On Limited Platinum Chains. Synthesis and Crystal Structure of a Green Tetranuclear Platinum Compound, *cis*-Diammine Tetraplatinum Squarate, $Pt_4(NH_3)_8(C_4O_4)_4 \cdot 4H_2O$. A Structural Analogue of Platinum Blues

GERALD BERNARDINELLI

Laboratoire de Cristallographie X, Université de Genève, 24 quai Ernest Ansermet, 1211 Geneva, Switzerland

PAULE CASTAN* and REGIS SOULES

Laboratoire de Chimie de Coordination du CNRS, UP no 8241 liée par convention à l'Université Paul Sabatier, 205, route de Narbonne, 31077 Toulouse Cedex, France

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Abstract

From the reaction of the *cis*-dichlorodiammine hydrolysis product with squaric acid, green crystals of *cis*-diammine tetraplatinum squarate are obtained. A single crystal X-ray diffraction analysis shows that the compound consists of a tetranuclear chain, whose adjacent platinum atoms are bridged by squaric ligands.

Introduction

Cooperative phenomena exhibited by linear platinum chain compounds have received considerable interest in recent years [1]. These compounds exhibit strongly anisotropic behavior and unexpected physical and chemical properties which are favored by the partial oxidation state of the metal. However, little attention has been paid to electron delocalization phenomena occurring in limited platinum chains. The only extensive studies have been performed on the so-called 'platinum blues' complexes [2, 3] and on related compounds [4] in which various oxidation states of the metal are possible. When they are structurally identified, these complexes consist of tetranuclear mixed-valent platinum units, and the charge transfer between platinum atoms accounts for the intense band in the optical spectrum [5] and for the paramagnetic behavior of these compounds [3, 6].

We report here a green tetranuclear platinum complex obtained from the dianion of 3,4-dihydroxycyclobutenedione (squaric acid) as bridging ligand.

Experimental

A mixture of *cis*-diammine–platinum(II) hydrolysis products [7] was prepared from 1 mmol of *cis*-$(NH_3)_2PtCl_2$ and 2 mmol of silver nitrate in 10 ml of water. The resulting mixture was left to stand overnight. After removing the silver chloride by centrifugation, the platinum solution was added to an aqueous solution of 2 mmol of squarric acid dissolved in 15 ml of water. Upon standing, the solution turned blue yielding a dark blue amorphous precipitate after 1 h. This precipitate was removed by filtration. From subsequent reaction of the solution, bright green crystals were obtained. Analytical* and X-ray crystallographic data** showed the composition to be $Pt_4(C_4O_4)_4(NH_3)_8 \cdot 4H_2O$.

Results and Discussion

The structure of *cis*-diamminetetraplatinum squarate green is shown in Fig. 1 and selected bond

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*Author to whom correspondence should be addressed.

**Anal.* Calc. for $Pt_4(C_4O_4)_4(NH_3)_8 \cdot 4H_2O$: C, 13.36; H, 2.22; N, 7.79; Pt, 54.32. Found: C, 13.04; H, 2.27; N, 7.30; Pt, 54.55%.

**X-ray analysis. Single crystals of $C_{16}H_{24}O_{16}N_8Pt_4(4H_2O)$ ($M_r = 1436.8$) were studied. Green crystal of dimensions 0.043 × 0.078 × 0.138 mm with faces (001) well developed and elongated along (010); monoclinic, $P2_1/n$, $a = 9.436(2)$, $b = 11.363(2)$, $c = 15.568(3)$ Å, $\beta = 94.42(1)°$, $V = 1664.6$ Å^3, $Z = 2$, $D_c = 2.886$ g cm^{-3}, Mo K$\alpha = 0.710(7)$ Å, $\mu = 170.2$ cm^{-1}, $F(000) = 1312$, $T = 294$ K. Philips PW1100 diffractometer, graphite monochromator, cell dimensions from 25 reflections ($2\theta = 22–32°$); data collections: $\sin \theta/\lambda \leqslant 0.51$, $\omega/2\theta$ scans, ω-scan angle = 1.5°, absorption correction by Gaussian grid integration on grid of 12 × 12 × 12 points, $2.000 \leqslant A^* \leqslant 3.464$, 2 standard reflections varied by a maximum of $1.4\sigma(I)$, 1791 independent reflections, 1397 observed reflections with $|F| \geqslant 4\sigma(F)$ and $|F| > 8$, distribution of data $\langle E^2 - 1 \rangle = 0.904$ indicated centrosymmetric space group; structure solved by MULTAN 80 [19]. Full matrix least-squares using $|F|$ values; 107 parameters refined; no secondary-extinction correction; all coordinates of the hydrogen atoms were calculated; $w(F) = 1$, $R = 5.4\%$. Atomic scattering factors and anomalous dispersion terms for Pt atoms from International Tables for X-Ray Crystallography [20]. All calculations performed with a local version of XRAY'76 [21] and ORTEP II [22].

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TABLE I. Selected Geometric Features of the Complex

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Bond lengths					
Pt(1)	Pt(2)	3.162(2)	Pt(2)	N(3)	2.014(5)
Pt(1)	Pt(1')	3.197(3)	Pt(2)	N(4)	2.018(2)
Pt(1)	N(1)	2.014(1)	Pt(2)	O(4)	2.037(5)
Pt(1)	N(2)	2.048(5)	Pt(2)	O(8)	2.039(6)
Pt(1)	O(1)	2.030(4)	C(5)	C(6)	1.462(7)
Pt(1)	O(5)	2.017(9)	C(5)	C(8)	1.425(6)
C(1)	C(2)	1.286(4)	C(6)	C(7)	1.516(9)
C(1)	C(4)	1.482(6)	C(7)	C(8)	1.408(7)
C(2)	C(3)	1.379(9)			
C(3)	C(4)	1.434(6)			

Atom 1	Atom 2	Atom 3	Angle (°)
Bond angles			
Pt(2)	Pt(1)	Pt(1')	168.0(3)
N(1)	Pt(1)	N(2)	91.6(2)
N(1)	Pt(1)	O(1)	89.2(1)
O(1)	Pt(1)	O(5)	90.0(4)
Pt(2)–N(3)	Pt(1)–N(1)		38.3(8)

Plane A	Plane B	Angle (°)
Dihedral angles		
Pt(1) coord plane	Pt(2) coord plane	12.3(4)
Pt(1) coord plane	squaric 1	65.4(0)
Pt(1) coord plane	squaric 2	75.0(0)
Pt(2) coord plane	squaric 1	71.9(5)
Pt(2) coord plane	squaric 2	65.7(7)
squaric 1	squaric 2	74.4(2)

lengths and angles are reported in Table I. Each platinum atom is coordinated by two ammine ligands in *cis* position and two oxygen atoms of the squarato dianions. Two quasi planar *cis* diammine platinum units are bridged by two squarato ligands and the average O...O distance (O(1)–O(3)) in the bridged squarate is significantly longer (3.32 Å) than for the free ligand (3.24 Å) [8] and than for the Pt–Pt

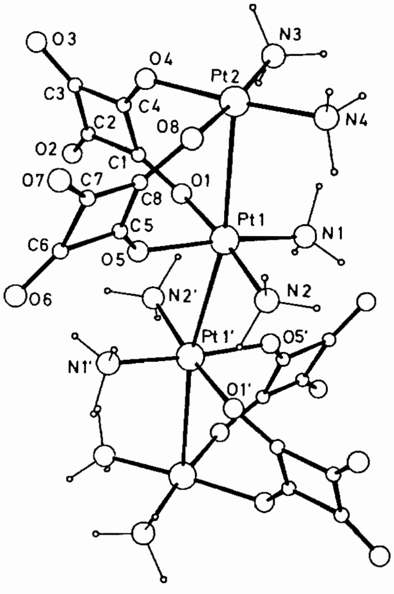

Fig. 1. Structure of $Pt_4(NH_3)_8(C_4O_4)_4 \cdot 4H_2O$.

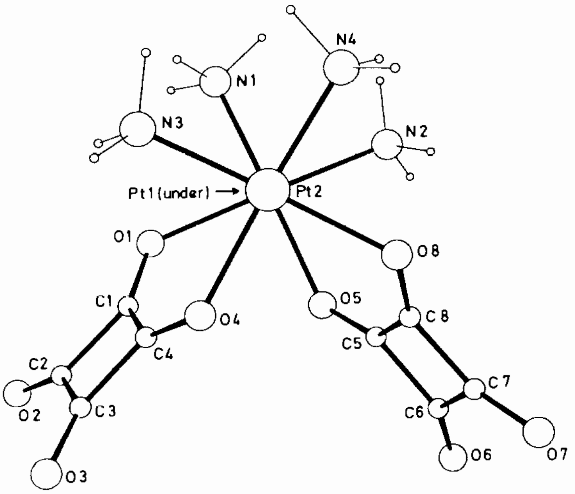

Fig. 2. Structure of the $Pt_2(NH_3)_4(C_4O_4)_2$ unit; perspective view along the Pt_2–Pt_1 axis.

bond length (3.16 Å). Two coordination planes are not strictly parallel and are canted at an angle of 12°3′, together with a 38° torsional twist about the Pt(1)–Pt(2) bond axis (Fig. 2).

Moreover two squarato bridged dimers are linked by a crystallographic center of inversion by a 3.2 Å platinum–platinum distance. The later bond is enhanced by hydrogen bonds between the hydrogen atoms of the coordinated amines and the oxygen atoms of the squarate entity (H...O *ca.* 2 Å).

The tetranuclear chain of platinum atoms consists of a large zigzag since the Pt(2)–Pt(1)–Pt(1′) angle is 168°. This structure may be compared to that of the α-pyridone blue [2] or to that of the tetranuclear platinum complexes of α-pyrrolidone which also consist of dinuclear entities linked by a short metal–metal distance [9, 10]. However, one of the main differences is that the platinum–platinum distances are quite a lot longer in the case of the squarato complex.

It is well known that the Pt–Pt distance in the amidate-bridged tetranuclear platinum compounds increases as the Pt oxidation state decreases [11], a correlation similar to that observed for one-dimensional platinum complexes [12]. Bearing this in mind, the Pt–Pt distances in the squarate-bridged complex described here are quite long, as expected for a Pt(II) complex. They are similar to those found in the tetranuclear *cis*-diammine platinum(II) 1-methylhydantoin yellow (3.13, 3.20 Å) [13] and should also be compared to those observed in the dinuclear barium tetrakis μ-squarato platinum(II) (3.06 Å) [14] or in other platinum(II) complexes bridged by amide ligands [13, 15].

Since examples of tetranuclear platinum compounds are still scarce and only limited to amide ligands, a green tetranuclear complex has been previously described and structurally identified using α-pyrolidone as amide ligand [11]. However it is a nonstoichiometric complex with an average oxidation state of 2.37, and it is easy to correlate the green color with some electronic delocalization along the platinum chain.

Taking into account that a fractional oxidation state of the metal neither appears in the chemical formulation nor in the structural determination for the squarate complex, this unusual color may rather be correlated with that observed for Magnus's green salt (MGS), $[Pt(NH_3)_4][PtCl_4]$. Though it may be recalled that the green color of the platinum Magnus-type salts has been considered to be a diagnostic for strong metal-metal interactions [16], it could be assumed that this unusual property would be impurity dominated [17].

The existence of traces of platinum(IV) or even platinum(III) in the title complex is opened to discussion. However, this hypothesis should be retained since the study of the amorphous blue compound obtained as a first step during the synthesis allows to assign an oxidation state above two. Like in MGS [18], the EPR signal may be due to an extrinsic mechanism related to hole states due to the presence of Pt(IV) complexes promoted during sample preparation.

Supplementary Material

Listings of angles and bond distances (Table S_1), positional parameters and their estimated standard deviations (Table S_2) are available from the authors on request.

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