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Dinuclear, Metal–Metal-Bonded Platinum(III) Compounds. 2. Synthesis and Properties of Complexes Containing the [Pt₂(HPO₄)₄(B)₂]²⁻ Anions (B = a Heterocyclic Tertiary Amine) or the [Pt₂(H₂PO₄)(HPO₄)₃(py)₂]⁻ Ion

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The reactions of phosphoric acid solutions containing the diplatinum(III) anion [Pt$_2$(HPO$_4$)$_4$]$^{2-}$ with heterocyclic tertiary amines afford yellow complexes of stoichiometry (BH)$_2$[Pt$_2$(HPO$_4$)$_4$(B)$_2$], where B = pyridine, 4-methylpyridine, or 3,4-dimethylpyridine. These products are probably contaminated with small amounts of the mixed salts (BH)[Pt$_2$(H$_2$P-O$_4$)(HPO$_4$)$_3$(B)$_2$]·H$_2$O, a complex of this type apparently being the principal product when 4-phenylpyridine is used as the nitrogen base. During attempts to grow suitable crystals of the pyridine (py)-containing complex (pyH)$_2$[Pt$_2$(HPO$_4$)$_4$(py)$_2$], we instead isolated (pyH)[Pt$_2$(H$_2$PO$_4$)(HPO$_4$)$_3$(py)$_2$]·H$_2$O, the identity of which was determined by an X-ray structure analysis. The crystals are orthorhombic, and the structure was solved and refined in space group $Pc2_1n$ (a nonstandard setting of $Pna2_1$). The unit cell dimensions are as follows: a = 8.460 (2) Å; b = 16.476 (6) Å; c = 19.466 (6) Å; V = 2713 (2) Å^3; Z = 4. The structure was refined to R = 0.031 and R_w = 0.039. The Pt–Pt distance is 2.494 (1) Å, the mean Pt–O(coord) distance is 2.004 [4] Å, and the mean P–O(coord) distance is 1.528 [4] Å. The Pt–N distances are 2.11 (2) and 2.18 (1) Å, with the py planes being almost perpendicular to each other and staggered with respect to the Pt–O bonds. The water molecule is loosely hydrogen bonded to the [Pt$_2$(H$_2$PO$_4$)(HPO$_4$)$_3$(py)$_2$] ion. The pattern of P–O distances, the occurrence of hydrogen-bonded O···O contacts, and the chemical analysis are all consistent with the formulation of this compound. Preliminary studies of the reaction of (pyH)$_2$[Pt$_2$(HPO$_4$)$_4$(py)$_2$] with triphenylphosphine and *tert*-butyl isocyanide have been carried out. Mononuclear products such as Pt(PPh$_3$)$_2$(O$_2$CCH$_3$)$_2$ (formed in glacial acetic acid) and Pt(CN-t-Bu)$_2$(CN)$_2$ attest to the relative ease with which reductive cleavage of the Pt–Pt bond occurs.

Introduction

Dimetal species having metal–metal single bonds based upon the electron-rich $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ or $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configuration are especially prevalent in rhodium(II) chemistry, the dirhodium(II) acetate complex Rh$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$ being the best known example.[2] Recent evidence attests to the existence of isoelectronic singly bonded species in the chemistry of diplatinum(III), of which the α-pyridone-bridged species [X-(NH$_3$)$_2$Pt(C$_5$H$_4$NO)$_2$Pt(NH$_3$)$_2$X]$^{2+}$ (X = NO$_2$ or NO$_3$),[3,4] the trifluoroacetate-bridged complex (*p*-CH$_3$C$_5$H$_4$N)$_2$Pt$_2$-(CH$_3$)$_4$(O$_2$CCF$_3$)$_2$,[5] and the sulfate-bridged complex K$_2$-[Pt$_2$(SO$_4$)$_4$(H$_2$O)$_2$][6] and its dimethyl sulfoxide adduct K$_2$-[Pt$_2$(SO$_4$)$_4$(Me$_2$SO)$_2$]·4H$_2$O[7] constitute the majority of structurally characterized examples.

A recent report describing the synthesis of a complex purported to be "(NH$_4$)$_2${(H)$_4$[Pt$_2$(PO$_4$)$_4$(H$_2$O)$_2$]}", and several derivatives thereof,[8] prompted further investigations of this and related materials in both of these laboratories with a view

to using them as starting materials for the synthesis of other diplatinum(III) species. As already reported, it has been possible to obtain an accurate structure determination of the sodium salt Na$_2$[Pt$_2$(HPO$_4$)$_4$(H$_2$O)$_2$],[9] thereby establishing the true identity of the [Pt$_2$(HPO$_4$)$_4$(H$_2$O)$_2$]$^{2-}$ unit. In a continuation of our efforts to develop and expand the useful chemistry of diplatinum(III) species, we have carried out a collaborative study into further aspects of the chemistry of salts containing the [Pt$_2$(HPO$_4$)$_4$]$^{2-}$ anion. Details of this work are reported herein and include the isolation and structural characterization of the novel complex (pyH)[Pt$_2$(H$_2$PO$_4$)-(HPO$_4$)$_3$(py)$_2$]·H$_2$O.

Experimental Section

Materials. All solvents and reagents were reagent grade unless specified otherwise. *cis*- and *trans*-Pt(NH$_3$)$_2$(NO$_2$)$_2$,[10] *tert*-butyl isocyanide,[11] (NH$_4$)$_2$[Pt$_2$(HPO$_4$)$_4$(H$_2$O)$_2$],[8] and (NH$_4$)$_2$[Pt$_2$(SO$_4$)$_4$-(H$_2$O)$_2$][6] were prepared by standard literature methods.

Reaction Procedures. Unless otherwise stated, all reactions were carried out with use of a mineral oil bubbler vented in an efficient fume hood. Reactions involving phosphines and *tert*-butyl isocyanide were carried out under an inert nitrogen atmosphere.

Preparation of (NH$_4$)$_2$[Pt$_2$(SO$_4$)$_4$(H$_2$O)$_2$] from (NH$_4$)$_2$[Pt$_2$(HP-O$_4$)$_4$(H$_2$O)$_2$]. A suspension of 0.10 g of (NH$_4$)$_2$[Pt$_2$(HPO$_4$)$_4$(H$_2$O)$_2$] in 10 mL of a 1:1 concentrated sulfuric acid–water mixture was heated to 100–110 °C for 2 h, during which time a deep red solution formed.

(1) (a) Purdue University. (b) Texas A&M University.
(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapter 7.
(3) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761.
(4) Hollis, L. A.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 2117.
(5) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.
(6) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR* **1976**, *226*, 76.
(7) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 2889.
(8) Muraveiskaya, G. S.; Abashkin, V. E.; Evstaf'eva, O. N.; Golovaneva, I. F.; Shchelokov, R. N. *Sov. J. Coord. Chem. (Engl. Transl.)* **1980**, *6*, 218.

(9) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709.
(10) "Handbuch der Präparativen Anorganischen Chemie"; Verlag Chemie: Stuttgart, 1981; Vol. 3, pp 1720–1725.
(11) Weber, W. P.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

A solution of 0.10 g of $(NH_4)_2SO_4$ in 20 mL of water was added and the mixture cooled in a refrigerator to yield a yellow solid (60% yield) whose spectral properties were identical with those exhibited by a sample of $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ prepared by the usual literature method.[6]

Preparation of Complexes of the Type $(BH)_2[Pt_2(HPO_4)_4(B)_2]$. A suspension of 0.25 g of *cis*- or *trans*-$Pt(NH_3)_2(NO_2)_2$ in 3–5 mL of phosphoric acid was heated at 110–120 °C until NO gas evolution ceased and a deep red brown solution resulted (usually 2 h). The hot reaction mixture was filtered to remove any insoluble material and added to a solution containing a 20-fold molar excess of base in 30 mL of absolute methyl alcohol. When it stood overnight in the refrigerator, this solution deposited a bright yellow precipitate. Anal. Calcd for $C_{20}H_{26}N_4O_{16}P_4Pt_2$ (B = pyridine; yield 54%): C, 21.99; H, 2.40. Found: C, 21.43; H, 2.47. Calcd for $C_{24}H_{34}N_4O_{16}P_4Pt_2$ (B = 4-methylpyridine; yield 35%): C, 25.09; H, 2.98. Found: C, 23.98; H, 3.17. Calcd for $C_{28}H_{42}N_4O_{16}P_4Pt_2$ (B = 3,4-dimethylpyridine; yield 58%): C, 27.92; H, 3.51. Found: C, 26.82; H, 3.84.

In the case of the reaction with 4-phenylpyridine, the bright yellow solid (yield 25%) had a stoichiometry that most closely approached that of (4-PhpyH)("H⁺")$[Pt_2(HPO_4)_4(4-Phpy)_2]·H_2O$. Anal. Calcd for $C_{33}H_{35}N_3O_{17}P_4Pt_2$: C, 31.46; H, 2.80. Found: C, 31.67; H, 3.08.

Reactions of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$. The following reactions were carried out under a N_2 atmosphere.

(i) Triphenylphosphine in Water. A suspension of 0.25 g of PPh_3 in 10 mL of water containing 0.10 g of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ was refluxed for 3 h. The heterogeneous reaction mixture when cooled yielded an orange solid. The solution was decanted and discarded, and the remaining orange solid was broken up and washed with several 30-mL portions of acetone and then recrystallized from approximately 250 mL of boiling methyl alcohol to yield a microcrystalline orange product that analysis showed to be $Pt_2(HPO_4)_3(PPh_3)_2(H_2O)_2$, yield 85%. Anal. Calcd for $C_{36}H_{37}O_{14}P_5Pt_2$: C, 34.90; H, 3.01. Found: C, 35.10; H, 3.20.

(ii) Triphenylphosphine in Acetic Acid. A mixture of 0.10 g of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ and 0.25 g of PPh_3 was refluxed for 30 min in 15 mL of glacial acetic acid, during which time an orange solid and an orange solution formed. The reaction mixture was cooled, and a quantity of the orange complex $Pt_2(HPO_4)_3(PPh_3)_2(H_2O)_2$ (25–30% yield) was filtered off. The filtrate was poured into 150 mL of distilled water and allowed to stand overnight. The resulting pale yellow solid was filtered off and washed with several 30-mL portions of diethyl ether to remove any unreacted PPh_3. The residue was recrystallized from methylene chloride–diethyl ether to give white crystals of $Pt(PPh_3)_2(O_2CCH_3)_2$.[12] Anal. Calcd for $C_{40}H_{36}O_4P_2Pt$: C, 57.35; H, 4.33. Found: C, 57.38; H, 4.33. If the initial reaction mixture is refluxed for 3 h instead of 30 min, then the yield of $Pt(PPh_3)_2(O_2CCH_3)_2$ increases to 80%.

(iii) *tert*-Butyl Isocyanide. A suspension of 0.20 g of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ in a solution of 1.0 mL of *tert*-butyl isocyanide in 5 mL of absolute methyl alcohol was refluxed until all the solid dissolved (~1 h). The reaction mixture was poured directly into 150 mL of diethyl ether. An immediate lemon yellow precipitate formed and was allowed to stand overnight. Recrystallization from methylene chloride–acetone afforded fluorescent yellow needles of $Pt(CN-t-Bu)_2(CN)_2$.[13,14] Anal. Calcd for $C_{12}H_{18}N_4Pt$: C, 34.87; H, 4.39; M_r, 413.4. Found: C, 35.20; H, 4.67; M_r (in CH_2Cl_2), 438.0. NMR (¹H, CD_2Cl_2): δ 1.60. IR: ν_{max} (in Nujol) 2266 s, 2244 s, 2166 ms cm⁻¹; ν_{max} (in CH_2Cl_2) 2256 s, 2235 s, 2164 m cm⁻¹.

Preparation of Single Crystals of $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]·H_2O$. After the isolation of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ the filtrate was allowed to stand for several days. Large crystals (linear dimensions of 1–3 mm) and clusters of crystals were thereby obtained. These were similar in color to that of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ and were initially assumed to have that composition. When X-ray crystallography revealed the presence of only one pyH⁺ ion, a chemical analysis was obtained. Anal. Calcd for $C_{15}H_{23}N_3O_{17}P_4Pt_2$: C, 17.47; H, 2.25; N, 4.07. Found: C, 17.40; H, 2.37; N, 4.08.

X-ray Crystallography. A large crystal of the compound was cut to a size of 0.5 × 0.4 × 0.3 mm and mounted on a glass fiber with epoxy cement. A Syntex P1 four-circle diffractometer equipped with

Table I. Crystallographic Data

formula	$(C_5H_6N)[Pt_2(H_2PO_4)-(HPO_4)_3(C_5H_5N)_2]·H_2O$
fw	1031.43
space group	$Pc2_1n$
a, Å	8.460 (2)
b, Å	16.476 (6)
c, Å	19.466 (6)
α, deg	90.0
β, deg	90.0
γ, deg	90.0
V, Å³	2713 (2)
Z	4
d_{calcd}, g/cm³	2.52
cryst size, mm	0.5 × 0.4 × 0.3
μ(Mo Kα), cm⁻¹	107.7
data collection instrument	P1 Syntex
radiation	Mo Kα
scan method	θ–2θ
data collection range, deg	2–25, θ
no. of unique data	2759
no. of data with $F_o^2 \geqslant 3\sigma(F_o^2)$	2103
no. of parameters refined	369
R^a	0.031
R_w^b	0.039
quality-of-fit indicator^c	0.953
largest shift/esd, final cycle	0.05

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

graphite-monochromated Mo Kα (λ_α = 0.71073 Å) radiation was used to collect 2759 reflections, of which 2103 had $I > 3\sigma(I)$. Lorentz, polarization, and absorption corrections were applied.

The systematic absences, namely, $hk0$ with $h + k = 2n$ and $0kl$ with $l = 2n$, were indicative of the space groups $Pc2_1n$ or $Pcmn$, which are equivalent to the *bca* setting of space group $Pna2_1$ and the $\bar{c}ba$ setting of $Pnma$, respectively.[15] The heavy-atom position was determined from a Patterson synthesis, and refinement was successful in the acentric group $Pc2_1n$. Subsequent difference Fourier maps revealed the remaining non-hydrogen atoms, and full-matrix least-squares refinement converged to final residuals of R = 0.031 and R_w = 0.039. Expressions for R and R_w and other pertinent crystallographic data are given in Table I. The final difference map contained four peaks between 1.00 and 1.66 e/Å³—all ghosts of the platinum atoms—which can be attributed partly to series termination and partly to strong and anisotropic absorption. A few of the thermal ellipsoids also showed a higher degree of anisotropy than expected, again indicating some residual effects of absorption. Refinement of the enantiomorph resulted in values of R = 0.038 and R_w = 0.050 at convergence.[16] A table of structure factor amplitudes is available as supplementary material.

Physical Measurements. Infrared spectra (4000–400 cm⁻¹) were recorded on Beckman IR-12 and Acculab 6 spectrophotometers. Nuclear magnetic resonance spectra were recorded in methylene chloride-d_2 with tetramethylsilane (Me₄Si) as an internal reference by a Perkin-Elmer R-32 90-MHz NMR spectrometer. A Varian 634 spectrophotometer was used to obtain the UV–vis spectra at 25 °C with water as solvent.

Elemental microanalyses were performed by Drs. C. S. Yeh and H. D. Lee of the Purdue University microanalytical laboratory and by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

Synthesis and Preliminary Characterization of Salts Containing the $[Pt_2(HPO_4)_4]^{2-}$ Unit. Our initial hope of studying the reaction chemistry of the singly bonded diplatinum species $[Pt_2(HPO_4)_4]^{2-}$ was restricted by the low yields and poor solubility in suitable solvents of the known complex $(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$.[8] However, we were able readily to

(12) Dobson, A.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1977**, *17*, 130.
(13) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 913.
(14) Solutions of $Pt(CN-t-Bu)_2(CN)_2$ were found to be colorless at all concentrations.

(15) Henry, N. F. M., Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. I.
(16) All calculations were performed with the Enraf-Nonius Structure Determination Package on the PDP 11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX.

Table II. Electronic Absorption Spectra of
$(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$ and Complexes of the Type
$(BH)_2[Pt_2(HPO_4)_4(B)_2]$

compd	λ_{max}, nm (ϵ)
$(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$[a]	500 (170), 390 (1740), 295 (2350)
$(pyH)_2[Pt_2(HPO_4)_4(py)_2]$	~350 sh, 330 (3150), 293 (9150)
$(4\text{-MepyH})_2[Pt_2(HPO_4)_4(4\text{-Mepy})_2]$	~350 sh, 330 (2840), 293 (9190)
$(3,4\text{-DiMepyH})_2[Pt_2(HPO_4)_4(3,4\text{-DiMepy})_2]$	~360 sh, 330 (2700), 293 (10 000)

[a] Data reported in ref 8 for this complex are as follows: 500 (93), 403 (1140), 333 nm (840).

Figure 1. ORTEP drawing of the $[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]^-$ anion. Thermal ellipsoid representations of the numbered atoms are at the 50% probability level.

convert the $[Pt_2(HPO_4)_4]^{2-}$ core into $[Pt_2(SO_4)_4]^{2-}$ by reaction of this salt with concentrated sulfuric acid at 110 °C. The product had spectroscopic properties identical with those exhibited by an authentic sample of $(NH_4)_2[Pt_2(SO_4)_4 \cdot 2H_2O]$ prepared by reaction of $Pt(NH_3)_2(NO_2)_2$ with concentrated sulfuric acid.[6] This led us to hope that the phosphate bridges could be replaced by other ligands if we could first prepare a more soluble starting complex.

In an effort to obtain more soluble salts of the $[Pt_2-(HPO_4)_4]^{2-}$ anion, we attempted to synthesize complexes of the type $(BH)_2[Pt_2(HPO_4)_4(B)_2]$, where B represents a heterocyclic tertiary amine. The reaction of methanol solutions of pyridine (py), 4-methylpyridine (4-Mepy), and 3,4-dimethylpyridine (3,4-DiMepy) with deep brown phosphoric acid solutions containing $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ afforded bright yellow precipitates of what, on the basis of microanalytical data and IR spectroscopy, were compounds for which the formulation $(BH)_2[Pt_2(HPO_4)_4(B)_2]$ seemed most appropriate.

These complexes were obtained as yellow air-stable crystalline materials that were slightly soluble in hot water but, as far as we could tell, insoluble in common organic solvents. Their IR spectra in the region 1200–800 cm^{-1} were very similar, regardless of the pyridine-type base used, and each showed phosphate vibrations that agreed extremely well with IR data for the corresponding ammonium salt $(NH_4)_2[Pt_2(HPO_4)_4-(H_2O)_2]$.[8]

The implication from both IR spectroscopy and the microanalytical data that the pyridine ligands are bound in the axial positions of the dinuclear complex anion (i.e., occupying the same positions that the water molecules do in the salt $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$[9]) is supported by the electronic absorption spectra of these three complexes (Table II). In spite of the absence of any definitive assignments for these transitions, we can draw two important conclusions. First, the spectra of all three complexes of the type $(BH)_2[Pt_2(HPO_4)_4(B)_2]$ are so similar as to imply an essential identity of structure. Second, the spectra are sufficiently different from that of the hydrated anion $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ that coordination of pyridine ligands in place of H_2O can be reasonably predicted.

One additional feature of note concerns the microanalytical data for these complexes. In all cases, the C microanalyses are low and the H analyses high for the formulation $(BH)_2-[Pt_2(HPO_4)_4(B)_2]$. Possible explanations for this are (1) the presence of water of hydration and (2) the presence of *small amounts* of $(BH)[Pt_2(H_2PO_4)(HPO_4)_3(B)_2] \cdot H_2O$ or $(BH)_2-[Pt_2(HPO_4)_4(B)(H_2O)]$ in the bulk materials. These possibilities would be extremely difficult to distinguish by spectroscopic means, but we note that, in the IR spectra of these three complexes, bands associated with $\nu(O-H)$ and $\delta(O-H)$ modes are present at ~3400 w, br, 2400–2200 w, br, and 1710 mw, br cm^{-1}. The 1700-cm^{-1} band could reasonably be assigned to $\delta(O-H)$ of H_2O. In support of possibility 2, we note
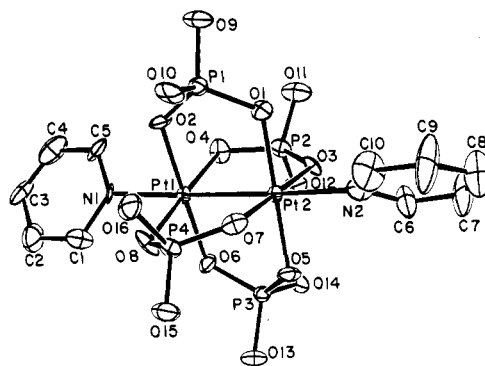
that, when we attempted to isolate the 4-phenylpyridine complex $(4\text{-PhpyH})_2[Pt_2(HPO_4)_4(4\text{-Phpy})_2]$, we instead isolated a material that gave analytical results close to those for $(4\text{-PhpyH})[Pt_2(H_2PO_4)(HPO_4)_3(4\text{-Phpy})_2] \cdot H_2O$ or $(4\text{-PhpyH})_2[Pt_2(HPO_4)_4(4\text{-Phpy})(H_2O)]$. While this complex is extremely insoluble in all organic solvents, thereby hindering its characterization, we were able to measure the electronic absorption spectrum of a very dilute aqueous solution. This spectrum is, as far as we can tell, very similar to those of other complexes that contain $[Pt_2(HPO_4)_4(B)_2]^{2-}$ anions (see Table II), displaying λ_{max} at ca. 340 sh and 290 nm. This is consistent with either of the above formulations.

More conclusive information became available during our attempts to grow crystals of these complexes for an X-ray crystallographic structure analysis. None of these complexes readily form crystals of sufficient size for X-ray work. However, we were eventually successful in growing a few large crystals from the reaction solution that afforded $(pyH)_2-[Pt_2(HPO_4)_4(py)_2]$ as the bulk material. However, these crystals proved not to be this particular complex but rather a compound we formulate as $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3-(py)_2] \cdot H_2O$, for reasons given below. Its isolation and characterization support the view that it and its analogues containing substituted pyridines are the principal contaminants present in $(BH)_2[Pt_2(HPO_4)_4(B)_2]$, where B = py, 4-Mepy, or 3,4-DiMepy.

Structure and Formulation of $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3-(py)_2] \cdot H_2O$. The final atomic coordinates for the 41 non-hydrogen atoms are listed in Table III. Tables IV and V list selected bond distances and angles, and Figure 1 illustrates the $[Pt_2(H_2PO_4)(HPO_4)_3]^-$ anion.

The Pt–Pt bond at 2.494 (1) Å is not significantly different from the 2.486 (2) Å separation in the related compound $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$.[3] Other chemically equivalent averaged dimensions[17] are as follows: Pt–O(coord), 2.004 [4] Å,[4] P–O(coord), 1.528 [4] Å; Pt–Pt–O, 89.8 [1]°; Pt–Pt–N, 177.5 [4]°. The phosphorus atom lies slightly out of the plane in each of the five-membered Pt–O–P–O–Pt rings, and these bends are all in the same rotational sense about the Pt–Pt bond. The $Pt_2O_8P_4$ unit, therefore, has essentially C_{4h} symmetry and resembles the comparable portions of the similar compounds $Mo_2(HPO_4)_4$[18] and $Pt_2(HPO_4)_4$.[9]

Two pyridine molecules are coordinated to the axial positions of the anion at distances of 2.179 (13) and 2.11 (2) Å. The

(17) A number in parentheses is an esd for a given individual value while a number in brackets is equal to

$$[\textstyle\sum_n \Delta_i^2 / n(n-1)]^{1/2}$$

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.

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

Table III. Final Positional Parameters (with Esd's)

atom	x	y	z
Pt(1)	0.03140 (6)	0.000	0.11560 (2)
Pt(2)	0.02594 (5)	−0.06584 (5)	0.00028 (3)
P(1)	−0.1384 (5)	0.1005 (2)	0.0016 (2)
P(2)	−0.2411 (5)	−0.1239 (3)	0.0985 (2)
P(3)	0.1921 (4)	−0.1689 (2)	0.1102 (2)
P(4)	0.2998 (4)	0.0580 (3)	0.0177 (2)
O(1)	−0.132 (1)	0.0155 (6)	−0.0318 (5)
O(2)	−0.084 (1)	0.0960 (6)	0.0764 (5)
O(3)	−0.154 (1)	−0.1368 (6)	0.0321 (5)
O(4)	−0.179 (1)	−0.0509 (6)	0.1390 (5)
O(5)	0.183 (1)	−0.1468 (6)	0.0332 (5)
O(6)	0.142 (1)	−0.0959 (6)	0.1546 (5)
O(7)	0.204 (1)	0.0057 (7)	−0.0307 (4)
O(8)	0.241 (1)	0.0488 (7)	0.0913 (5)
O(9)	−0.308 (1)	0.1329 (7)	−0.0039 (6)
O(10)	−0.028 (1)	0.1613 (7)	−0.0354 (7)
O(11)	−0.415 (1)	−0.1161 (7)	0.0873 (6)
O(12)	−0.214 (1)	−0.2000 (6)	0.1443 (5)
O(13)	0.362 (1)	−0.1975 (7)	0.1280 (5)
O(14)	0.086 (1)	−0.2404 (6)	0.1274 (5)
O(15)	0.471 (1)	0.0404 (8)	0.0131 (7)
O(16)	0.278 (1)	0.1476 (7)	−0.0049 (6)
O(17)	0.963 (2)	0.051 (1)	0.6746 (8)
N(1)	0.027 (1)	0.0575 (7)	0.2164 (6)
N(2)	0.009 (2)	−0.123 (1)	−0.0964 (7)
N(3)	0.021 (2)	0.372 (1)	0.5592 (8)
C(1)	0.163 (2)	0.061 (1)	0.2528 (9)
C(2)	0.167 (3)	0.101 (1)	0.3160 (9)
C(3)	0.027 (2)	0.130 (1)	0.3439 (8)
C(4)	−0.107 (2)	0.123 (1)	0.3068 (9)
C(5)	−0.106 (2)	0.0875 (8)	0.2412 (9)
C(6)	−0.028 (2)	−0.202 (1)	−0.0995 (9)
C(7)	−0.053 (3)	−0.237 (1)	−0.162 (1)
C(8)	−0.039 (3)	−0.196 (2)	−0.223 (1)
C(9)	0.010 (4)	−0.117 (2)	−0.218 (1)
C(10)	0.031 (2)	−0.081 (1)	−0.1565 (9)
C(11)	−0.043 (3)	0.291 (1)	0.564 (1)
C(12)	−0.065 (3)	0.263 (1)	0.624 (1)
C(13)	−0.027 (4)	0.301 (2)	0.678 (2)
C(14)	0.053 (4)	0.377 (2)	0.677 (1)
C(15)	0.065 (3)	0.413 (2)	0.613 (1)

Table IV. Selected Bond Distances (Å)[a]

Pt(1)–Pt(2)	2.494 (1)	P(2)–O(3)	1.505 (12)
–O(2)	2.011 (10)	–O(4)	1.529 (12)
–O(4)	2.023 (10)	–O(11)	1.494 (14)
–O(6)	1.988 (10)	–O(12)	1.555 (12)
–O(8)	2.004 (11)	P(3)–O(5)	1.544 (11)
–N(1)	2.179 (13)	–O(6)	1.540 (11)
Pt(2)–O(1)	1.994 (10)	–O(13)	1.549 (12)
–O(3)	2.016 (11)	P(3)–O(14)	1.520 (11)
–O(5)	1.989 (11)	P(4)–O(7)	1.512 (13)
–O(7)	2.006 (11)	–O(8)	1.523 (11)
–N(2)	2.11 (2)	–O(15)	1.478 (13)
P(1)–O(1)	1.545 (12)	–O(16)	1.553 (13)
–O(2)	1.528 (12)	O(17)–O(4)	3.02 (2)
–O(9)	1.532 (13)	–O(8)	2.98 (2)
–O(10)	1.550 (13)	–O(15)	3.20 (2)

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

Table V. Selected Bond Angles (deg)[a]

Pt(1)–Pt(2)–O(1)	90.1 (3)	Pt(2)–Pt(1)–O(2)	89.5 (3)
–O(3)	89.4 (3)	–O(4)	90.3 (3)
–O(5)	89.4 (3)	–O(6)	90.4 (3)
–O(7)	90.1 (3)	–O(8)	88.8 (3)
–N(2)	176.9 (4)	–N(1)	178.1 (4)

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

pyridine ring planes make a dihedral angle to each other along the Pt–Pt bond of 87.9°. It is interesting to compare this value and arrangement of the rings with the 58.9° angle observed
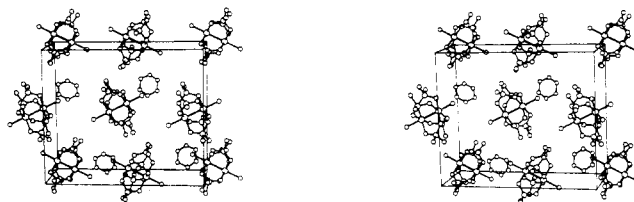

Figure 2. ORTEP stereoview plot of $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]$. The carbon atoms of the axial pyridine groups have been omitted for clarity.
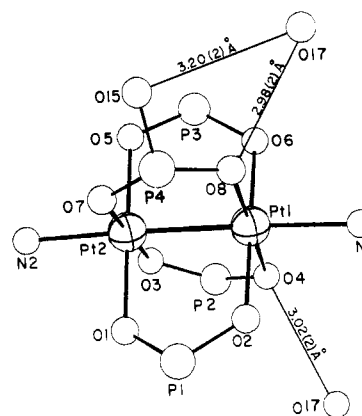

Figure 3. ORTEP plot showing the relationship of the water oxygen atom, O(17), to the diplatinum anion. Various peripheral phosphate oxygen atoms have been omitted for clarity.

in $Rh_2(OOCCH_3)_4(py)_2$[19] and the nearly coplanar relationship in $Mo_2(OOCCF_3)_4(py)_2$.[20]

We now turn to the formulation, including correct charge assignments, of this compound, where a problem arises from the inability of X-ray diffraction to locate hydrogen atoms in a structure such as this. The microanalytical data for the compound obtained as the first and major product of the reaction were in agreement with the formula $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$. However, the crystal structure determination revealed at an early stage only one pyridinium cation (as illustrated in the stereoview of Figure 2). This leaves the central question of whether the platinum dimer anion charge is 2− or 1−. We consider first the former.

If the anion has a charge of 2−, then the lone oxygen atom found in the lattice, O(17), must belong to a hydronium cation. Figure 3 shows the hydrogen-bonding scheme of O(17). This oxygen atom is located between two diplatinum units and forms contacts with coordination sphere oxygen atoms O(4) and O(8) of different dimers at distances of 3.02 (2) and 2.98 (2) Å, with an O(4)–O(17)–O(8) angle of 122.3°. The next nearest contact made by O(17) is with a peripheral oxygen atom, O(15), at 3.20 (2) Å. This distance is not indicative of a hydrogen bond at all, and even the other two O(17) to oxygen distances are much longer than would be expected (2.4–2.6 Å[21]) for hydrogen bonds formed by an H_3O^+ ion. We thus conclude with confidence that oxygen atom O(17) represents a water molecule. The diplatinum anion, therefore, has a charge of 1−.

At this juncture there are two possibilities. (1) All the bridging bidentate ligands are HPO_4^{2-} groups (as in the previously studied $[Pt_2(HPO_4)_4]^{2-}$ and $[Mo_2(HPO_4)_4]^{2-}$ ions[9,18]) and the platinum atoms each have a mean oxidation number of $+3^1/_2$. (2) One of the bridging bidentate groups is a $H_2PO_4^-$ ion and the platinum atoms both have an oxidation number

(19) Koh, Y. B.; Christoph, G. G. *Inorg. Chem.* **1978**, *17*, 2590.
(20) Cotton, F. A.; Norman, J. G., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5697.
(21) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

Table VI. Short Oxygen–Oxygen Contacts (A) Indicative of Hydrogen Bonding

Intermolecular Contacts			
O(9)(P–OH)– O(15)(P=O)	2.439 (18)	O(11)(P=O)– O(13)(P–OH)	2.447 (17)
O(10)(P–OH)– O(14)(P=O)	2.465 (18)		

Intramolecular Contacts			
O(10)–O(16)	2.660 (18)	O(12)–O(14)	2.644 (16)

of +3. We now present the reasons why we conclude that the second possibility is the correct one.

To begin with, the presence of a Pt_2^{7+} group is unlikely because the Pt–Pt bond length here, 2.494 (1) Å, is very similar to those in the three structurally characterized Pt_2^{6+} compounds with fourfold symmetry: $K_2[Pt_2(SO_4)_4(H_2O)_2]$, 2.466 (?) Å;[8] $K_2[Pt(SO_4)_4(Me_2SO)_2]\cdot4H_2O$, 2.471 (1) Å;[7] Na_2-$[Pt_2(HPO_4)_4(H_2O)_2]$, 2.486 (2) Å.[9] In the case of the isoelectronic dirhodium compounds, a loss of one electron to go from the $[Rh_2(O_2CCH_3)_4(H_2O)_2]$ molecule to the $[Rh_2$-$(O_2CCH_3)_4(H_2O)_2]^+$ ion results in a 0.07-Å decrease in the bond length, since an antibonding electron is being removed.[2,22]

On the other hand, the pattern of peripheral P–O distances and the occurrence of O···O contacts sufficiently short to indicate hydrogen bonding (Table VI) are fully consistent with the occurrence of one $H_2PO_4^-$ ligand along with three of the familiar HPO_4^{2-} ones. In the P(2) and P(4) phosphate ions the outer P–O distances correspond well with the expected P=O and P–OH groups, the former distances being 1.494 (14) and 1.478 (13) Å and the latter 1.555 (12) and 1.553 (13) Å. Moreover, O(12)–H is hydrogen bonded to O(14) and O-(16)–H is hydrogen bonded to O(10), the respective O···O distances being 2.64 (2) and 2.66 (2) Å.

In the other two phosphate groups the outer P–O bond lengths range only from 1.520 (11) to 1.550 (13) Å, and each of these four oxygen atoms is strongly hydrogen bonded to an oxygen atom in a neighboring molecule. The three hydrogen atoms still to be assigned to P–OH groups in the $Pt_2(H_2P-O_4)(HPO_4)_3$ unit can then be placed on three of the four oxygen atoms O(9), O(10), O(13), and O(14), but it is not possible to say with certainty which three. It is, perhaps, possible that two or more arrangements occur in a disordered fashion. In Figure 4 we show the arrangement that seems to be most probable, since it assigns the P=O bond to the shortest of the four P–O distances among the four under consideration.

Some Reactions of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$. Several reactions of this complex were carried out to ascertain the stability of the phosphate-bridged core to nucleophiles. For this purpose reactions with triphenylphosphine and *tert*-butyl isocyanide were explored. In methyl alcohol or water, $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$ reacted with triphenylphosphine to produce a highly insoluble, orange, air-stable solid whose IR spectrum is consistent with the presence of bridging phosphate ligands,[23] triphenylphosphine, and water. Microanalytical data support a formulation approximating to $Pt_2(HPO_4)_3$-$(PPh_3)_2(H_2O)_2$ in which one of the phosphato bridges of the $[Pt_2(HPO_4)_4]^{2-}$ anion has been replaced. Unfortunately, the extreme insolubility of this complex and our failure to obtain

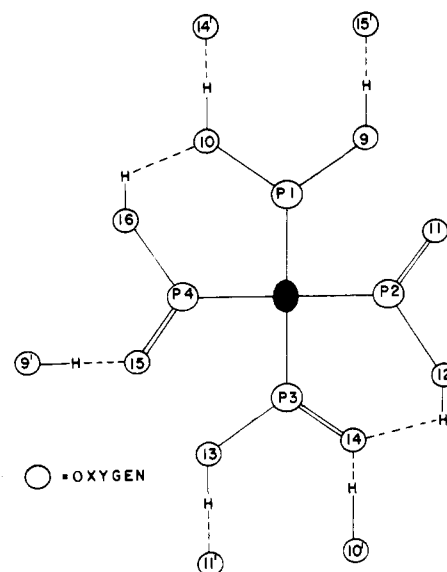**Figure 4.** Schematic representation of the probable arrangement of hydrogen atoms in one $Pt_2(H_2PO_4)(HPO_4)_3$ group and its hydrogen-bonded neighbors.

it as suitable single crystals hindered attempts to adequately characterize it. When this reaction is carried out in hot glacial acetic acid, this same orange compound is formed as the initial product (reaction time ca. 30 min) but as the reaction time is increased considerable quantities of the reductive cleavage product $Pt(PPh_3)_2(O_2CCH_3)_2$ are formed. This latter complex was found to be the major product (>80% yield) when reaction was continued for several hours.

When *tert*-butyl isocyanide was reacted with $(pyH)_2[Pt_2$-$(HPO_4)_4(py)_2]$, only the reductive cleavage product $Pt(CN$-t-$Bu)_2(CN)_2$ was observed even with short reaction times (~30 min). The presence of cyanide ions in the product, $Pt(CN$-t-$Bu)_2(CN)_2$, was not surprising in light of the fact that $[PtCl_4]^{2-}$ and *tert*-butyl isocyanide when heated together in either water or alcohol[24] result in the hydrolysis of the isocyanide ligand to produce *tert*-butyl alcohol and the same cyano complex as that found in our reaction. The $[PtCl_4]^{2-}$ ion has also been shown to react with *tert*-butyl isocyanide in methylene chloride under mild reflux to yield the same cyano complex.

(22) Ziolkowski, J. J.; Moszner, M.; Głowiak, T. *J. Chem. Soc., Chem. Commun.* **1977**, 760.

(23) Absorptions due to the phosphate ligands are at 1100 s, 1080 s, 990 s, and 910 m cm^{-1} in the IR spectrum of $Pt_2(HPO_4)_3(PPh_3)_2(H_2O)_2$. Corresponding absorptions are, for comparison, at 1070 s, 1050 s, 990 s, and 890 m cm^{-1} in the spectrum of $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$.

(24) Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley: New York, 1969; p 169.