than expected. All four ions contain Mn and on the basis of closed-polyhedral structures without double bonds have electron deficiencies of $2^{1}/_{2}$ or $2^{2}/_{3}$. In fact, all clusters which satisfy that description are relatively unreactive. We speculate that these ions are stabilized by electronic effects perhaps related to those associated with adsorbate-induced structural changes observed on metal surfaces. Six clusters with low electron deficiencies were more reactive than expected. With one exception, these reactive clusters have on the basis of closed-polyhedral structures and no delocalized bonding ($X = 0$) electron deficiencies of $^{3}/_{4}$ or $^{5}/_{6}$. The interesting exception is $Mn_6(CO)_{20}^+$ in $Mn_2(CO)_{10}$ with an $X = 0$ electron deficiency of $^{1}/_{2}$. In $ReMn(CO)_{10}$ and $Re_2(CO)_{10}$ it is the $M_6(CO)_{19}^+$ ions that are anomalously reactive. We speculate that these reactive ions have open or distorted structures forced upon them by ligand crowding around the central metal core. The open structures are then more susceptible to reaction. We note that these exceptional cases are the only ones of the 76 clusters observed in this and the previous study[2] of clustering reactions in the group 7 metal carbonyls.

Acknowledgment. We wish to thank Professor A. Wojcicki (Ohio State University), who kindly provided the sample of $ReMn(CO)_{10}$, Dr. B. K. Teo (AT&T Bell Laboratories), and Professor J. W. Lauher (State University of New York at Stony Brook), who provided many useful suggestions, and the National Science Foundation for partial support of this research under Grant CHE 81-10516.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $MnRc(CO)_{10}$, 14693-30-2.

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One- and Two-Electron Chemistry in the Reaction of Nitrogen Dioxide and Nitrosyl Halides with Binuclear Pyrophosphito Complexes of Platinum(II) and Platinum(III)

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Received October 26, 1984

Nitrogen dioxide adds to the bridged binuclear Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4^{4-}$ to give the Pt(III)–Pt(III) complex $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$. The NO_2 ligands coordinate the axial positions in this Pt(III)–Pt(III) complex, and this has been confirmed by X-ray crystallography. Crystals grown from an acidic aqueous solution of $Pt_2(P_2O_5H_2)_4^{4-}$ and $NaNO_2$ have the formula $H_{40}N_2O_{42}P_8Pt_2Na_8$. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 13.958$ (3) Å, $b = 19.413$ (2) Å, $c = 15.538$ (5) Å, $\beta = 106.19$ (2)°, and $Z = 4$. The molecular structure shows respective Pt–Pt and Pt–N distances of 2.7333 (3) and 2.153 (6) Å, with half the ligand protons replaced by hydrated sodium ions. Reductive elimination of NO_2 gives $Pt_2(P_2O_5H_2)_4^{4-}$. Halide ion X^- (X = Cl, Br) reacts with $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ to give $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$. Excess iodide ion gives $Pt_2(P_2O_5H_2)_4I_2^{4-}$, and 1 equiv of *N*-iodosuccinimide reacts with $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ to give $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$. Nitric oxide does not add to $Pt_2(P_2O_5H_2)_4^{4-}$, and nitrosyl chloride gives $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$. Carbonylation of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ gives CO_2 and $Pt_2(P_2O_5H_2)_4^{4-}$ with no observable nitrosyl intermediate.

The coordination chemistry of platinum is dominated by complexes with Pt in oxidation states 0, II, and IV.[2] Interconversions between these complexes involve two-electron changes, and consequently, reactions of monomeric platinum complexes with one-electron reagents have received considerably less study.[3] Nevertheless, for multimetallic chain complexes of platinum the odd-electron mixed-valence compounds are quite commonly found, because the paramagnetic form is stabilized by intermetallic delocalization.[4] Using the delocalization concept with binuclear complexes, we have carried out pairwise one-electron oxidations at each platinum in the Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4^{4-}$ in the presence of Cl^- to convert it to the Pt(III)–Pt(III) complex $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ with outer-sphere oxidants.[5] This next paper now describes the reactions of the binuclear complex $Pt_2(P_2O_5H_2)_4^{4-}$ with the one-electron *inner*-sphere oxidant NO_2, and for the first time, we show how addition and elimination reactions of the stable NO_2 radical can be used to interconvert between Pt(II)–Pt(II) and Pt(III)–Pt(III) complexes.[6] Lippard et al. have used nitrous acid to convert Pt(II)–Pt(II) complexes into axially disubstituted nitro Pt(III)–Pt(III) complexes.[7] With Lippard's μ-pyridonato complexes, however, NO_2 elimination does not appear to be facile, and this paper for the first time shows how to prepare Pt(III)–Pt(III) complexes with both nitro and halo ligands in the axial positions.

Experimental Section

^{31}P NMR spectra were measured at 80.98 MHz on a Nicolet NTC 200 NMR spectrometer. Samples were dissolved in D_2O contained in 12-mm tubes. Chemical shifts are reported in ppm with positive shifts to high frequency of 85% H_3PO_4. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Model 383 spectrometer. Reagents and solvents were commercial samples and were used without further purification. The complex $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ was prepared by the literature method,[8] and solutions of this compound and $K_4[Pt_2(P_2O_5H_2)_4X_2]$ are strongly acidic.

$K_4[Pt_2(P_2O_5H_2)_4(NO_2)_2]$ (1). Method A. The complex $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (200 mg, 0.17 mmol) was dissolved in deionized water (3 mL). Nitrogen dioxide was slowly bubbled through the solution for 10 min, during which time the solution turned from green to orange-brown. The reaction is complete when no green emission (514 nm) is observable.[8] Dropwise addition of acetone (20 mL) precipitated the complex as an orange powder, which was filtered and air-dried; yield 110 mg (51%). A

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Table I. Crystal Data and Data Collection Details

formula	$H_{40}N_2O_{42}P_8$-Pt_2Na_8	abs coeff μ(Mo Kα), cm^{-1}	77.7
mol wt	1558.28	λ (Mo Kα), Å	0.71069
a, Å	13.958 (3)	monochromator	graphite
b, Å	19.413 (2)	method	ω–2θ scan technique
c, Å	15.538 (5)		
β, deg	106.19 (2)	2σ limits, deg	46 (max)
d_{calcd}, g cm^{-3}	2.460	octants collcd	$\pm h,+k,+l$
V, Å^3	4043.3	total no. of unique reflcns	2924
Z	4	no. of data used ($I \geq 2.5\sigma(I)$)	2431
space group	$C2/c$ (No. 15)		

satisfactory microanalysis cannot be obtained for the complex because of its ready loss of NO_2. Solid samples decompose thermally within hours even under anaerobic conditions.

Method B. The complex $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (300 mg, 0.26 mmol) was dissolved in deionized water (3 mL). Sodium nitrite (150 mg) was added in portions. The acidic solution immediately changed color to orange-brown, and there was an effervescent formation of nitrogen dioxide. Isolation by the procedure used in method A gave 175 mg (52%) of product complex.

Carbonylation of $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$. Carbon monoxide was bubbled through a solution of $K_4[Pt_2(P_2O_5H_2)_4(NO_2)_2]$ dissolved in 10 mL of carbon dioxide free deionized water. The effluent gas was passed through carbon dioxide free saturated aqueous barium hydroxide in a stream of nitrogen gas. After 4 h the solution contained $Pt_2(P_2O_5H_2)_4{}^{4-}$, and barium carbonate (10 mg) had precipitated.

Halide Replacement Reactions. (a) Reactions with Halide Ion. A sample of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (100 mg) was dissolved in D_2O (5 mL). The solution was filtered through glass wool into a 12-mm NMR tube. The solution was purged with nitrogen (10 min), and sodium nitrite was added to completely convert the complex into $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$. A solution containing 5 equiv of either KCl, KBr, or KI in D_2O (1 mL) was rapidly added, a Teflon vortex plug was inserted, and the NMR tube finally was sealed with a close-fitting cover cap. The closed tubes were used to follow the reactions by ^{31}P NMR spectroscopy.

(b) *N*-Iodosuccinimide. By the same procedure as for the halide ion reactions, a sealed NMR tube was prepared containing equal equivalents of $Pt_2(P_2O_5H_2)_4{}^{4-}$ and *N*-iodosuccinimide.

Reaction of $Pt_2(P_2O_5H_2)_4{}^{4-}$ with Nitrosyl Chloride. The complex $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (200 mg, 0.17 mmol) was dissolved in deionized water (1 mL). Nitrosyl chloride was bubbled through the solution for 20 min, during which time the solution color changed from green to yellow. Excess NOCl was then purged from the solution by using a rapid stream of nitrogen gas. Dropwise addition of ethanol (20 mL) gave a precipitate of $K_4[Pt_2(P_2O_5H_2)_4Cl_2]$[9] as a yellow powder, yield 125 mg (60%)

Preparation of Crystals of $Na_8[Pt_2(P_2O_5H)_4(NO_2)_2]\cdot 18H_2O$ Suitable for X-ray Diffraction. The complex $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (109 mg, 0.09 mmol) was dissolved in deionized water (2 mL). The solution was filtered through glass wool into a 5-mm NMR tube. Sodium nitrite (220 mg 3.2 mmol) was added to the solution in the tube, and the tube was quickly sealed with a close-fitting NMR cap. The tube was shaken to dissolve all the solids. After 30 days, crystals of crystallographic quality were formed. The needles were maintained in the mother liquor.

Collection of the X-ray Diffraction Data. A well-formed clear orange crystal was cut to a cube of side 0.35 mm and sealed in a glass Lindeman tube. Without this latter procedure, the highly hydrated crystals lose both water of crystallization and nitrogen dioxide to give materials that do not diffract X-rays. Diffraction data at 293 K were collected on an Enraf-Nonius CAD-4 diffractometer with a graphite beam monochromator. An empirical absorption correction was applied by using the packaged program routine in the diffractometer software. No crystal decay was apparent from monitoring two check reflections. The position of the platinum atom was obtained from a Patterson map, and all other non-hydrogen atoms were picked out from difference Fourier maps. Satisfactory refinement could not be achieved in space group *Cc*, and the correct space group is $C2/c$ with the molecule having a crystallographic 2-fold axis that is perpendicular to the Pt–Pt bond and passes through two of the pyrophosphate bridging oxygens. Crystal data and data collection details are reported in Table I.

Structure Determination and Refinement. All the calculations were carried out by using the SHELX 76 crystallographic system of programs.[10] The atomic scattering factors for non-hydrogen atoms were taken from the SHELX library.[11] In the final cycles of full-matrix least-squares refinement, the 11 crystallographically independent water oxygen atoms were refined isotropically and all other non-hydrogen atoms were refined anisotropically. The average shift over estimated error for the 177 parameters was less than 0.005. The highest peak in the final difference maps is less than 1 e Å^{-3} and lies near the platinum atom. The weighting scheme that gave the best analysis of variance in ranges of $|F|$ and σ was $w = 1/(\sigma^2(F) + 0.00055F^2)$, and this gave final $R = 0.031$ and $R_w = 0.041$ where the reliability indices referred to are $R = \sum|\Delta F|/|F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum w|F_0|^2]^{1/2}$.

Table II. Fractional Coordinates of Atoms with Standard Deviations

atom	x	y	z
Pt	0.90109 (2)	0.37069 (1)	0.24661 (2)
P(1)	0.93593 (15)	0.35084 (10)	0.40360 (14)
P(2)	0.89933 (14)	0.49241 (10)	0.26432 (13)
P(3)	0.85948 (15)	0.38483 (11)	0.08876 (13)
P(4)	0.89033 (16)	0.25005 (11)	0.21916 (16)
O(1)	1.00000	0.5267 (4)	0.25000
O(2)	0.9437 (4)	0.3449 (3)	0.0523 (4)
O(3)	1.00000	0.2162 (5)	0.25000
O(11)	0.8973 (4)	0.2793 (3)	0.4228 (4)
O(12)	0.9010 (4)	0.4040 (3)	0.4589 (4)
O(21)	0.8860 (4)	0.5248 (3)	0.3476 (4)
O(22)	0.8687 (4)	0.4611 (3)	0.0604 (4)
O(31)	0.7621 (4)	0.3541 (3)	0.0373 (4)
O(32)	0.8183 (4)	0.5223 (3)	0.1804 (4)
O(41)	0.8378 (4)	0.2136 (3)	0.2847 (4)
O(42)	0.8432 (4)	0.2248 (3)	0.1271 (4)
N(1)	0.7455 (5)	0.3708 (3)	0.2420 (4)
O(4)	0.6885 (4)	0.3259 (3)	0.2007 (4)
O(5)	0.7094 (4)	0.4166 (3)	0.2799 (4)
Na(1)	1.00000	0.50000	0.50000
Na(2)	0.77195 (22)	0.48532 (16)	0.41749 (22)
Na(3)	1.01750 (24)	0.01000 (18)	0.39387 (24)
Na(4)	0.6734 (3)	0.24816 (20)	0.0532 (3)
Na(5)	1.00000	0.6704 (3)	0.25000
O(91)	0.8658 (5)	0.6695 (3)	0.3233 (4)
O(92)	0.3688 (4)	0.5760 (3)	0.3421 (4)
O(93)	0.8767 (5)	0.6535 (4)	0.1133 (5)
O(94)	0.5806 (5)	0.5649 (3)	0.5418 (5)
O(95)	0.6495 (4)	0.4247 (3)	0.4682 (4)
O(96)	0.6511 (5)	0.5733 (3)	0.3624 (5)
O(97)	0.50000	0.4542 (5)	0.25000
O(98)	1.00000	0.7904 (6)	0.25000
O(99)	0.5135 (9)	0.3005 (6)	0.0590 (9)
O(991)	0.5408 (11)	0.3109 (8)	0.0104 (11)
O(100)	0.8143 (7)	0.7921 (5)	0.0845 (6)

Results and Discussion

Two of the most stable inorganic free radicals are nitrogen dioxide and nitric oxide. Addition of NO_2 to an aqueous solution of the Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4{}^{4-}$ results in a rapid reaction to give the binuclear Pt(III)–Pt(III) complex $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$. The reaction is reversible since in the absence of excess NO_2 reductive elimination back to $Pt_2(P_2O_5H_2)_4{}^{4-}$ readily occurs at ambient temperature (eq 1). The adduct shows a single

$$Pt_2(P_2O_5H_2)_4{}^{4-} + 2NO_2 \rightleftharpoons Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-} \quad (1)$$

^{31}P NMR resonance at δ 30.9 (^1J(PtP) = 2211 Hz). This ^1J(PtP) value in the region of 2200 Hz confirms that each platinum center has been oxidized to platinum(III).[8] An aqueous solution Raman spectrum of $Pt_2(P_2O_5H_2)_4(NO_2)_2{}^{4-}$ shows ν(Pt–Pt) at 151 cm^{-1}, with ν(Pt–N), ν_{sym}(N–O), and δ_{sym}(N–O) at 267, 1320, and 820 cm^{-1}, respectively. Thus the nitrite ligands are N-bonded to platinum(III), and the complex has a strong homometallic Pt–Pt bond.[12] A weak Pt–N bond is indicated from the low-energy position of ν(Pt–N).[13] The solid-state IR spectrum shows

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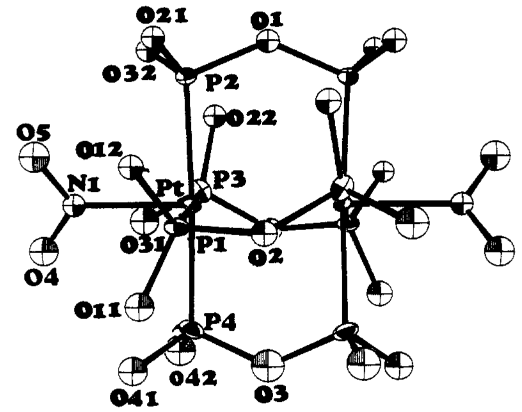


Figure 1. ORTEP diagram of the molecular structure of the anion $Pt_2(P_2O_5H)_4(NO_2)_2^{8-}$. Hydrogen atoms were not located; see text.

Table III. Selected Bond Distances and Angles in the Anion $Pt_2(P_2O_5H)_4(NO_2)_2^{8-}$

Distances (Å)			
Pt-Pt	2.7333 (3)	P(2)-O(21)	1.496 (6)
Pt-P(1)	2.3802 (21)	P(2)-O(32)	1.579 (6)
Pt-P(2)	2.3798 (20)	P(3)-O(2)	1.635 (6)
Pt-P(3)	2.3736 (21)	P(3)-O(22)	1.561 (6)
Pt-P(4)	2.3779 (23)	P(3)-O(31)	1.496 (7)
Pt-N(1)	2.153 (6)	P(4)-O(3)	1.611 (6)
P(1)-O(2)	1.632 (6)	P(4)-O(41)	1.578 (6)
P(1)-O(11)	1.549 (6)	P(4)-O(42)	1.482 (7)
P(1)-O(12)	1.508 (6)	N(1)-O(4)	1.234 (9)
P(2)-O(1)	1.625 (5)	N(1)-O(5)	1.248 (9)

Angles (deg)			
P(1)-Pt-Pt′	92.58 (7)	P(1)-Pt-N(1)	87.14 (18)
P(2)-Pt-Pt′	92.21 (7)	P(3)-Pt-N(1)	90.68 (18)
P(3)-Pt-Pt′	89.63 (7)	P(4)-Pt-N(1)	88.98 (18)
P(4)-Pt-Pt′	91.14 (7)	Pt(1)-N(1)-O(4)	121.0 (5)
P(1)-Pt-N(1)	87.14 (18)	Pt(1)-N(1)-O(5)	121.4 (5)
P(2)-Pt-N(1)	87.71 (18)	O(4)-N(1)-O(5)	117.6 (7)
P(1)-Pt-P(2)	92.75 (7)	P(1)-O(2)-P(3)	125.2 (3)
P(1)-Pt-P(4)	90.52 (7)	P(2)-O(1)-P(2)′	131.6 (3)
P(2)-Pt-P(3)	89.84 (7)	P(4)-O(3)-P(4)′	131.8 (3)
P(3)-Pt-P(4)	86.76 (7)		

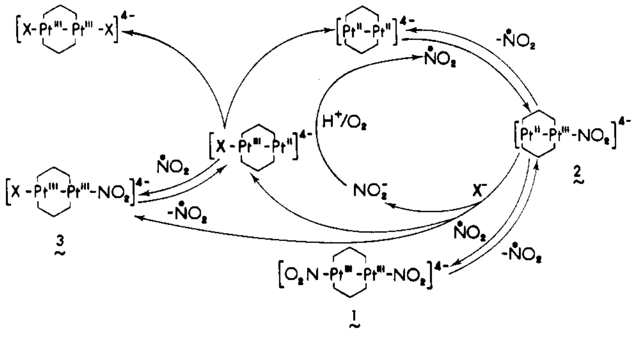
$\nu_{asym}(NO_2)$ at 1425 cm^{-1} and $\nu_{sym}(NO_2)$ at 1300 cm^{-1}.[13]

Structure. The structure of the complex has been confirmed by X-ray crystallography. The structure corresponds to the molecular formula $Na_8[Pt_2(P_2O_5H)_4(NO_2)_2]\cdot18H_2O$, and because the complex readily loses NO_2, it is necessary to seal the crystal in a Lindeman tube. The anion $Pt_2(P_2O_5H)_4(NO_2)_2^{8-}$ has a binuclear "lantern-type" structure with eclipsed equatorial P-bonded *mono*hydrogen pyrophosphito ligands. The axially bonded nitro ligands are η^1-bonded (Figure 1). The final atomic coordinates are given in Table II. Selected bond distances and angles in this anion are given in Table III, and bond distances and angles about the sodium ions are given in Table IV. The two bridging pyrophosphito ligands, which lie across a crystallographic 2-fold rotation axis, have a wide 131.6 (3)° POP angle with a slightly staggered conformation (O(1)-P(2)-Pt-Pt′ = 13° and O(3)-P-(4)-Pt-Pt′ = 20°). The third POP ligand adopts a different conformation with a POP angle of 125.2 (3)°, O(2)-P(1)-Pt-Pt′ = 0.6°, and O(2)-P(3)-Pt-Pt′ = 33°. Structurally this anion is similar to the bis(η^1-nitro)bis(μ-α-pyridonato)diplatinate(III) anion,[7] which also has axially substituted bis(η^1-nitro) groups bonded through nitrogen and N,O-bridging α-pyridonato ligands across two platinum(III) centers. The Pt-N distance in this μ-pyrophosphito complx is 2.153 (6) Å, which is statistically identical with the values 2.172 (10) and 2.168 (11) Å found in the μ-pyridonato complex,[7] but the O(4)-N(1)-O(5) angle of 117.6 (7)° is slightly smaller in this pyrophosphito complex.

Table IV. Bond Distances (Å) about the Crystallographically Distinct Sodium Ions

Na(1)-O(12)	2.301 (5)	Na(2)-O(12)	2.347 (6)
Na(1)-O(12)′	2.301 (5)	Na(2)-O(21)	2.295 (6)
Na(1)-O(21)	2.504 (5)	Na(2)-O(22)	2.483 (6)
Na(1)-O(21)′	2.504 (5)	Na(2)-O(5)	2.463 (7)
Na(1)-O(22)	2.401 (5)	Na(2)-O(95)	2.382 (7)
Na(1)-O(22)′	2.401 (5)	Na(2)-O(96)	2.385 (7)
Na(3)-O(95)	2.508 (7)	Na(4)-O(2)	2.671 (7)
Na(3)-O(96)	2.395 (8)	Na(4)-O(31)	2.449 (8)
Na(3)-O(92)	2.380 (7)	Na(4)-O(42)	2.372 (8)
Na(3)-O(94)	2.463 (8)	Na(4)-O(91)	2.629 (8)
Na(3)-O(94)′	2.398 (8)	Na(4)-O(99)	2.474 (14)
Na(3)-O(97)	2.434 (6)	Na(4)-O(991)	2.201 (17)
Na(5)-O(1)	2.789 (6)	Na(5)-O(93)	2.355 (8)
Na(5)-O(91)	2.449 (8)	Na(5)-O(93)′	2.355 (8)
Na(5)-O(91)′	2.449 (8)	Na(5)-O(98)	2.331 (8)

Scheme I. Interconversion between $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ and Added Halide X^- (X = Cl, Br) Ions



Each half-dimer unit has five crystallographically independent sodium ions, each having octahedral coordination. Ions Na(1) and Na(5) are in special positions with occupancy factors of 0.5. Each half-dimer unit has 11 water molecules with O(97) and O(98) on special positions and O(99) and O(991) with occupancy factors of 0.56 and 0.44. The sodium ions are not bonded to oxygen in an ordered manner but are variously O-bonded to P—Ō, P═O, and H_2O groups. The two crystallographically independent hydrogen atoms associated with P_2O_5H have not been determined unambiguously. From residual density, one proton appears to be between O(11) and O(41) and the other appears to be close to O(32). The following H-bonded groups are likely: P-O(11) to water O(99); P-O(41) to water O(92) and O(91); P-O(32) to water O(93) and O(92). The fourth long P-O bond (P-O(22)) is unprotonated and coordinated to Na(1) and Na(2). Although proton replacement by alkali-metal ions occurs with dimethyl phosphito complexes,[14] this crystal is the first known case of this replacement being observed in these pyrophosphite-bridged complexes.

Reactions. Binuclear Pt(III)-Pt(III) pyrophosphito complexes undergo halide ion substitution in the axial positions. We have proposed earlier[5] that the thermal reaction involves halide ion loss (eq 2) and that the photochemical reaction involves halogen atom loss in aqueous solution (eq 3). This facile photochemical halogen

$$Pt_2(P_2O_5H_2)_4X_2^{4-} + 2Y^- \xrightarrow{pH > 5} Pt_2(P_2O_5H_2)_4Y_2^{4-} + 2X^- \quad (2)$$

$$Pt_2(P_2O_5H_2)_4X_2^{4-} + Y^- \xrightarrow{h\nu} Pt_2(P_2O_5H_2)_4XY^{4-} + X^- \quad (3a)$$

$$Pt_2(P_2O_5H_2)_4XY^{4-} + Y^- \xrightarrow{h\nu} Pt_2(P_2O_5H_2)_4Y_2^{4-} + X^- \quad (3b)$$

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Table V. ^{31}P NMR Spectral Parameters for Complexes $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$ ($X = NO_2$, Cl, Br, I)[a]

X	δ_1	δ_2	$^1J_1$(PtP), Hz	$^1J_2$(PtP), Hz	$^2J_1$(PtP), Hz	$^2J_2$(PtP), Hz	^3J(PP), Hz
NO_2	30.9	*b*	2211	*b*	*b*	*b*	*b*
Cl	32.9	26.7	2262	2254	106	103	16.5
Br	29.4	26.4	2258	2264	104	101	16
I	27.8	22.5	2290	2232	93	101	16

[a] Assignments are δ_1/J_1 for the phosphorus nuclei closest to the axial nitro substituent. These assignments are based on comparison with the published ^{31}P NMR spectra of $Pt_2(P_2O_5H_2)_4X_2^{4-}$ (X = Cl, Br, I)[9] and with the observed broadening of δ_1 due to a two-bond coupling with the ^{14}N nuclei of the NO_2 ligand. [b] Lines not observed because of equivalence, or parameters not calculated because of higher order effects.

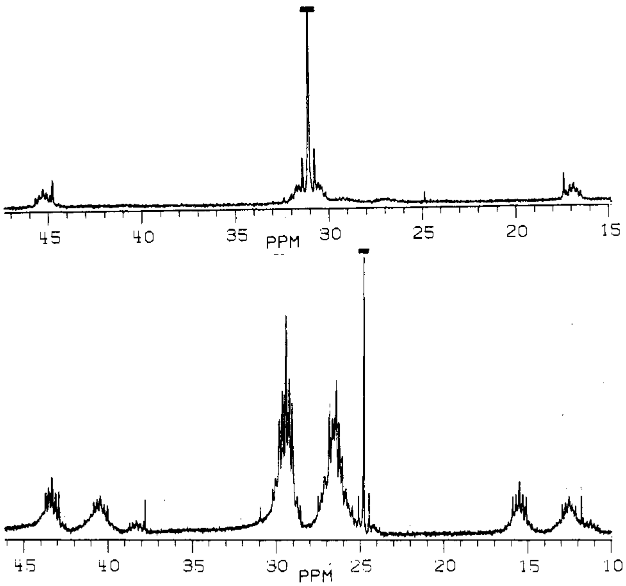

Figure 2. ^{31}P NMR spectra of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ with added Br^-. The upper spectrum measured immediately after addition shows mainly $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ at δ 30.9. The lower spectrum, measured after 20-h reaction time, shows the product to be mainly $Pt_2(P_2O_5H_2)_4Br(NO_2)^{4-}$ with two multiplets centered at δ 29.4 and 26.4. The sharp peak at δ 24.8 is due to some $Pt_2(P_2O_5H_2)_4Br_2^{4-}$ being formed.

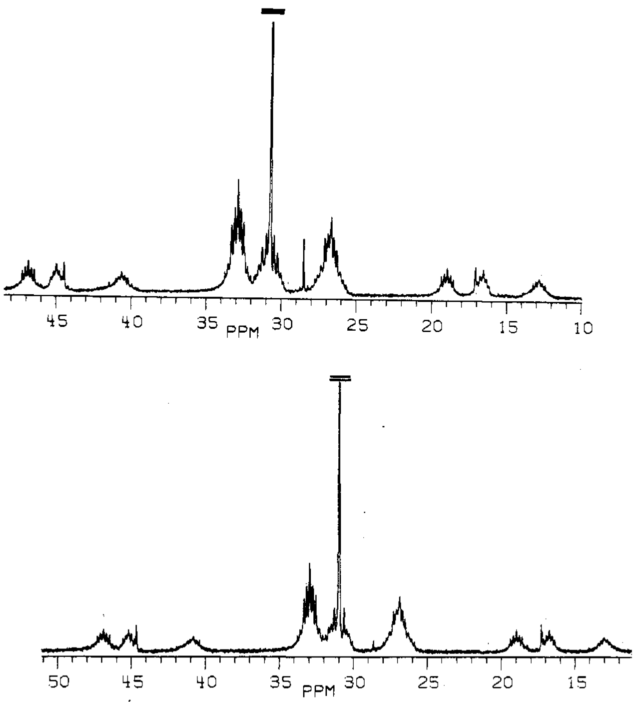

Figure 3. ^{31}P NMR spectra of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ with added Cl^-. The lower spectrum after 16 h shows the product to be mainly $Pt_2(P_2O_5H_2)_4Cl(NO_2)^{4-}$ with two multiplets centered at δ 32.9 and 26.7. Significant quantities of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ at δ 30.9 remain. The upper spectrum after 48 h shows that $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ at δ 28.6 is now beginning to be formed.

replacement occurs in acid solution to first yield the mixed complex $Pt_2(P_2O_5H_2)_4XY^{4-}$ (eq 3a), and then subsequent reaction converts this intermediate into $Pt_2(P_2O_5H_2)_4Y_2^{4-}$ (eq 3b). This new axially disubstituted nitro complex undergoes a similar replacement chemistry, except that now the loss of the NO_2 group from $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ is a thermal process.[15,16] If halide ion X^- (X = Cl, Br) is present, intermediate **2** ($Pt_2(P_2O_5H_2)_4(NO_2)^{4-}$) with a vacant axial coordination site will be trapped to give $Pt_2(P_2O_5H_2)_4X(NO_2)^{5-}$. Intermediate **2**, formed by NO_2 dissociation, will be present in very low equilibrium concentration because it is an odd-electron Pt(II)-Pt(III) complex, which will be rapidly trapped by free NO_2 to revert back to $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$. Under our reaction conditions, we observe no formation of $Pt_2(P_2O_5H_2)_4^{4-}$. If, however, the free-radical trap α-methylstyrene is added to the solution, addition of NO_2 to the double bond results in induced alkene polymerization and an irreversible loss of NO_2. Removal of NO_2 from the equilibrium in (1) favors reductive elimination and $Pt_2(P_2O_5H_2)_4^{4-}$ formation. The second intermediate, $Pt_2(P_2O_5H_2)_4X(NO_2)^{5-}$, will be oxidized to $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$ (**3**) by nitrogen dioxide. This replacement reaction is shown in eq 4, and the overall changes are diagramed

$$Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-} + X^- \rightarrow \underset{\mathbf{3}}{Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}} + NO_2^- \quad (4)$$

in Scheme I. The ^{31}P NMR data for these complexes are collected in Table V. Scheme I shows the equilibria among the species $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$, $Pt_2(P_2O_5H_2)_4(NO_2)^{4-}$, and $Pt_2(P_2O_5H_2)_4^{4-}$, as well as the formation of $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$ from added X^-. The nitrite ion formed in (4) is rapidly converted back to NO_2 in the acidic medium, thereby remaining in the reaction cycle. Spectral changes for the conversion of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ into $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$ (X = Cl, Br) are shown in Figures 2 and 3, and in Table V we collect the ^{31}P NMR spectral data for the complexes. In each case a small amount of $Pt_2(P_2O_5H_2)_4X_2^{4-}$ (X = Cl, Br) forms at the later stages of the reaction, this being more pronounced when the halide is bromide. These dihalo products can be explained by the same mechanistic sequence, if $Pt_2(P_2O_5H_2)_4X(NO_2)^{4-}$ dissociates NO_2 to give the mixed-valence species $Pt_2(P_2O_5H_2)_4X^{4-}$. In the presence of NO_2 this intermediate

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(15) At 10 °C an acidified solution containing $Pt_2(P_2O_5H_2)_4^{4-}$ and $Pt_2(P_2O_5H_2)_4(^{15}NO_2)_2^{4-}$ (90% ^{15}N) shows reversible coalescence in the ^{31}P NMR spectrum from a singlet to an apparent triplet ($^2J(P^{15}N) = {}^3J(P^{15}N) = 2$ Hz).

(16) Other mechanisms have been considered. By analogy with the mechanisms for monomeric platinum(IV) complexes, we cannot ignore the possibility that the substitution occurs by an REOA pathway,[17] by a mechanism involving platinum(II)-catalyzed (i.e. $Pt_2(P_2O_5H_2)_4^{4-}$) substitution,[18] or by a dissociative pathway involving loss of nitrite ion as the first step.[19] We believe that the REOA and platinum(II)-catalyzed pathways are unlikely because a coordinated nitrite, like a complexed water molecule,[20] is a poor bridging ligand. We cannot discount nitrite ion loss as a first step. Simple dissociative pathways are not usually observed for kinetically inert d^6 platinum complexes, and if such a mechanism was followed, we believe that nitrite loss from $Pt_2(P_2O_5H_2)_4Cl(NO_2)^{4-}$ would be similarly favored over nitrite ion loss from $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ (except for, of course, the statistical factor of 2). Since free dissociated nitrite ion will be rapidly converted into NO_2 in the acidic reaction medium, the number of available mechanistic probes is rather few.

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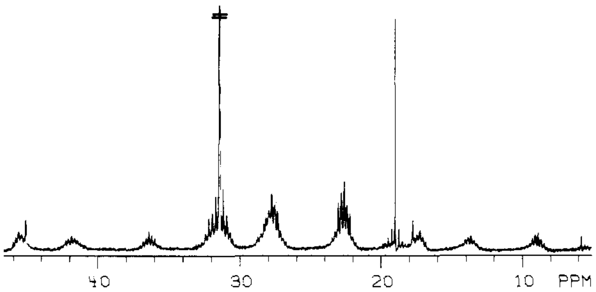

Figure 4. ^{31}P NMR spectrum of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ with added *N*-iodosuccinimide after 24 h. The spectrum shows that $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$ is formed, having two multiplets at δ 27.8 and 22.5, along with some unreacted $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ at δ 30.9 and a small amount of $Pt_2(P_2O_5H_2)_4I_2^{4-}$ at δ 19.0.

will rapidly convert back to **3**, but in competition with this reverse reaction there is the disproportionation of $Pt_2(P_2O_5H_2)_4X^{4-}$ into $Pt_2(P_2O_5H_2)_4X_2^{4-}$ and $Pt_2(P_2O_5H_2)_4^{4-}$, a reaction which is fast.[21] The other complex formed in this disproportionation reaction, $Pt_2(P_2O_5H_2)_4^{4-}$, will subsequently react with the excess NO_2 in solution to give back $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$.

If excess iodide (X = I) is added, the product is $Pt_2(P_2O_5H_2)_4I_2^{4-}$ with no observed $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$. This is to be anticipated because iodide ion will be oxidized to iodine by NO_2 and iodine will rapidly add to $Pt_2(P_2O_5H_2)_4^{4-}$,[8] which is formed in equilibrium with $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ (eq 1). The complex $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$ can be synthesized, however, by treating $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ with 1 equiv of *N*-iodosuccinimide (NIS). In aqueous solution, NIS reacts by iodonium ion chemistry rather than by a free-radical pathway,[22] and the formation of $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$ (**4**) can be explained by the redox pathway shown in eq 5. The solution after 12 h contains **4** in high yield,

$$Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-} + I^+ \rightarrow Pt_2(P_2O_5H_2)_4I(NO_2)^{4-} + NO_2^+ \quad (5)$$

and only small quantities of $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ and $Pt_2(P_2O_5H_2)_4I_2^{4-}$ are present (Figure 4). Apparently complex **4** does not undergo disproportionation readily in solution, and also there is an implication that NO_2 loss from $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$ is preferential over NO_2 loss from $Pt_2(P_2O_5H_2)_4I(NO_2)^{4-}$.

Our attempts to prepare nitrosyl complexes of these binuclear platinum(III) pyrophosphito complexes have been unsuccessful. Three routes have been tried. The obvious route, addition of NO to $Pt_2(P_2O_5H_2)_4^{4-}$, does not occur. Under anaerobic conditions there is no reaction between these compounds in aqueous solution. A plausible alternate route involves the reduction of a coordinated nitrite to a nitrosyl ligand by carbon monoxide. Although such a reaction is usually considered to follow a pathway involving prior coordination of carbon monoxide to a coordinatively unsaturated metal center,[23] we find that CO_2 is indeed formed from $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$. Nevertheless, the Pt(II)–Pt(II) complex $Pt_2(P_2O_5H_2)_4^{4-}$ is the only observable complex (eq 6), and no

$$Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-} + 2CO \rightarrow Pt_2(P_2O_5H_2)_4^{4-} + 2NO + 2CO_2 \quad (6)$$

platinum(III) nitrosyls are detected. A third alternate route for the synthesis of nitrosyl complexes is the oxidative addition of nitrosyl chloride.[24] Addition of NOCl to $Pt_2(P_2O_5H_2)_4^{4-}$ instead gives the dichloro complex $Pt_2(P_2O_5H_2)Cl_2^{4-}$ (eq 7). This reaction

$$Pt_2(P_2O_5H_2)_4^{4-} + 2NOCl \rightarrow Pt_2(P_2O_5H_2)_4Cl_2^{4-} + 2NO \quad (7)$$

can be rationalized as a one-electron process involving initial halogen abstraction from NOCl by $Pt_2(P_2O_5H_2)_4^{4-}$ to give $Pt_2(P_2O_5H_2)_4Cl^{4-}$. This mixed-valence intermediate can then form $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$, either by disproportionation or by chlorine abstraction from NOCl. By analogy, the reaction between $PtCl_2$(phen) and NOCl gives $PtCl_4$(phen).[25]

We believe that our failure to observe nitrosyldiplatinum(III) complexes is a consequence of the platinum center being too electron poor to stabilize the bond with the strongly π-accepting nitrosyl ligand. This observation reinforces our previous position that these metal-bonded diplatinum(III) complexes show chemistry analogous to that of monomeric platinum(IV) compounds.[5]

Acknowledgment. We thank Professor Paul Stein for the Raman data.

Registry No. **1**, 97295-61-9; **3** (X = Cl), 97295-63-1; **3** (X = Br), 97295-64-2; **3** (X = I), 97295-65-3; $K_4[Pt_2(P_2O_5H_2)_4]$, 80011-26-3; NO_2, 10102-44-0; CO, 630-08-0; $K_4[Pt_2(P_2O_5H_2)_4Cl_2]$, 85335-49-5; $Na_8[Pt_2(P_2O_5H)_4(NO_2)_2]\cdot XH_2O$, 97295-62-0; $Pt_2(P_2O_5H_2)_4I_2^{4-}$, 87355-25-7.

Supplementary Material Available: Lists of observed and calculated structure factors (Table S1), fractional coordinates of atoms with standard deviations (Table S2), thermal vibrational parameters with standard deviations (Table S3), and bond distances and angles (Table S4) (18 pages). Ordering information is given on any current masthead page.

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