Structural Characterization of the 3,4-dimethylpyridinium Salt of the $[Pt_2(HPO_4)_4(3,4\text{-}Me_2py)_2]^{2-}$ Ion

F. ALBERT COTTON*, SCOTT HAN

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, Tex. 77843, U.S.A.

HAROLD L. CONDER and RICHARD A. WALTON*

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

Received November 27, 1982

The previously reported compound, $(3,4\text{-}Me_2C_5H_3NH)_2[Pt_2(HPO_4)_4(3,4\text{-}Me_2C_5H_3N)_2]$, has been structurally characterized by X-ray crystallography. The anion resides on an inversion center and the principal bond lengths and angles are: Pt–Pt, 2.494(1) Å; Pt–O, 2.012[6] Å; P–O(coord), 1.545[7] Å; P=O, 1.489[12] Å; P–OH, 1.565[11] Å; Pt–Pt–O, 90.5[2]°. The $Pt_2(HPO_4)_4$ unit has virtual C_{4h} (4/m) symmetry. The compound crystallizes in space group $P2_1/n$ with the following unit cell dimensions: a = *8.418(2)* Å; b = *20.122(8)* Å; c = *11.433(2)* Å; β = *107.02(2)*°; V = *1852(1)* Å^3; *Z = 2.*

Introduction

In an earlier report [1] the reactions of phosphoric acid solutions containing (presumably) the diplatinum(III,III) anion, $[Pt_2(HPO_4)_4]^{2-}$, with heterocyclic amines, B, to give products of the type $(BH)_2[Pt_2(HPO_4)_4B_2]$ were reported. Crystallographic examination of what was expected to be a representative compound of the above type with B = pyridine revealed that the crystalline material examined was actually $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3py_2]\cdot H_2O$. We have continued our study of the general class of $(BH)_2[Pt_2(HPO_4)_4B_2]$ compounds and can now report the crystal and molecular structure of one such compound, *viz.*, that in which B is 3,4-dimethylpyridine.

Experimental

The compound was prepared according to the previously reported procedure [1]. A crystal of

TABLE I. Crystallographic Data.

Formula	$(C_7N_{10}N)_2[Pt_2(HPO_4)_4(C_7H_9N)_2]$
Formula weight	1202.72
Space group	$P2_1/n$
a, Å	8.418(2)
b, Å	20.122(8)
c, Å	11.433(2)
α, degrees	90.0
β, degrees	107.02(2)
γ, degrees	90.0
V, Å^3	1851.7(9)
Z	2
d_{calc}, g/cm^3	2.157
Crystal size, mm	0.1 × 0.2 × 0.2
μ(MoKα), cm^{-1}	78.70
Data collection instrument	P$\bar{1}$ Syntex
Radiation	Mo Kα
Scan method	$\theta-2\theta$
Data collection range	4–50, 2θ
No. unique data,	2194
$F_o^2 \geqslant 3\sigma(F_o^2)$	1845
Number of parameters refined	239
R^a	0.062
R$_w$^{b}	0.086
Quality-of-fit indicator^c	2.030
Largest shift/esd, final cycle	0.12

$^a R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b R_w = \Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

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*Authors to whom correspondence should be addressed.

0020-1693/83/$3.00

TABLE II. Final Atomic Positions and Their Estimated Standard Deviations.

Atom	*x*	*y*	*z*
Pt(1)	0.04241(9)	0.03622(4)	0.09247(6)
P(1)	−0.3123(7)	0.0695(3)	−0.0826(5)
P(2)	−0.0924(7)	−0.1010(3)	0.1423(5)
O(1)	−0.181(2)	0.0812(8)	0.040(1)
O(2)	0.269(2)	−0.0089(9)	0.147(1)
O(3)	−0.055(2)	−0.0281(8)	0.187(1)
O(4)	0.137(2)	0.1021(8)	0.001(1)
O(5)	−0.481(2)	0.0615(8)	−0.069(1)
O(6)	−0.315(2)	0.1328(8)	−0.165(1)
O(7)	−0.041(2)	0.1497(8)	−0.202(1)
O(8)	0.251(2)	0.1241(9)	−0.174(1)
N(1)	0.115(2)	0.0978(8)	0.255(1)
N(2)	0.557(3)	0.089(1)	0.173(2)
C(1)	0.234(3)	0.076(1)	0.358(2)
C(2)	0.284(2)	0.114(1)	0.454(2)
C(3)	0.220(3)	0.179(1)	0.457(2)
C(4)	0.113(3)	0.202(1)	0.350(2)
C(5)	0.062(3)	0.158(1)	0.253(2)
C(6)	0.405(3)	0.085(2)	0.572(2)
C(7)	0.268(4)	0.225(2)	0.568(2)
C(8)	0.676(3)	0.065(1)	0.273(2)
C(9)	0.734(3)	0.105(1)	0.384(2)
C(10)	0.654(3)	0.168(1)	0.379(2)
C(11)	0.536(3)	0.189(2)	0.274(2)
C(12)	0.488(3)	0.145(2)	0.179(3)
C(13)	0.875(4)	0.079(2)	0.494(3)
C(14)	0.712(3)	0.216(2)	0.490(3)

TABLE III. Selected Bond Distances and Angles.[a]

Distances (Å)			
Pt(1)–Pt(1)′	2.494(1)	P(1)–O(2)	1.524(13)
Pt(1)–O(1)	2.015(11)	P(1)–O(5)	1.479(12)
Pt(1)–O(2)	2.038(10)	P(1)–O(6)	1.580(11)
Pt(1)–O(3)	2.005(11)	P(2)–O(3)	1.555(13)
Pt(1)–O(4)	1.991(11)	P(2)–O(4)	1.570(11)
Pt(1)′–N(1)	2.164(11)	P(2)–O(7)	1.498(12)
P(1)–O(1)	1.529(12)	P(2)–O(8)	1.550(11)

Angles (Deg.)	
Pt(1)–Pt(1)′–O(1)	90.0(3)
Pt(1)–Pt(1)′–O(2)	90.6(3)
Pt(1)–Pt(1)′–O(3)	91.0(3)
Pt(1)–Pt(1)′–O(4)	90.2(3)
Pt(1)–Pt(1)′–N(1)	179.1(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

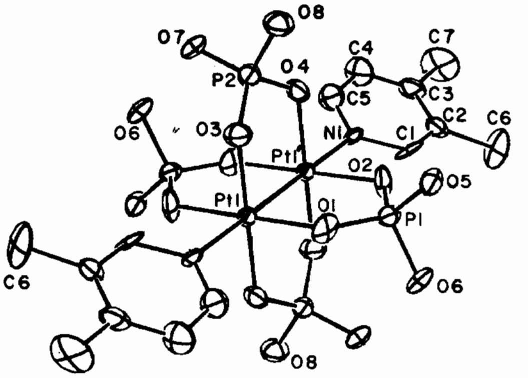

Fig. 1. ORTEP plot of the $[Pt_2(HPO_4)_4(Me_2C_5H_3N)_2]^{2-}$ anion. Thermal ellipsoids of the atoms are at the 50% probability level.

dimensions 0.2 × 0.2 × 0.1 mm was coated with epoxy cement, mounted on a glass fiber, and placed on a Syntex P$\bar{1}$ four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 Å). Of 2194 unique data collected, those 1845 with $I > 3\sigma(I)$ were used to solve and refine the structure. Lorentz, polarization and absorption corrections (by the ψ-scan method) were applied.

The usual procedures of preliminary examination to determine the crystal class and measure unit cell dimensions were used. Systematic absences identified the space group as $P2_1/n$. The pertinent crystallographic data are collected in Table I.

The Patterson function revealed the heavy atom position and subsequent difference Fourier maps followed by full-matrix least squares cycles revealed the remaining non-hydrogen atoms. Converged discrepancy indices were R = 0.062 and R_w = 0.086. The peaks over 1.0 e/Å^3 in the final difference map were ghost peaks extremely close to the platinum atoms. One methyl carbon atom of the dimethylpyridinium cation was left isotropic as attempts to refine it anisotropically produced imaginary amplitudes of vibration. We attribute this to a remnant of absorption even though, as stated previously, an absorption correction was applied [2].

Table II gives final atomic coordinates and Table III shows selected bond lengths and angles. Figure 1 depicts the $[Pt_2(HPO_4)_4(Me_2C_5H_3N)_2]^{2-}$ anion. The thermal parameters and a list of the observed and calculated structure factors are available as supplementary material from F.A.C.

Discussion

The compound we have now studied is, indeed, a representative $(BH)_2[Pt_2(HPO_4)_4B_2]$ compound. Two 3,4-dimethylpyridinium cations are found. The closest noncovalent contact distance observed is an N–H···O hydrogen bond, 2.75(2) Å, between the cation nitrogen atom and one of the P=O oxygen atoms. There are also longer contacts between this nitrogen atom and O(1) and O(2) at distances of 3.03(2) Å and 3.07(2) Å, respectively.

The $[Pt_2(HPO_4)_4(Me_2C_5H_3N)_2]^{2-}$ anion resides on a crystallographic inversion center. The $Pt_2(HPO_4)_4$ portion of it has essentially C_{4h} (4/m) symmetry. Distances and angles averaged [3] for this assumed ideal symmetry are: Pt–O, 2.012[6] Å; P–O(coord), 1.545[7] Å; P=O, 1.489[12] Å; P–OH, 1.565[11] Å; Pt–Pt–O, 90.5[2]°.

This central $Pt_2(HPO_4)_4$ unit, with its essential C_{4h} symmetry, is thus very similar to those previously seen in $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ [4] and the $Mo_2(HPO_4)_4$ compounds [5].

Two axial 3,4-dimethylpyridine groups are coordinated linearly to the Pt–Pt bond at an angle of 179.1(3)° with a Pt–N distance of 2.164(11) Å. The rings are coplanar to each other similar to the arrangement seen in $Mo_2(OOCCF_3)_4(py)_2$ [6]. We note that in $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]\cdot H_2O$ the rings make a dihedral angle of 87.9° to each other [1] and in $Rh_2(OOCCF_3)_4(py)_2$ they pack at an angle of 58.9° [7].

The Pt–Pt bond length here, 2.494(1) Å, is not different, in any chemically significant way, from those previously found in $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ [4], 2.486(2) Å, or $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3py_2]\cdot H_2O$ [1], 2.494(1) Å. Indeed, the latter is identical to the present one, and all other dimensions in the two structures are so similar that we have here further evidence that the $[Pt_2(H_2PO_4)(HPO_4)_3py_2]^-$ ion has, indeed, been correctly formulated as a diplatinum (III,III) species.

Acknowledgement

We are grateful to the National Science Foundation for financial support.

References

1 H. L. Conder, F. A. Cotton, L. R. Falvello, S. Han and R. A. Walton, *Inorg. Chem.*, in press.

2 All calculations were performed on the PDP 11/60 computer using the Enraf-Nonius Structure Determination Package at B. A. Frenz and Associates, College Station, Texas.

3 We use ( ) to represent an esd for a given individual value and [ ] as $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value in a set of *n* such values from the arithmetic mean of the n values.

4 F. A. Cotton, L. R. Falvello and S. Han, *Inorg. Chem.*, *21*, 1709 (1982).

5 A. Bino and F. A. Cotton, *Inorg. Chem.*, *18*, 3562 (1979).

6 F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, *94*, 5697 (1972).

7 J. J. Ziolkowski, M. Moszner and T. Glowiak, *J. Chem. Soc. Chem. Comm.*, 760 (1977).