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PREPARATION, CHEMICAL CHARACTERIZATION AND THERMAL STUDY OF 2-AMINOPYRIDINIUM SALTS OF SQUARE-PLANAR 1,2-DITHIOOXALATO-*S,S′* METAL COMPLEXES (M = Ni^{II}, Pd^{II} AND Pt^{II})

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Abstract—Reaction of an aqueous solution of 2-aminopyridinium chloride with the appropriate $K_2[M(S_2C_2O_2)_2]$ salt yielded microcrystalline powders of three complexes of the formulae $(HC_5H_6N_2)_2[Ni(S_2C_2O_2)_2]$ (**1**), $(HC_5H_6N_2)_2[Pd(S_2C_2O_2)_2]$ (**2**) and $(HC_5H_6N_2)_2[Pt(S_2C_2O_2)_2]$ (**3**), which were characterized by elemental analysis, IR and UV–vis spectroscopies, thermal analysis (TG, DTG and DTA) and X-ray powder diffraction techniques. The IR and UV–vis spectra support the presence of the aromatic cation and the complex anions. Single crystals of **1** were grown in silica hydrogel at room temperature employing test tubes. However, this compound is not stable on X-ray exposure and only the unit cell parameters were determined. The three compounds are isostructural, and crystallize in the monoclinic space group $C2/c$ with $Z = 8$. Thermal studies give evidence that the mechanism and the final solid products are strongly influenced by the atmospheric conditions. The final decomposition products were identified by elemental analysis and the X-ray powder diffraction technique. In an argon–oxygen atmosphere, thermal degradation led to a mixture of nickel sulphides, oxides and sulphate for **1**, metallic palladium and palladium(II) oxide for **2**, and platinum(0) for **3**. Thermal decompositions in an inert atmosphere yielded nickel(II) sulphide, a mixture of Pd–PdS and metallic platinum, respectively.

The coordination chemistry of sulphur donor ligands is an active area of research with interest arising from the study of the properties of their metal complexes and from the applications of these complexes to areas such as analytical chemistry, catalysis and biological chemistry.[1] One of these sulphur ligands is the multifunctional dithiooxalate dianion (dto^{2-}, $S_2C_2O_2^{2-}$), which shows unique coordination properties due to the presence of four donor atoms and the possibilities of charge delocalization on its atoms.

In view of this interest, we have studied the reaction between aromatic organoammonium molecules and several square-planar inorganic metal(II) 1,2-dithiooxalato-*S,S′* anions, in order to obtain a deeper insight into the cation, the metal effects on the crystal packing and the strength of the intermolecular interactions in these types of compounds.[2–5]

On the other hand, the studies on this kind of square-planar d^8 metal complexes involving sulphur donor ligands focus mainly on the structural properties and very little has been published to date about the decomposition of thiooxalate complexes in general and 1,2-thiooxalate complexes in particular.[6–9] 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.[10]

The aim of this paper is to describe the prep-

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aration, chemical characterization and crystal data of isostructural 2-aminopyridinium salts of 1,2-dithiooxalate-*S*,*S′* metallate anions, $[M(S_2C_2O_2)_2]^{2-}$, where M is Ni^{II}, Pd^{II} or Pt^{II}.

EXPERIMENTAL

General and instrumental

Elemental analysis, IR and UV–vis spectra, differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG) were carried out according to the procedure described in a previous paper.[6] Density values were measured by flotation in a mixture of CCl_4–$CHBr_3$. The unit cell parameters of $(HC_5H_6N_2)_2[Ni(S_2C_2O_2)_2]$ (**1**) were determined on an Enraf–Nonius CAD4 four-circle diffractometer with graphite monochromated radiation Mo-K_α. X-ray powder diffraction patterns of microcrystalline powders of the compounds $(HC_5H_6N_2)_2[Pd(S_2C_2O_2)_2]$ (**2**) and $(HC_5H_6N_2)_2[Pt(S_2C_2O_2)_2]$ (**3**) and the final products of thermal decompositions were recorded at room temperature with a Philips PW 1710 instrument equipped with graphite monochromated Cu-K_α radiation. The diffraction positions were corrected using silicon as internal standard and the GUINIER program.[11] 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]

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 synthesized by a method reported previously[13] and isolated with sufficient purity. Firstly, the three compounds were prepared by room temperature mixing of aqueous solutions of 2-aminopyridinium chloride and the appropriate $K_2[M(S_2C_2O_2)_2]$ salt in an approximately 2 : 1 molar ratio (Table 1). The resultant microcrystalline powders were isolated by vacuum filtration, washed with ethanol, then ether and recrystallized in *N*,*N*-dimethylformamide. After several weeks, crystals of the three compounds were collected by suction filtration, washed with ethanol and finally dried in open air. The purity of the complexes was checked by elemental analyses and characterized by IR (Table 1) and UV–vis spectroscopies (Table 2).

Unfortunately, crystals of the three compounds were twinned and were not suitable for X-ray analysis. Suitable single crystals of **1** were grown in silica hydrogel using test tubes. The gel was formed by

Table 1. Analytical data and characteristic bands in the IR spectra of complexes **1**–**3**

		Reagent, g (mmol)		Found (Calc.) (%)					IR (cm^{-1})					
Complex	Colour	HBCl	$K_2[M(dto)_2]$	C	N	H	M	Yield (%)	$\nu(C{=}O)$	$\nu(C{=}O)$	$\nu(C{=}C)$ $\nu(C{-}S)$	$\delta(C{=}O)$ $\nu_{as}(C{-}S)$	$\nu(C{-}S)$	$\nu(M{-}S)$
1	Black	0.45 (3.45)	0.60 (1.59)	34.3 (34.4)	11.4 (11.5)	2.8 (2.9)	12.1 (12.0)	88	1560vs 1550vs	1420m	1095s	960s	630m	435w 360w
2	Yellow	0.30 (2.30)	0.43 (1.01)	31.1 (31.3)	10.5 (10.4)	2.7 (2.6)	19.9 (19.8)	83	1560vs 1550s	1425w	1095s	955w	630m	405w 365w
3	Red	0.06 (0.46)	0.10 (0.19)	27.0 (26.9)	8.9 (9.0)	2.4 (2.3)	31.1 (31.2)	87	1555vs 1540vs	1430w	1085s	950m	630m	425w 395w

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

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

1	2	3	Assignment
566.3 (2.5)		465.3 (5.2)	$M \rightarrow L(\pi^*)$
566.3 (2.5)		338.5 (3.7)	$d_{xy} \rightarrow d_{x^2-y^2}$
507.7 (3.3)		433.3 (6.5)	$M \rightarrow L(\pi^*)$
		413.5 (5.8)	
298.7 (21.0)	387.9 (7.1)		$L(\pi) \rightarrow M$
263.5 (12.3)	235.9 (35.0)	235.1 (38.0)	$L(\pi) \rightarrow L(\pi^*)$
231.1 (19.8)	277.9 (43.0)		$L(\sigma) \rightarrow M$
298.7 (21.0)		293.5 (12.4)	$\pi \rightarrow \pi^*$
231.1 (19.8)	235.9 (35.0)	235.1 (38.0)	$n \rightarrow \pi^*$

addition of 30 cm^3 of sodium silicate solution (density 1.06 g cm^{-3}) to a solution containing 0.03 g of $K_2[Ni(S_2C_2O_2)_2]$ in 15 cm^3 of 1 M acetic acid, with a strong and continuous mechanical stirring. This mixture was placed in eight test tubes (∅ = 8 mm, height = 70 mm). When the gel was firm, an aqueous solution of 2-aminopyridinium chloride was added to the top of the tube. Red–brown crystals with extremely well formed faces appeared in all the tubes after a few days, the dimensions of the largest crystals being 1.0 × 1.5 × 1.5 mm. Attempts to obtain single crystals of compounds **2** and **3** by this method were not successful.

RESULTS AND DISCUSSION

Spectroscopic characterization

The IR spectra of compounds **1**–**3** are similar in the 3000–2700 cm^{-1} region, where N—H and C—H stretching bands are present, which confirm the presence of 2-aminopyridinium cations. The other characteristic bands of the aromatic cation are observed between 1650 and 600 cm^{-1}. Some differences are found in the 1600–350 cm^{-1} range, where the absorption peaks attributable to the complex anions are detectable. A comparison of the results with the observed spectra of similar reported compounds[3–9] leads to the assignments described in Table 1.

Table 2 lists the maximum peaks of the UV–vis spectra of the three compounds. The spectra show absorptions at *ca* 235 and 295 nm, attributable to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the 2-aminopyridinium cations,[14] which are not affected by the complex anions. For complex **2**, the second band is masked by the intense $L(\sigma) \rightarrow M$ band at 277.9 nm. The rest of the spectra correspond to electronic transitions into the complex anions[7,15,16] and the discrepancies are due to the existence of different M—S bonds.

X-ray diffraction study

A prismatic single crystal of **1** with dimensions 0.30 × 0.30 × 0.40 mm was mounted on an Enraf–Nonius CAD4 four-circle diffratometer, and its accurate unit cell parameters were obtained from least-squares fitting on the setting angles for 25 reflections with $2\theta = 14$–$28°$. Unfortunately, crystals of **1** were not stable to X-ray exposure and a strong decay of three standard reflections was observed (> 25%) during the intensity data collection. Thus, it was not possible to solve its crystal structure.

Compounds **2** and **3** crystallized in insufficient quality to be studied by X-ray single crystal diffraction, but their cell parameters have been obtained by least-squares refinement, using the LSUCRE[17] program, of indexed powder diffraction patterns. Table 3 gives the crystal data for the three isostructural complexes.

Thermal analysis

Several studies[6–9] on the thermal decomposition of various dithiooxalate complexes have demonstrated that the surrounding atmosphere, the nature of the metal and the experimental conditions play an important role in the thermal stability and behaviour of these compounds, as well as the final products, which may develop novel catalytic properties.

The results of the thermal studies of compounds **1**–**3** in argon–oxygen and argon atmospheres are presented in Table 4, and the TG–DTG–DTA curves are shown in Figs 1–3.

In both atmospheres, the TG–DTG–DTA curves

Table 3. Crystal data for compounds **1–3**

	1[a]	**2**[b]	**3**[b]
Formula	$C_{14}H_{14}N_4NiO_4S_4$	$C_{14}H_{14}N_4O_4PdS_4$	$C_{14}H_{14}N_4O_4PtS_4$
Formula weight	489.22	536.95	625.61
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	23.522(7)	23.56(1)	23.62(1)
b (Å)	8.868(2)	8.848(6)	8.872(5)
c (Å)	22.147(5)	22.22(3)	22.21(2)
β (°)	124.03(2)	124.60(8)	124.98(4)
V (Å^3)	3829(2)	3813(4)	3812(3)
Z	8	8	8
D_c (g cm^{-3})	1.70	1.87	2.18
D_0 (g cm^{-3})	1.71(1)	1.86(1)	2.17(1)

[a] Single-crystal X-ray diffraction analysis.
[b] Powder X-ray 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	190	260	225 (+)	68.70	1	200	280	250 (−)	71.50
2[c]	260	340		5.30	2[c]	280	350		6.50
3	340	440	420 (+)	6.50					
4	485	600	520 (+)	+3.00	3[c]	350	600		1.50
				(77.50)					(79.50)
Compound **2**									
1[d]	200	290		64.60	1	210	300	255 (−)	65.20
2	290	370	360 (+)	13.00	2[c]	300	500		2.80
				(77.60)	3[c]	500	900		9.50
									(77.50)
Compound **3**									
1[d]	210	260		42.50	1	215	330	260 (−)	42.00
2[c]	260	320		4.50	2[c]	330	600		2.90
3	320	365	335 (+)	20.00	3[c]	600	900		19.10
4[c]	365	530		1.20	4[c]	900	1000		4.00
				(68.20)					(68.00)

[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.
[d] Endothermic and exothermic overlapped peaks in DTA curve.

indicate that the thermal decompositions are not simple, since most of the stages overlap. This fact, together with the great diversity of possible intermediate products, precludes exhaustive interpretations and only the final inorganic degradation residues have been identified by X-ray powder diffraction techniques.

The thermal analysis of **1** in the oxidative atmosphere shows that the compound undergoes decomposition by a strong mass loss between 190 and 260°C corresponding to two overlapped exothermic peaks in the DTA curve, followed by a slight progressive mass loss and one exothermic process up to 440°C. A constant weight was

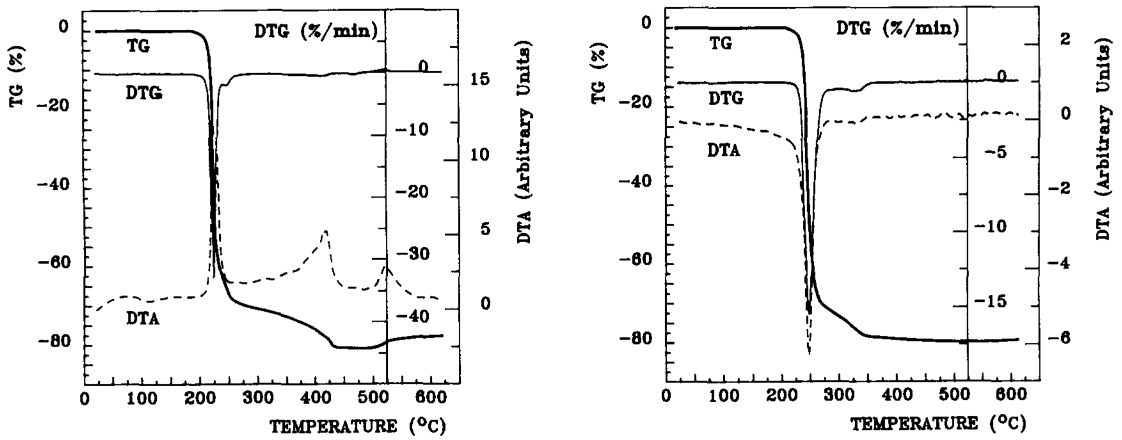

Fig. 1. Thermogravimetric curves of compound **1** in argon–oxygen (left) and argon (right) atmospheres.

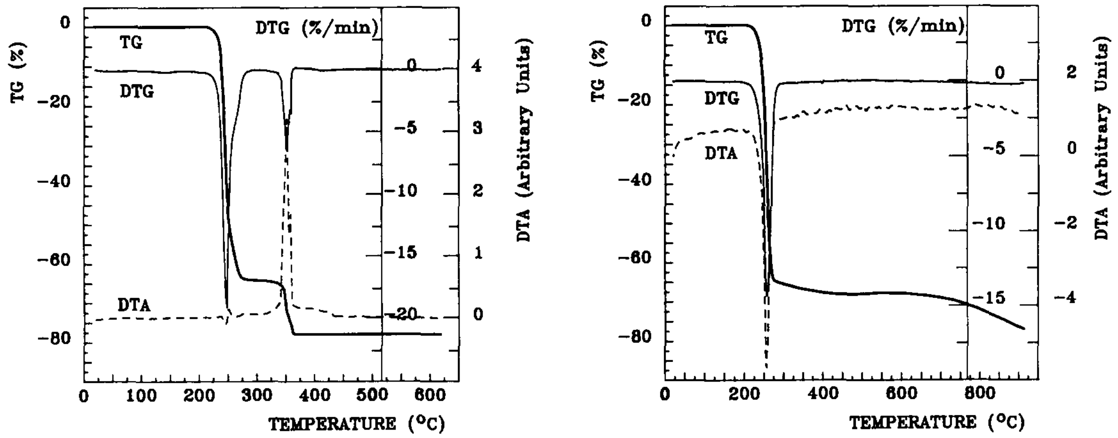

Fig. 2. TG–DTG–DTA curves for the thermal decomposition of compound **2** in argon–oxygen (left) and argon (right) atmospheres.

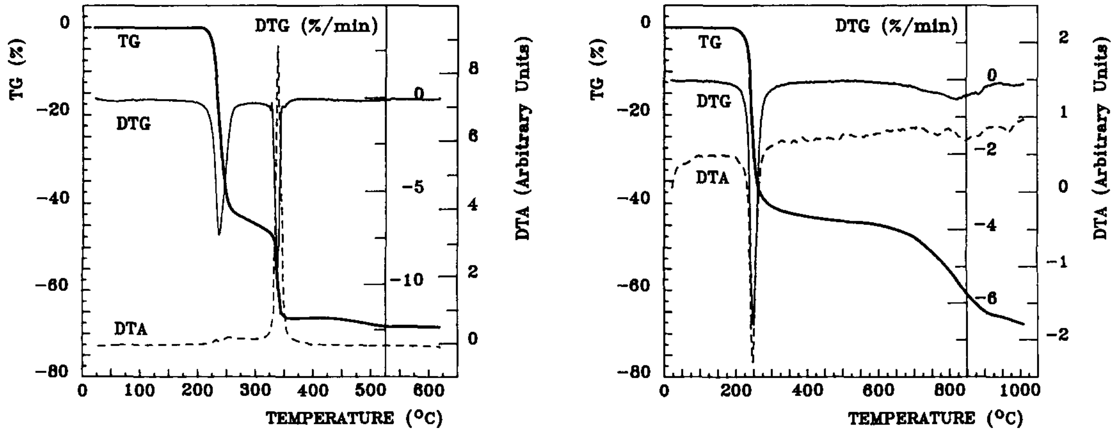

Fig. 3. Thermograms of compound **3** in argon–oxygen (left) and argon (right) atmospheres.

achieved after losing 80.50% of the original weight. This constant weight indicated that nickel(II) sulphide was formed. This conclusion was confirmed by X-ray diffraction (ASTM 2-1280). Above 485°C, an exothermic mass gain takes place related to the oxidation of the NiS to yield nickel sulphate and non-stoichiometric nickel oxides.[18] In the inert atmosphere, the complex is more stable than in the argon–oxygen atmosphere and the degradation starts at 200°C, where an abrupt mass loss occurs corresponding to a strong endothermic peak in the DTA curve, followed by two progressive mass losses without clear peaks in the DTA and DTG curves, until 600°C. The chemical analysis of the black final residue gave no indication of carbon, nitrogen or hydrogen being present in the composition, and it was mainly identified as NiS. However, the X-ray powder diffractogram also showed the presence of some diffraction maxima which could not be identified according to the different nickel oxides and sulphides of the JCPDS, but may be ascribed to non-stoichiometric sulphides, since it is well known that the heating of metallic sulphides in an inert atmosphere yields this kind of compound.[19]

In the oxidative atmosphere, compound **2** is stable up to 200°C, at which temperature a first great mass loss occurs corresponding to the pyrolysis of organic cations and the breakdown of the dithiooxalato ligands. Between 290 and 370°C, two overlapping exothermic processes take place. The final residue was identified as a mixture of palladium(0) (ASTM 5-0681) and palladium(II) oxide (ASTM 6-0515). In the argon atmosphere, the compound is stable up to 210°C and the thermal decomposition occurs in an endothermic step centred at 255°C, followed by two progressive mass losses which lead to a residue identified as a mixture of palladium(0) (ASTM 5-0681) and PdS (ASTM 10-429).

The thermal decomposition of **3** under an oxidative atmosphere starts at 210°C, with a strong mass loss followed by a progressive mass loss, a strong exothermic peak in the DTA curve centred at 335°C and a slight mass loss to yield metallic platinum (ASTM 4-802) as the final product above 530°C.

In the inert atmosphere, this compound is stable up to approximately 215°C, when a first mass loss takes place corresponding to an endothermic peak in the DTA curve. This decomposition step is followed by three progressive mass losses with poorly resolved peaks in the DTG curve and no clear peaks in the DTA curve. The final product of thermal decomposition above 1000°C is platinum(0).

These thermoanalytical results show that the three compounds are slightly more stable in an inert atmosphere than in an oxidative one. Also, they indicate that the thermal stability is influenced by the compound's density and there is a shift towards higher temperature limits of the first thermal decomposition step in the denser compounds.

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