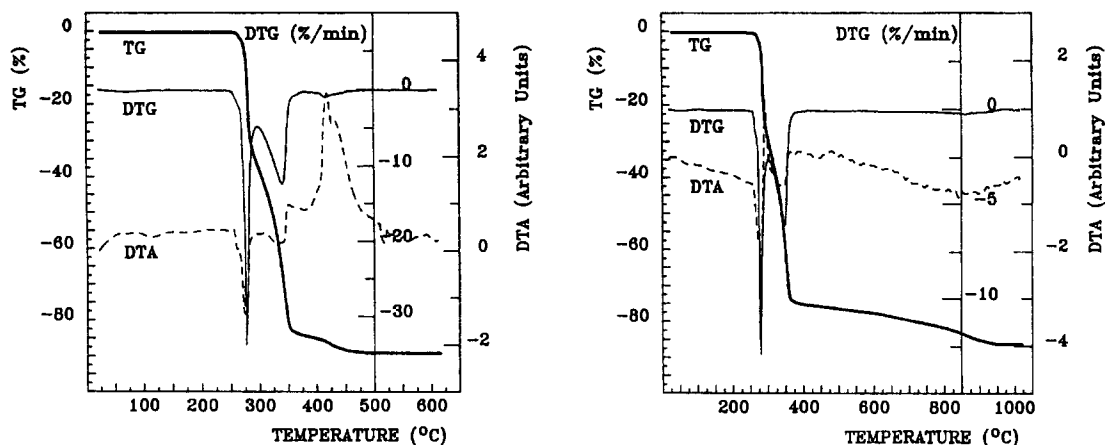


Fig. 2. Thermograms of compound **2** in argon–oxygen (left) and argon (right) atmospheres.

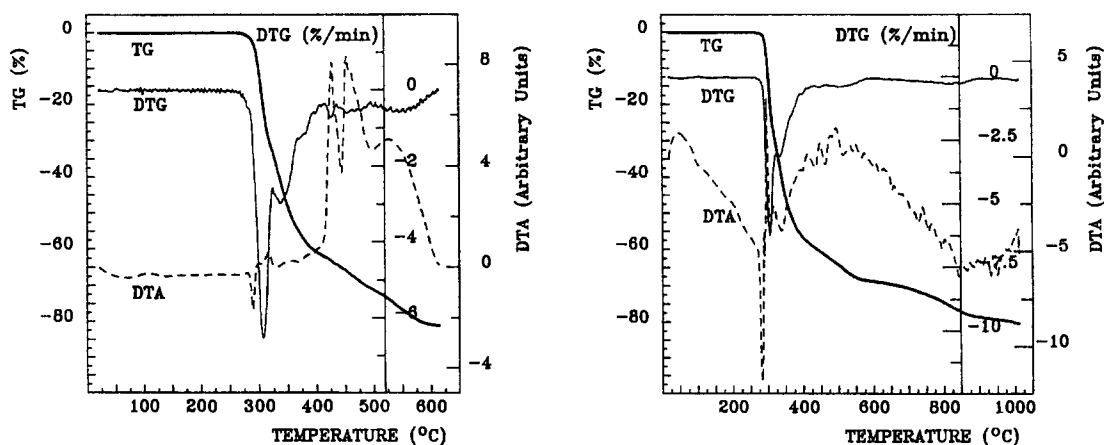


Fig. 3. Thermogravimetric curves of compound **3** in argon–oxygen (left) and argon (right) atmospheres.

dithiooxalate ligand. Between 305 and 450°C, two progressive overlapped mass losses occur, followed by a strong exothermic peak centred at 510°C. The great diversity of possible products precludes exhaustive interpretations of these last degradation processes; however, they could be due to the reordering of the inorganic residue obtained after the breakdown of the dithiooxalate ligands and the pyrolysis of the tetraphenylphosphonium cations during the first strong exothermic step. The solid residue at 600°C was identified as a mixture of nickel(II) sulphide and nickel oxides.

In the inert atmosphere, the decomposition begins with two endothermic processes between 230 and 380°C followed by two progressive mass losses, to give a solid black final residue which was identified as NiS, but its X-ray powder diffractogram also shows the presence of some diffraction maxima, not recorded in the JCPDS files, which could be ascribed to non-stoichiometric sulphides.

This behaviour is well known for metallic sulphides heated in an inert atmosphere.²⁰

The thermogravimetric curve of the palladium(II) complex in the argon–oxygen atmosphere shows that its thermal degradation starts above 255°C with two endothermic mass losses. These steps are followed by one strong exothermic peak around 420°C in the DTA curve. A constant mass was reached at 500°C and the residue was identified as palladium(0) (ASTM 5-0681). No PdS or other palladium sulphides could be detected.

In the inert atmosphere, **2** undergoes decomposition at 245°C with two endothermic steps followed by a progressive mass loss. A constant mass was achieved at 950°C, and the final residue was identified as a mixture of metallic palladium and PdS (ASTM 10-429).

The thermal decomposition of the platinum compound under oxidative atmosphere starts at 270°C, with an endothermic peak in the DTA curve centred

at 290°C followed by progressive mass losses and two very strong exothermic peaks in the DTA curve centred at 425 and 450°C, respectively, to yield at 600°C a residue identified as platinum(0) (ASTM 4-802). In the inert atmosphere, this compound is stable up to approximately 270°C beyond which an abrupt mass loss takes place corresponding to endothermic peaks in the DTA curve. These decomposition steps are followed by three progressive mass losses to give, at 1000°C, platinum(0) as final residue.

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