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Dinuclear, Metal–Metal-Bonded Platinum(III) Compounds. 4. Structural Studies of Several Compounds with Sulfate or Hydrogenphosphate Ions

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Three compounds containing Pt_2^{6+} *units have been accurately characterized by X-ray crystallography:* $K_2[Pt_2(SO_4)_4(H_2O)_2]$, *1;* $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, *2;* $[(C_5H_5)_4N]_2[Pt_2(H_2PO_4)_2{\cdot}(HPO_4)_2Cl_2]{\cdot}H_2O$, *3. All three compounds crystallize in space group* $P\bar{1}$. *Crystallographic data are as follows. For compound 1:* $a = 7.453(3)$ Å, $b = 7.524(3)$ Å, $c = 7.593(3)$ Å, $\alpha = 102.01(4)^\circ$, $\beta = 111.45(3)^\circ$, $\gamma = 99.80(3)^\circ$, $V = 373.1(9)$ Å^3, $Z = 1$. *For compound 2:* $a = 7.912(1)$ Å, $b = 7.893(2)$ Å, $c = 13.732(4)$ Å, $\alpha = 82.66(2)^\circ$, $\beta = 98.29(2)^\circ$, $\gamma = 114.27(2)^\circ$, $V = 780.2(6)$ Å^3, $Z = 2$. *For compound 3:* $a = 10.136(3)$ Å, $b = 11.660(6)$ Å, $c = 8.392(3)$ Å, $\alpha = 111.30(3)^\circ$, $\beta = 88.04(3)^\circ$, $\gamma = 109.47(2)^\circ$, $V = 867.0(6)$ Å^3, $Z = 1$. *The Pt–Pt distances (Å) in the three compounds are: 1, 2.461(1); 2, 2.487(2), 2.485(1); 3, 2.529(1). The structure of compound 1 was reported earlier by others but not fully refined or described. The structure of compound 2 is here reported fully for the first time. Compound 3 is a new compound with an unprecedented assortment of* $H_2PO_4^-$ *and* HPO_4^{2-} *bridging ligands. In each of the three compounds the* $Pt_2(O_2XO_2)_4$ *arrangement entails non-planar* Pt_2O_2X *rings, all bent in the same direction to afford* C_{4h} *symmetry. The outer P=O and P–OH bonds can be distinguished by their different lengths. The Pt–Pt distance in 3 is appreciably longer than any other one for a species of this general class.*

Introduction

In recent years there has been considerable interest, both here [1–4] and elsewhere [5], in the preparation and structural characterization of diplatinum(III,III) complexes, *i.e.*, compounds containing the Pt_2^{6+} unit in which there is a net Pt–Pt single bond. Most of the compounds examined so far have bridging sulfate groups or the stereoelectronically equivalent HPO_4^{2-} groups, but there are also other kinds. A complete list of those known will be found in the Discussion section of this paper. These Pt_2^{6+} species are isoelectronic with the Rh_2^{4+} complexes, of which a much greater number and variety are known. It is presumed that the electronic arrangements in the two series are qualitatively similar and it is on this basis that a Pt–Pt bond of order one, a net sigma bond, is believed to be present.

This report deals with three compounds, each of which was studied for a different, and not always deliberate, reason. The compound $K_2[Pt_2(SO_4)_4(H_2O)_2]$, *1*, was the first one of this class to have its identity confirmed by X-ray crystallography [5]. The structure report is somewhat incomplete and when we found that we had, inadvertantly, collected a good data set for this same compound, we considered it worthwhile to refine the structure so that a more complete description of it could be presented. Our results are in good agreement with those of Porai-Koshits and coworkers [5]. Compound *2*, $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, is one for which the structure was previously reported only in a preliminary communication. Compound *3*, $[Et_4N]_2(Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]{\cdot}H_2O$, is a new one and of an interesting type because it illustrates once again the fact that the bridging ligands, within the same compound, may coexist in different states of protonation.

Experimental

Crystallization of $K_2[Pt_2(SO_4)_4(H_2O)_2]$, *1*

A sample of this compound was made according to the method originally described by Muraveiskaya *et al.* [12]. An attempt was made to oxidize the $[Pt_2(SO_4)_4]^{2-}$ unit to $[Pt_2(SO_4)_4]^{3-}$ by dissolving a 0.10 g sample of *1* in 20 ml of H_2O and adding 0.1 ml of bromine. The solution was stirred for 0.5 h and then filtered. During this time the color of the solution changed from pale orange to deep red-orange. Subsequent evaporation in air gave a black amorphous powder and yellow crystals of what proved, by X-ray crystallography, to be unreacted $K_2[Pt_2(SO_4)_4(H_2O)_2]$.

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Preparation of $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, 2

A mixture of 0.10 g (0.31 mmol) of $Pt(NH_3)_2(NO_2)_2$ and 5 ml of 85% H_3PO_4 was heated with stirring at 100 °C for 2 h until a deep red solution formed. This solution was cooled, diluted with 10 ml of water and 0.5 g (3.8 mmol) of $(NH_4)_2HPO_4$ was added. The resulting solution was kept at −10 °C for 2 days. A yellow, powdery precipitate which had formed was washed with cold water, ethanol, and ether. This solid was redissolved in 20 ml of warm water and 5 ml of 0.1 *M* $[Et_4N]NO_3$ (made from $[Et_4N]Cl$ and $AgNO_3$) was added. The $[Et_4N]NO_3$ solution used in this instance apparently contained a large amount of sodium ion as an impurity and thus the Na salt of the complex was unexpectedly formed. The solution was filtered and crystals of *2* grew by slow evaporation of the filtrate in air.

Preparation of $[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$, 3

The yellow solid first isolated in the preparation of *2*, assumed to have the formula $(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$ (0.10 g, 0.12 mmol), was dissolved in 20 ml of water and 0.039 g (0.24 mmol) of Et_4NCl was added. The solution became red and was filtered to remove any undissolved matter. Crystals in the form of plates were then obtained by slow evaporation of this solution in air. The Et_4NCl adduct appears to be more soluble than the starting aquo species.

Crystallographic Studies

The crystallographic work was mostly routine and followed procedures that have previously been described*. Many of the relevant data are summarized in Table I and extended accounts of the handling of each structure are available upon request. In the case of compound *2* we were unable to find a disorder model, or any other model, that allowed successful anisotropic refinement of O(8) and O(14); these two atoms were therefore refined with isotropic thermal vibration parameters and no disorder. However, it is probable that they are actually disordered

TABLE I. Crystallographic Data.

	(*1*)	(*2*)	(*3*)
Formula	$K_2[Pt_2(SO_4)_4(H_2O)_2]$	$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$	$[(CH_3CH_2)_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$
Formula weight	888.66	856.11	1125.55
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	7.453(3)	7.912(1)	10.136(3)
b, Å	7.524(3)	7.983(2)	11.660(6)
c, Å	7.593(3)	13.732(4)	8.392(3)
α, degrees	102.01(4)	82.66(2)	111.30(3)
β, degrees	111.45(3)	98.29(2)	88.04(3)
γ, degrees	99.80(3)	114.27(2)	109.47(3)
V, Å^3	373.1(9)	780.2(6)	867.0(6)
Z	1	2	1
d_{calc}, g/cm^3	3.96	3.64	2.16
Crystal size, mm	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.05
μ(MoKα), cm^{-1}	201.2	193.9	85.48
Data collection instrument	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Syntex P$\bar{1}$
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)
Scan method	$\theta, 2\theta$	$\theta, 2\theta$	$\theta, 2\theta$
Data collection range	4.0–50.0, 2θ	2.0–50.0, 2θ	4.0–60.0, 2θ
No. unique data	1415	3053	2286
$F_o^2 \geqslant 3\sigma(F_o^2)$	1146	1673	2146
Number of parameters refined	118	225	194
R^a	0.052	0.045	0.047
$R_w{}^b$	0.063	0.061	0.064
Quality-of-fit indicator^c	2.100	1.631	1.422
Largest shift/esd, final cycle	0.01	0.06	0.23

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

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*Calculations for compounds (*1*) and (*2*) were performed on the PDP 11/60 computer equipped with the Enraf-Nonius Structure Determination Package at B. A. Frenz and Associates, Inc., College Station, Texas. Calculations for compound (*3*) were done on the VAX 11/780 computer using the Enraf-Nonius Structure Determination Package ('VAXSDP') at the Department of Chemistry, Texas A&M University, College Station, Texas.

in some way. In addition, we noted that the crystal lattice was nearly monoclinic metrically, but not within experimental error. However, we attempted a refinement of the structure in the higher-symmetry setting, and ruled out monoclinic symmetry. In compound *3*, atom O(9) belongs to a water molecule that appears to be disordered as two half atoms related by an inversion center; it refined satisfactorily when so treated. Tables of observed and calculated structure factors are available as supplementary material.

Results and Discussion

Atomic coordinates for the three compounds are listed in Tables II–IV. Table V gives selected bond distances and angles for all three compounds. Complete tables of bond lengths and angles are available as supplementary material.

TABLE II. Final Positional Parameters and Their Estimated Standard Deviations for $K_2[Pt_2(SO_4)_4(H_2O)_2]$, *(1)*.

Atom	*x*	*y*	*z*
Pt(1)	0.13006(8)	0.45300(8)	0.12154(8)
K(1)	0.2136(6)	0.9574(6)	0.7168(6)
S(1)	0.2312(6)	0.8746(6)	0.1744(6)
S(2)	0.1873(6)	0.4425(6)	−0.2593(5)
O(1)	0.318(1)	0.711(1)	0.210(2)
O(2)	−0.058(2)	0.197(1)	0.031(1)
O(3)	0.381(2)	1.013(2)	0.162(2)
O(4)	0.162(2)	0.942(2)	0.321(2)
O(5)	0.236(2)	0.367(2)	−0.082(2)
O(6)	0.028(2)	0.544(2)	0.324(2)
O(7)	0.319(2)	0.625(2)	−0.209(2)
O(8)	0.190(2)	0.298(2)	−0.413(2)
O(9)	0.351(2)	0.370(2)	0.330(2)

TABLE III. Final Positional Parameters and Their Estimated Standard Deviations for $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, *(2)*.

Atom	*x*	*y*	*z*
Pt(1)	−0.0465(1)	0.0899(1)	0.05039(7)
Pt(2)	0.5922(1)	0.4620(1)	0.44715(6)
P(1)	0.1357(8)	0.3061(8)	−0.1368(5)
P(2)	0.3554(7)	0.1178(8)	0.1062(5)
P(3)	0.8126(7)	0.6297(8)	0.6410(5)
P(4)	0.6039(7)	0.8541(7)	0.4019(5)
Na(1)	−0.114(1)	0.188(1)	−0.4095(8)
Na(2)	0.624(2)	0.370(2)	−0.1349(11)
O(1)	−0.176(2)	−0.136(2)	0.139(1)
O(2)	0.084(2)	0.323(2)	−0.034(1)
O(3)	0.190(2)	0.142(2)	0.143(1)
O(4)	−0.283(2)	0.041(2)	−0.038(1)
O(5)	0.810(2)	0.523(2)	0.555(1)
O(6)	0.386(2)	0.405(2)	0.341(1)
O(7)	0.702(2)	0.724(2)	0.393(1)
O(8)	0.489(2)	0.199(2)	0.502(1)
O(9)	−0.140(2)	0.239(2)	0.136(1)
O(10)	0.743(2)	0.391(2)	0.355(1)
O(11)	−0.033(2)	0.282(2)	−0.215(1)
O(12)	0.302(2)	0.477(2)	−0.166(1)
O(13)	0.470(2)	0.301(2)	0.048(1)
O(14)	0.483(2)	0.088(2)	0.193(1)
O(15)	0.910(2)	0.572(2)	0.731(1)
O(16)	0.913(2)	0.840(2)	0.613(1)
O(17)	0.744(2)	1.052(2)	0.400(1)
O(18)	0.446(2)	0.829(2)	0.319(1)

TABLE IV. Final Positional Parameters and Their Estimated Standard Deviations for $[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$, *(3)*.

Atom	*x*	*y*	*z*
Pt(1)	0.45735(6)	0.09652(6)	0.04928(8)
Cl(1)	0.3735(4)	0.2827(3)	0.1450(5)
P(1)	0.3504(4)	−0.0923(4)	0.2457(5)
P(2)	0.7567(4)	0.1609(4)	0.2091(5)
O(1)	0.444(1)	−0.157(1)	0.132(1)
O(2)	0.631(1)	0.206(1)	0.214(2)
O(3)	0.363(1)	0.037(1)	0.233(1)
O(4)	0.712(1)	0.010(1)	0.118(1)
O(5)	0.381(1)	−0.072(1)	0.434(1)
O(6)	0.812(1)	0.197(1)	0.399(1)
O(7)	0.195(1)	−0.188(1)	0.195(1)
O(8)	0.875(1)	0.231(1)	0.131(1)
O(9)	0.056(2)	0.115(2)	0.073(3)
N(I)	0.746(1)	0.652(1)	0.320(2)
C(1)	0.596(2)	0.634(2)	0.248(2)
C(2)	0.818(2)	0.789(2)	0.451(3)
C(3)	0.723(2)	0.553(2)	0.402(2)
C(4)	0.838(2)	0.631(2)	0.168(3)
C(5)	0.497(2)	0.668(2)	0.387(3)
C(6)	0.832(2)	0.900(2)	0.390(3)
C(7)	0.857(2)	0.542(2)	0.464(3)
C(8)	0.786(3)	0.492(2)	0.034(3)

TABLE V. Selected Bond Distances and Angles[a]

(a) $K_2[Pt_2(SO_4)_4(H_2O)_2]$, *(1)*

Atom	Distance (Å)	Atom	Distance (Å)
Pt(1)–Pt(1)	2.461(1)	S(1)–O(2)	1.527(8)
Pt(1)–O(1)	2.006(8)	S(1)–O(3)	1.436(9)
Pt(1)–O(2)	1.996(7)	S(1)–O(4)	1.429(8)
Pt(1)–O(5)	2.017(8)	S(2)–O(5)	1.521(9)
Pt(1)–O(6)	2.002(8)	S(2)–O(6)	1.524(9)
Pt(1)–O(9)	2.111(7)	S(2)–O(7)	1.428(9)
S(1)–O(1)	1.516(8)	S(2)–O(8)	1.427(8)

(continued overleaf)

TABLE V *(continued)*

Atom	Angle (deg)
Pt(1)–Pt(1)–O(1)	90.6(2)
Pt(1)–Pt(1)–O(2)	89.1(2)
Pt(1)–Pt(1)–O(5)	90.4(2)
Pt(1)–Pt(1)–O(6)	89.4(3)
Pt(1)–Pt(1)–O(9)	179.4(3)

(b) $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, *(2)*

Atom	Distance (Å)	Atom	Distance (Å)
Pt(1)–Pt(1)	2.487(2)	P(1)–O(11)	1.544(13)
Pt(1)–O(1)	2.008(11)	P(1)–O(12)	1.507(12)
Pt(1)–O(2)	2.022(12)	P(2)–O(3)	1.553(15)
Pt(1)–O(3)	2.024(13)	P(2)–O(4)	1.536(15)
Pt(1)–O(4)	2.000(12)	P(2)–O(13)	1.556(12)
Pt(1)–O(9)	2.161(13)	P(2)–O(14)	1.505(13)
Pt(2)–Pt(2)	2.485(1)	P(3)–O(5)	1.541(14)
Pt(2)–O(5)	2.030(12)	P(3)–O(6)	1.533(12)
Pt(2)–O(6)	1.973(12)	P(3)–O(15)	1.490(12)
Pt(2)–O(7)	1.995(10)	P(3)–O(16)	1.562(12)
Pt(2)–O(8)	1.999(10)	P(4)–O(7)	1.562(13)
Pt(2)–O(10)	2.140(13)	P(4)–O(8)	1.538(13)
P(1)–O(1)	1.519(13)	P(4)–O(17)	1.517(12)
P(1)–O(2)	1.559(14)	P(4)–O(18)	1.533(12)

Atom	Angle (deg)
Pt(1)–Pt(1)–O(1)	91.3(4)
Pt(1)–Pt(1)–O(2)	90.6(4)
Pt(1)–Pt(1)–O(3)	90.6(4)
Pt(1)–Pt(1)–O(4)	91.0(4)
Pt(1)–Pt(1)–O(9)	177.5(3)
Pt(2)–Pt(2)–O(5)	90.5(4)
Pt(2)–Pt(2)–O(6)	90.8(4)
Pt(2)–Pt(2)–O(7)	90.8(4)
Pt(2)–Pt(2)–O(8)	90.6(4)
Pt(2)–Pt(2)–O(10)	178.2(3)

(c) $[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$, *(3)*

Atom	Distance (Å)	Atom	Distance (Å)
Pt(1)–Pt(1)	2.529(1)	P(1)–O(5)	1.532(10)
Pt(1)–Cl(1)	2.448(4)	P(1)–O(7)	1.560(11)
Pt(1)–O(1)	2.005(9)	P(2)–O(6)	1.564(10)
Pt(1)–O(2)	2.007(10)	P(2)–O(8)	1.489(10)
Pt(1)–O(3)	1.999(10)	Cl(1)–O(9)	3.10(2)
Pt(1)–O(4)	1.986(10)	O(8)–O(9)	2.57(2)

Atom	Angle (deg)
Pt(1)–Pt(1)–Cl(1)	179.7(1)
Pt(1)–Pt(1)–O(1)	90.4(3)
Pt(1)–Pt(1)–O(2)	90.4(3)
Pt(1)–Pt(1)–O(3)	89.3(3)
Pt(1)–Pt(1)–O(4)	89.6(3)
Cl(1)–O(9)–O(8)	118.9(8)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

$K_2[Pt_2(SO_4)_4(H_2O)_2]$, 1

The structure of the central $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ anion is shown in Fig. 1. The Pt–Pt bond length is 2.461(1) Å. This is not significantly different from the previously reported distance [5] of 2.466 if an esd (not specified in Ref. 5) of 0.001 or 0.002 is assumed for the latter. However, it is significantly different in a statistical sense from the bond distance of 2.471(1) Å reported for $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$ [2].

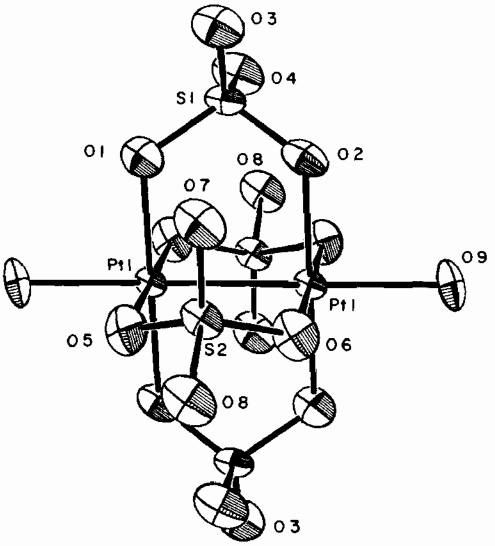

Fig. 1. ORTEP drawing of the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ anion in compound *1*. Thermal ellipsoids are at the 40% probability level.

The Pt–O(SO_4) bonds make angles with the Pt–Pt axis that average 89.9[1]°* and have a mean length of 2.005[4] Å. The axially coordinated oxygen atom of the water molecule is essentially colinear, 179.4(3)°, with the Pt–Pt bond at a bond distance of 2.111(7) Å. In the sulfate groups the average S–O(coord) distance is 1.522[5] Å, whereas the average S=O(terminal) bond length is 1.430[5] Å. This difference, 0.092(7) Å is significant. Each of the sulfur atoms is bent out of the O–Pt–Pt–O plane in the ring to which it belongs and these bends are all in the same rotational sense about the Pt–Pt axis. This effectively reduces the symmetry of the $Pt_2(SO_4)_4$ unit from D_{4h} symmetry to C_{4h} symmetry. The structure of the central $Pt_2(SO_4)_4$ unit, with its C_{4h} symmetry is very similar to the previously reported $[Re_2(SO_4)_4]^{2-}$ [13], $[Mo_2(SO_4)_4]^{4-}$ [14] and $[Mo_2(HPO_4)_4]^{2-}$ [15] groups.

The potassium atoms have a coordination number of 7 with various oxygen atoms. Two of these oxygen

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

atoms are of the kind coordinated to platinum atoms and contact the potassium ion at a mean distance of 2.995[9] Å. The other five contacts are with peripheral sulfate oxygen atoms. Four of these belong to one Pt dimeric unit and they coordinate at a mean distance of 2.926[5] Å. The remaining coordinated peripheral oxygen atom is from a neighboring unit and is coordinated to the potassium ion at a distance of 3.030(9) Å.

$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, *2*

Figures 2 and 3 depict the two independent dinuclear anions in the unit cell. They are essentially identical and show only small random differences from each other. The Pt–Pt bond lengths in the two units are 2.487(2) Å and 2.485(1) Å giving an average bond length 2.486[2] Å. This distance is significantly different in a statistical sense from the 2.461(1) Å seen in the sulfate analogue, compound *1*. However, it is doubtful whether the difference, 0.025(2) Å, is significant chemically.

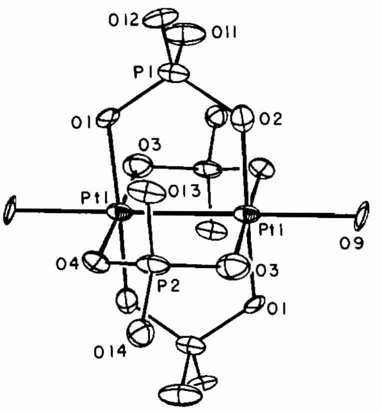

Fig. 2. ORTEP drawing of one of the two crystallographically independent but essentially identical $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ anions in compound *2*. The atoms are represented by thermal ellipsoids scaled to enclose 40% of the electron density.

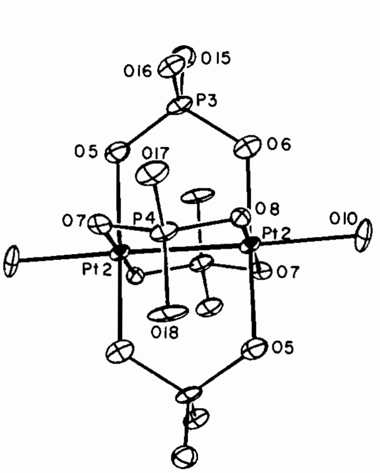

Fig. 3. ORTEP diagram of the second $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion in compound *2*. The thermal ellipsoids of the numbered atoms are at the 40% probability level.

Other important dimensions, chemically averaged over both anions, are Pt–O(phosphate), 2.006[4] Å; Pt–O(H_2O), 2.15[1] Å; P–O(coord), 1.543[5] Å; P=O, 1.505[7] Å; P–OH, 1.549[7] Å; ∠Pt–Pt–O, 90.8[2]°; ∠Pt–Pt–O(H_2O), 177.9[3]°. Each phosphorus atom lies slightly out of the Pt_2O_2 plane and the P=O and P–OH groups alternate cyclicly. Thus the $Pt_2(HPO_4)_4$ unit has C_{4h} symmetry. This arrangement is comparable to the one described previously in compound *1*.

The Na^+ ions reside on general positions in the unit cell. Each is surrounded by a distorted octahedron of oxygen atoms. Figure 4, a stereoview of the unit cell, shows the close non-covalent contacts of oxygen atoms with the sodium ions. These interactions give further evidence that the sodium ions are really sodium ions and not ammonium or hydronium ions. For example, Na(1) subtends an angle of 83° between O(5) (Na(1)–O(5), 2.940(15) Å) and O(11) (Na(1)–O(11), 2.781(17) Å). One would expect larger angles in the case of a central nitrogen or oxygen atom. The Na–O distances range from 2.79(2) to 3.16(2) Å with an average value of 2.96 Å. A summary of all structural parameters relating to hydrogen bonding as well as close sodium to oxygen contact distances is available in a table as supplementary material.

$[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$, *3*

The molecular structure of the diplatinum anion is shown in Fig. 5. The conformation of the $Pt_2(H_2PO_4)_2(HPO_4)_2$ portion is virtually identical to that of the $Pt_2(HPO_4)_4$ portion of compound *2*.

The Pt–Pt bond length in this compound is of interest, because, at 2.529(1) Å, it is significantly greater than the separation of 2.486(2) Å seen in the related aquo species, compound *2*, and greater than that in any other Pt_2^{6+} species with sulfate or phosphate bridging ligands. Table VI lists all the known metal–metal distances for such compounds. The bond length in this compound is close to the Pt–Pt bond length observed in $[Pt_2(NH_3)_4)(C_5H_4NO)_2(NO_3)(H_2O)](NO_3)_3\cdot H_2O$, 2.539(1), a Pt^{6+} compound with only two bridging ligands [7, 8]. Other species containing longer Pt–Pt distances are $[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)]^{2+}$ with a distance of 2.547(1) Å [8], the analog of this ion with NO_2^- groups in place of NO_3^- where the distance is 2.575(1) Å [8], the $[Pt_2(P_2O_5H_2)_4Cl_2]^{4-}$ ion where it is 2.695(1) Å [10] and $Pt_2(O_2CCF_3)_2(CH_3)_4(p\text{-}CH_3C_6H_4N)_2$ where it is 2.557(1) Å [9].

The chlorine atoms in *3* are coordinated axially to the Pt–Pt bond at a distance of 2.448(4) Å (∠Pt–Pt–Cl = 179.7(1)°). The average Pt–O separation is 1.999[6] Å with a mean Pt–Pt–O angle of 89.9[2]°. The Pt_2O_2P unit has the same kind of C_{4h} symmetry

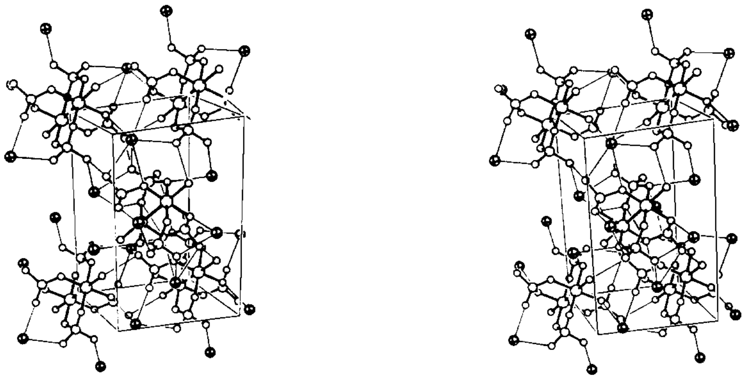

Fig. 4. A stereoview of the unit cell of $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, *2*, showing the molecular packing, extensive hydrogen bonding and copious close non-covalent contacts present in these species.

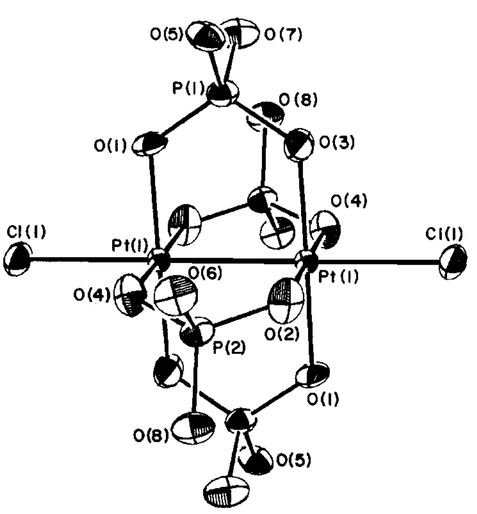

Fig. 5. ORTEP drawing of the $[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]^{2-}$ ion, in compound *3*. The atom numbering scheme is defined and the thermal ellipsoid representations are at the 35% probability level.

TABLE VI. Summary of Pt–Pt Bond Lengths in Pt_2^{6+} Sulfato and Phosphato Compounds.

Compound	Distance (Å)
$K_2[Pt_2(SO_4)_4(H_2O)_2]$[a]	2.461(1)
$K_2[Pt_2(SO_4)_2(OSMe_2)_2]$[b]	2.471(1)
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$[c,a]	2.486(2)
$(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]\cdot H_2O$[d]	2.494(1)
$(DMPyH)_2[Pt_2(HPO_4)_4(DMPy)_2]$[e]	2.494(1)
$[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$[a]	2.529(1)

[a]This work. [b]Ref. 2. [c]Ref. 1. [d]Ref. 3. [e]Ref. 4.

seen before. It is not clear why the Pt–Pt distance is longer in this compound than in other sulfate and phosphate bridged species.

Our identification of two of the phosphate bridges as $H_2PO_4^{1-}$ groups has the following structural support. In the phosphate group containing P(2) we can differentiate between P–OH and P=O bonds, with lengths of 1.564(10) Å and 1.489(10) Å, respectively. The difference, 0.075(14) Å, is statistically significant and leads us to the conclusion that two bridging groups containing P(2) and P(2)′ atoms are HPO_4^{2-}. However, the distances are 1.532(10) Å and 1.560(11) Å in the other groups; the difference is only 0.028(15) Å, and both are close to the expected P–OH value. The difference between the two is not significant at the 3σ level. Previous examples of the differentiation between P=O and P–OH groups in compounds of this type are provided by compound *2* of this paper where these distances are, respectively, 1.505(6) Å and 1.549(6) Å (a difference of only 0.044(8) Å), the $[Pt_2(HPO_4)_4DMPy_2]^{2-}$ ion [4] where the distances of 1.489(12) Å and 1.565(11) Å give a difference of 0.076(15) Å and the $[Pt_2(H_2PO_4)(HPO_4)_3py_2]^-$ ion [3] where two crystallographically independent HPO_4^{2-} ions have distances of 1.494(14) Å and 1.555(12) Å ($\Delta = 0.061(18)$ Å), and 1.478(13) Å and 1.553(13) Å ($\Delta = 0.075(18)$ Å). The averages of all previous P=O and P–OH distances in these compounds are 1.492 Å and 1.556 Å. Comparisons between these average values and the distances found in structure *3* support our $Pt_2(H_2PO_4)_2(HPO_4)_2$ formulation.

Only two cationic tetraethylammonium groups are present in the lattice, and there is no indication of any other cation. If the anionic unit contained four HPO_4^{2-} groups then the overall positive charge falls two short. The possibility that the solvent water molecule O(9) is actually part of a hydronium cation is not attractive since O(9) forms only two hydrogen bonds, one with O(8) at 2.57(2) Å and one with the chlorine atom at 3.10(2) Å. We conclude that this compound is $[Et_4N]_2[Pt(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$, even though hydrogen atoms attached to the phosphate groups are not directly observed.

With regard to the occurrence of $H_2PO_4^-$ ions as bridges in structures of this type, there are now three examples, *viz.*, the $[Pt_2(H_2PO_4)(HPO_4)_3py_2]^-$ ion [3], the $[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]^{2-}$ ion, reported here and the $Rh_2(H_2PO_4)_4(H_2O)_2]$ molecule whose structure was recently reported by Porai-Koshits *et al.* [16].

Acknowledgement

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Supplementary Material Available

Tables of structure factors, bond lengths and angles, thermal parameters and root-mean-square amplitudes for all three compounds, and a summary of close non-covalent contacts for compound *2* (59 pages).

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