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Squarate Complexes of Diamine Palladium(II) and Platinum(II)

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Abstract

Reactions of *cis*-diaminediaqua palladium and platinum dinitrates and of *trans*-diaminediaqua platinum dinitrate give complexes of the type $Pd(tmeda)(OH)(C_4O_4)Pd(tmeda)(C_4O_4H)$ (tmeda = tetramethylethylenediamine) (**1**), $(en)M(C_4O_4)_2M(en)$ (en = ethylenediamine (M = Pd, Pt) and *trans*-$[Pt(NH_3)_2C_4O_4]_n$, respectively. The structures of these compounds are discussed on the basis of their spectroscopic data.

Introduction

Squaric acid gives rise to a wide variety of complexes with transition metal compounds. A mononuclear complex has been reported in which squaric acid is bound to Pt as an olefin [1]. Binuclear complexes were obtained in which the dianion of squaric acid bridges two metal atoms (M = Pt [2, 3], Cu [4], Cr [5], Re [6]). In the case of vanadium the squarate is supposed to be *cis*-bound to the same metal ion [7]. However, with most transition metal ions one-dimensional chain and three-dimensional polymers are obtained due to pi-electron delocalisation of the squarate dianion [8–11]. In these polymers the squarate anion does not behave as a chelate ligand, as has been shown by detailed studies of Weiss and coworkers [11].

The current interest in squaric acid coordination chemistry motivated us to study the reaction of *cis*-diaminediaqua Pt(II) and *cis*-Pd(II) dinitrates in which the initial arrangement of the *cis*-diamino ligands should have an influence on the structure of the product.

Results and Discussion

Equimolar amounts of $[Pt(en)(H_2O)_2]^{2+}$ or $[Pd(en)(H_2O)_2]^{2+}$ and $K_2C_4O_4$ give rise to insoluble products (**4**, **5**) which according to elemental analysis have the composition $M(en)C_4O_4$ (M = Pd, Pt). *Cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ also gives an insoluble complex (**2**) containing one water molecule. The lack of solubility, which can be attributed either to a polymeric nature or to strong intermolecular hydrogen bonding between the carbonyl groups of squarate and the hydrogens of the amine ligands, limited investigations to infra-red studies. In order to diminish hydrogen bonding, 1,1′,2,2′-tetramethylethylenediamine (tmeda) was chosen as a nitrogen ligand. When $[Pd(tmeda)(H_2O)_2]^{2+}(NO_3^-)_2$ was reacted with $K_2C_4O_4$ a product (**1**) soluble in both water and methanol was obtained. According to molecular weight determination, **1** appears to be a binuclear complex containing a 1:1 ratio of squarate to metal either as a cyclic dimer dihydrate or as an open chain dimer monohydrate.

In the ^1H NMR spectrum of **1** in deuterated methanol, four methyl signals are observed at 2.81, 2.70, 2.64 and 2.34 ppm. In D_2O these signals become very broad, indicating a dynamic process. Multiplicity of the methyl signals and the dynamic properties rule out a cyclic dimer and are rather consistent with an open chain structure in which the methyl groups have different environment. In the ^{13}C NMR spectrum seven methyl ^{13}C-signals are observed at 52.9, 53.5; 53.6; 53.8, 54.1, 54.2 and 54.7 ppm ($Pd(tmeda)(NO_3)_2$ shows only one methyl carbon at 51.2 ppm and one methylene carbon at 64.0 ppm); three methylene carbons at 66.1, 66.4 and 66.7 ppm and four carbons of the squarate ring at 198.4, 202.9, 203.1 and 203.6 ppm. The NMR-spectra at low temperatures (−40 °C in CH_3OH) reveal that several dynamic processes are occurring, probably due to inter- and/or intramolecular hydrogen exchange. Also probable is the existence of several rotamers due to the hindered rotation about the three non equivalent metal squarate bonds in the neighbourhood of the bulky tmeda ligand. A similar type of isomerism has been observed by Cramer and Dahlstrom for $[Pt(tmeda)(guanosine)_2]^{2+}$ [18]. These data support the suggestion that the two Pd atoms and the two squarate ligands are not equivalent in the molecule. Aqueous solutions of **1** are acidic and show conduc-

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TABLE I. Selected IR Absorptions of Diamine Palladium(II) and Platinum(II) Squarates

1	**2**	**3**	**4**	**5**
3420vs	3420m, b	3400sh, b		
	3240s, b	3260s, b	3200s	3200s
	3120sh, b	3100s, b	3100s	3100s
2200vw	2200vw		2400vw	2210vw
				2180vw
1776w	1792w	1780vw	1792w	1770vw
			1780w	
1640m	1640m, b	1640sh	1630s	1620m
			1585m	
			1560m	1555s
1520s	1520sh			1525s
	1500s, b	1500s, b	1500s	1505s
			1470s	
1450m	1460s, b		1450m	1450s
1418m		1420sh	1430m	
1380w				1380sh
			1350w	
	1330m, b	1320sh	1310w	
	1310m, b			

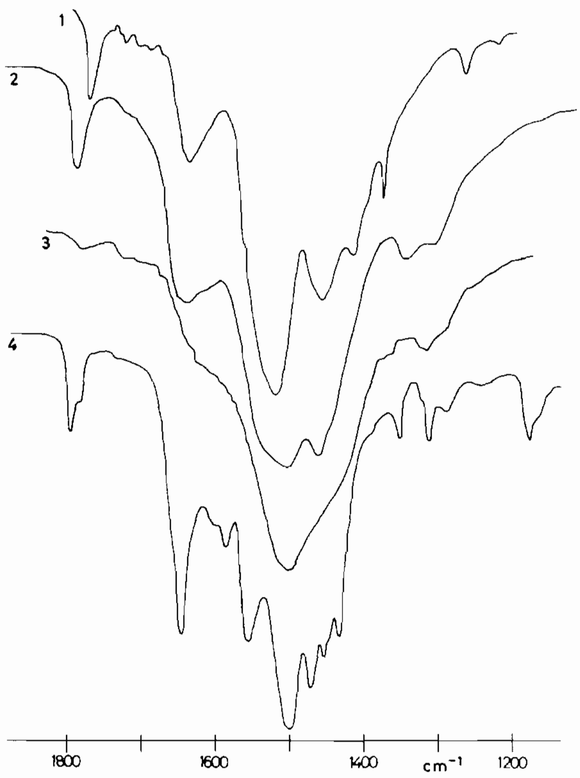
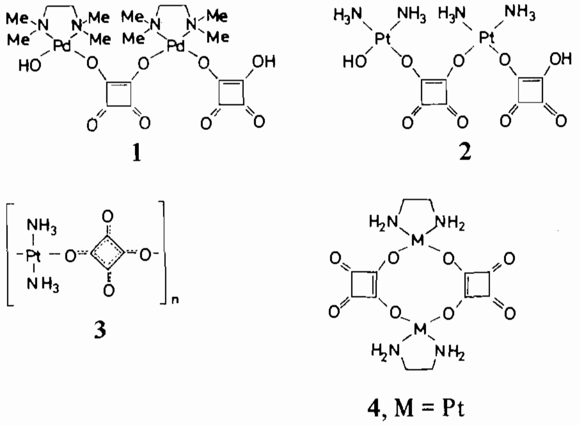


Fig. 1. IR Spectra of 1–4 in KBr pellets.

tivity (Λ = 70 cm^2/Ω mol in water: 28 cm^2/Ω mol in methanol).



1

2

3

4, M = Pt
5, M = Pd

Scheme 1.

The IR-spectrum of **1** contains a very strong OH stretching absorption at 3420 cm^{-1}; a weak carbonyl band at 1776 cm^{-1} (see Table I and Fig. 1), indicating the presence of an uncoordinated carbonyl group of squarate; and broad bands at 1640, 1520 and 1450 cm^{-1} of the $C\cdots C\cdots C\cdots O$ system, which have been reported for (en)Cu(μ-CO)(μ-C_4O_4)Cu(en) [4] and $(CO)_5Re(\mu\text{-}C_4O_4)Re(CO)_5$ [6].

According to these data the structure **1** is proposed as a mixture of several rotamers.

The insoluble *cis*-diamine Pt(II) **2** exhibits a very similar IR-absorption pattern with additional NH stretching bands at 3240 and 3120 cm^{-1}, indicating analogous structures for **1** and **2**. The *trans*-diamine Pt(II) squarate **3** which was prepared in order to compare IR spectra, has very broad bands similar to polymeric squarates [12] but different from the spectrum of the *cis* isomer **2**. We assume that **3** has a polymeric nature.

M(en)C_4O_4 (M = Pd, Pt, **4**, **5**) do not have absorptions at 3400 cm^{-1}; they show two relatively narrow stretching vibrations of the coordinated NH_2 groups at 3200 and 3100 cm^{-1} and two weak carbonyls at 1780 and 1792 cm^{-1} (ν_{as} and ν_sC=O). In the region 1630–1400 cm^{-1} well-resolved bands appear (see Fig. 1). We assume that **4** and **5** have a cyclic dimeric structure.

Experimental

Physical Measurements

Full range (4000–200 cm^{-1}) infrared spectra were obtained on a Perkin-Elmer model 325 as potassium bromide pellets and in nujol. ^{1}H NMR spectra were recorded on a Jeol FX 90 instrument and ^{13}C NMR on a Bruker WP 200. Molecular weight determination was performed with a Knauer vapour pressure osmometer.

Starting Materials

The starting compounds $PdCl_2$(en) [13, 14] and $PdCl_2$ (tmeda) [15] were prepared as reported. The conversion of Palladium complexes into the cor-

TABLE II. Analytical Data of the Pd(II) and Pt(II) Diaminosquarates

Compound	Yield (%)	Colour	Formula (formula weight)	Analyses: Found (calculated) (%)		
				C	H	N
1	76	orange	$C_{10}H_{18}N_2O_5Pd$ (351.6)[a]	33.83 (34.15)	5.45 (5.15)	8.43 (7.96)
2	88	light yellow	$C_4H_8N_2O_5Pt$ (359.0)	13.32 (13.37)	2.28 (2.28)	7.86 (7.79)
3	73	light yellow	$C_4H_8N_2O_5Pt$ (358.0)	12.65 (13.37)	2.64 (2.28)	7.56 (7.79)
4	75	light yellow	$C_6H_8N_2O_4Pt$ (367.2)	19.40 (19.62)	2.31 (2.19)	7.60 (7.62)
5	77	yellow	$C_6H_8N_2O_4Pd$ (278.5)	25.30 (25.87)	3.03 (2.89)	9.84 (10.05)

[a] Found 708 osmometrically in methanol.

responding aqua species was performed according to Lim and Martin [16]. Diaqua diamine platinum nitrates were prepared according to Lippert's procedure [17] by heating diaminedichloroplatinum with two equivalents of $AgNO_3$ for 2 h at 80 °C. After filtration of AgCl the solutions of aquated complexes were lyophilized, and the complexes were stored as solids to avoid formation of bridged hydroxides.

$Pd(OH)(tmeda)(C_4O_4)Pd(tmeda)C_4O_4H \cdot H_2O$ (1)

$[Pd(tmeda)(H_2O)_2](NO_3)_2$ (728 mg, 2 mmol) and $K_2C_4O_4$ (380 mg, 2 mmol) were dissolved in 10 ml distilled water and allowed to stand overnight at room temperature. Water was removed by lyophilisation; the residue was triturated with absolute ethanol (8 ml) over a period of 3 h and filtered from the insoluble KNO_3. The product precipitated from the solution upon addition of ether; it was centrifugated and dried in high vacuum. For analytical data see Table II.

General Procedure for Preparation cis-$Pt(NH_3)_2(OH)(C_4O_4)Pt(NH_3)_2(C_4O_4H) \cdot H_2O$ (2), trans-$Pt(NH_3)_2C_4O_4 \cdot H_2O$ (3), $Pt(en)C_4O_4$ (4) and $Pd(en)C_4O_4$ (5)

The aqua complex (1 mmol) dissolved in 5 ml water was mixed with $K_2C_4O_4$ (1 mmol) and stirred overnight. The precipitated product was filtered, washed several times with water and with alcohol, and dried in high vacuum. Heterogenous conditions were also used, in which the solid diaminodiaqua Pt(II) compound was added to the solution of squarate; however, analytical data obtained from homogeneous reaction conditions were found to be superior.

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