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Binuclear Platinum Diphosphite Complexes. Crystal Structures of $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$, a New Linear Chain Semiconductor, and $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$

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Abstract: The structures of crystals of $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ (pop = $(HO_2P)_2O^{2-}$), "Pt_2Br", and $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$, "$Pt_2Cl_2$", have been determined. The structure of "Pt_2Br" features a symmetric Pt–Br–Pt unit in an infinite linear chain (Pt–Pt–Br–Pt–Pt–Br–; $\sigma_{\parallel} = \sim 10^{-4}$–$10^{-3}\ \Omega^{-1}\ cm^{-1}$) with d(Pt–Pt) = 2.793 (1) and d(Pt–Br) = 2.699 (1) Å; "Pt_2Cl_2" is a discrete binuclear ion, with d(Pt–Pt) = 2.695 (1) and d(Pt–Cl) = 2.407 (2) Å. Both Pt–Pt distances are shorter than those (2.925 (1) Å) in $K_4[Pt_2(pop)_4]\cdot 2H_2O$, "$Pt_2$"; the order d("Pt_2") > d ("Pt_2Br") > d("Pt_2Cl_2") accords with an electronic structural model in which "Pt_2" is $(d\sigma)^2(d\sigma^*)^2$, "Pt_2Br" is $(d\sigma)^2(d\sigma^*)^1$, and "Pt_2Cl_2" is $(d\sigma)^2$.

Complexes containing linear chains of transition-metal atoms have been the subject of much contemporary research.[1-3] In such complexes, the ligands must be able to adopt a square-planar configuration about the transition-metal atom and have an appropriate shape to allow close stacking of ML_4 units; in most published work CN^-, CO, or $C_2O_4^{2-}$ has been used. Incorporation of planar ML_4 units into discrete $M_2(L–L)_4$ building blocks could lead to new types of linear chain species, and a particularly attractive binucleating ligand (L–L) in this respect is the diphosphite ion (pop, $(HO_2P)_2O^{2-}$; P···P distance = ~2.9 Å), which, when coordinated through the phosphorus atoms, can hold two metal atoms sufficiently closely to allow appreciable bonding interactions.[4-6]

During our investigations[5,6] of the oxidation chemistry of $Pt_2(pop)_4^{4-}$ in aqueous solutions, we have obtained golden metallic appearing species in which Pt is in a formal oxidation state of 2.5 ($K_4[Pt_2(pop)_4X]$, X = Cl, Br, I). Structural studies show that in crystals of these partially oxidized compounds there are infinite linear chains of Pt–Pt–X–Pt–Pt atoms. The halide ions act to bridge the gap between adjacent $Pt_2(pop)_4$ units and thus provide a continuous path for electrical conduction.[7] Measurements of the conductivities of single crystals of the Br compounds gave values in the range 5×10^{-4}–$10^{-3}\ \Omega^{-1}\ cm^{-1}$, indicating that the material is (at least) a semiconductor. Here we present detailed crystal structure analyses of $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ ("Pt_2Br") and of the nonconducting, fully oxidized Pt(III)–Pt(III) species $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$ ("Pt_2Cl_2"), and we compare these two structures with that of the starting material $K_4[Pt_2(pop)_4]\cdot 2H_2O$ ("Pt_2").[4,8] A preliminary report on "Pt_2Cl_2" has been published.[6]

Experimental Section

Preparation of $K_4[Pt_2(pop)_4]\cdot 2H_2O$, "$Pt_2$". The Pt(II) species was prepared as described previously;[5,9] dark green crystals were obtained when no precautions were taken against air oxidation, whereas yellowish crystals were obtained when deaerated solutions were used.[9] The green and yellow crystals exhibit identical diffraction patterns and have the same density (2.7 (1) g cm^{-3}).

Preparation of $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$, "$Pt_2Br$". Bromine water (5 mL) was added to an aqueous solution of "Pt_2" (0.4 g (0.4 mmol) in 10 mL of H_2O), followed by slow addition of a KCl solution (1 g/10 mL of H_2O). Tetragonal crystals with a copper-bronze sheen were obtained; the yield was about 70%. Anal. Calcd for $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$: P, 20.0; Br, 6.45; Cl, 0. Found: P, 19.61; Br, 7.04, Cl, 0. λ_{max} (ϵ_{max} in cm^{-1} mol^{-1} dm^3) for $K_4[Pt_2(pop)_4Br]$ in aqueous solution: 367 (19 740), 308 nm (21 070). (Orange crystals of $K_4[Pt_2(pop)_4Br_2]$[6] were obtained when KBr was used as the precipitating agent.) Conductivity was measured by the standard two-point probe technique, using a crystal ~0.6 mm long with a cross section of 0.3 × 0.15 mm. The measured value of $\sigma_{\parallel}$—the dc conductivity along the Pt–Pt direction—at room temperature is between 5×10^{-4} and $1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

Preparation of $K_4[Pt_2(pop)_4I]$, "Pt_2I". This compound was prepared by a procedure similar to the one used for "Pt_2Br" except that an aqueous solution of KI_3 (0.3 g of I_2 and 1 g of KI in 15 mL of water) served as both oxidizing and precipitating agent. Anal. Calcd for $K_4[Pt_2(pop)_4I]$: I, 10.16; P, 19.38. Found: I, 10.05; P, 19.58. λ_{max} (ϵ_{max} in cm^{-1} mol^{-1} dm^3) for $K_4[Pt_2(pop)_4I]$ in aqueous solution: 440 (6400), 367 (21 400), 330 nm (5600). Unlike the Cl and Br compounds, reaction with an excess of halide (KI_3) stops at the formation of "Pt_2I" rather than proceeding to "Pt_2I_2", presumably because of the low solubility of "Pt_2I". Due to the small size of the crystals we were unable to measure the value of $\sigma_{\parallel}$ for "Pt_2I"; however, measurements on a compressed powder sample (KBr pellet, 25 °C) gave a value of $2.8 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, which is considerably higher than the single crystal $\sigma_{\parallel}$ values of representative mixed-valence platinum species (e.g., $\sigma_{\parallel}$ for $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$ at 25 °C is $\sim 10^{-8}\ \Omega^{-1}\ cm^{-1}$).[10] We also have been able to prepare "Pt_2I" with NH_4^+ as the cation, but not with Ba^{2+} or Ph_4As^+.

Preparation of $K_4[Pt_2(pop)_4Cl]$, "Pt_2Cl". Chlorine water (2–3 mL) was added to an aqueous solution of "Pt_2" (0.4 g in 10 mL of H_2O). Slow addition of solid KNO_3 (2 g) yielded small golden metallic crystals of $K_4[Pt_2(pop)_4Cl]$. They were filtered off and air dried. Alternatively, $K_4[Pt_2(pop)_4Cl]$ may be prepared by the slow addition of solid KNO_3 to equimolar amounts of $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4Cl_2]$ in solution (0.3 g each of "Pt_2" and "Pt_2Cl_2" in 20 mL of H_2O). λ_{max} (ϵ_{max} in cm^{-1} mol^{-1} dm^3) for $K_4[Pt_2(pop)_4Cl]$ in aqueous solution: 367 (20 540), 282 nm (16 630).

Preparation of $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$, "$Pt_2Cl_2$". Chlorine gas was bubbled through an aqueous solution of 0.4 g (0.4 mmol) of "Pt_2" and 0.5 g (7 mmol) of KCl for 1–2 min, and then 1–2 g of solid KCl was added. The yellow microcrystalline precipitate of "Pt_2Cl_2" was recrystallized from aqueous solution by slow evaporation. Typical yield was 60–70%.

Crystal Structure Determinations. (a) "Pt_2Br". Preliminary photographs indicated a tetragonal cell and Laue symmetry $4/mmm$. Sys-

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Table I. Crystal Data

	$K_4[Pt_2(pop)_4]\cdot 2H_2O^a$ "Pt_2"	$K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ "Pt_2Br"	$K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$ "Pt_2Cl_2"
fw	1158.4	1256.1	1229.4
$F(000)$	1080	1170	574
a, Å	13.335 (1)	13.236 (8)	9.426 (2)
b, Å	13.335	13.236	9.534 (1)
c, Å	7.989 (1)	8.191 (3)	8.743 (1)
α, deg	90.0	90.0	99.07 (1)
β, deg	90.0	90.0	101.66 (1)
γ, deg	90.0	90.0	118.94 (1)
V, Å^3	1420.6 (4)	1435 (1)	642.8 (2)
d_{measd}, g cm^{-3}	2.75 (5)	>2.8	>2.8
d_{calcd}, g cm^{-3}	2.71	2.91	3.17
space group	$P4/mbm^b$	$P4/mbm$	$P\bar{1}$
Z	2^b	2	1

^{a} Reference 4. ^{b} Reference 8.

Table II. Parameters (Coordinates $\times 10^4$) for $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$

atom	no. in cell	x	y	z	B, Å^2
Pt	4	0	0	3295.3 (3)	1.03 (1)^a
Br	2	0	0	0	3.33 (4)^a
K(1)	4	2733 (2)	$x + {}^1/_2$	0	3.72 (8)^a
K(2)	4	3889 (1)	$x + {}^1/_2$	${}^1/_2$	3.13 (6)^a
P	16	1194 (1)	1297 (1)	3209 (1)	1.65 (5)^a
O(1)	16	2164 (2)	1016 (3)	2222 (5)	2.8 (2)^a
O(2)	16	840 (3)	2315 (2)	2622 (5)	3.0 (2)^a
O(3)	8	1673 (4)	1481 (4)	${}^1/_2$	3.3 (3)^a
W(1)^b	4	1014 (7)	$x + {}^1/_2$	5401 (20)	5.7 (4)
W(2)^c	2	490 (12)	$x + {}^1/_2$	2637 (34)	11.3 (7)

^{a} $B_{\text{eq}} = (8\pi^2/3)(U(11) + U(22) + U(33); \sigma(B_{\text{eq}}) = 1/(6)^{1/2}\text{-}\langle\sigma(U_{ii})/U_{ii}\rangle B_{\text{eq}}$. ^{b} Sites are half-occupied. ^{c} Sites are quarter-occupied.

tematic absences in the diffractometer data were $0kl$ with k odd, consistent with space groups $P4bm$ (no. 100), $P\bar{4}b2$ (no. 117), and $P4/mbm$ (no. 127). Intensity statistics suggested the centrosymmetric space group $P4/mbm$ and the successful structure solution confirmed it. A crystal 0.22 × 0.22 × 0.31 mm was centered on a Syntex $P2_1$ diffractometer equipped with graphite-monochromated Mo Kα X radiation. Cell dimensions (Table I) were obtained from the setting angles of 15 reflections with $42° < 2\theta < 55°$. Data were evaluated by θ–2θ scans at 2°/min from $2\theta(K\alpha_1\ -1°)$ to $2\theta(K\alpha_2 + 1°)$; 2441 reflections were scanned in the 2θ range 3°–75° and yielded 2097 independent reflections, 1809 of which had $I > 0$. The three check reflections collected every 97 reflections showed no significant variations. Variances $\sigma^2(I)$ were assigned on the basis of counting statistics plus an additional term, $(0.024I)^2$, to account for fluctuations proportional to the diffracted intensity. Intensities were corrected for Lorentz and polarization effects and for absorption (μ = 128.1 cm^{-1}; crystal faces {110}, {001}). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares to a final R $(=(\sum||F_o| - |F_c||/\sum|F_o|))$ of 0.058 for the 1809 reflections with $F_o^2 > 0$ and a goodness of fit $(=[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2})$ of 1.50 (n (number of reflections) = 2096, p (number of parameters) = 58). The structure solution was considerably simplified because, with two formula units in the cell, most of the atoms must occupy special positions. At a late stage of the refinement, a difference map suggested that a water molecule lies in a partially occupied site. This site, W(2), lay unrealistically close (~2.2 Å) to the other water, W(1), which lay on a mirror plane. However, the anisotropic term $U(33)$ of W(1) was so large (~0.2 Å^2) as to suggest that it is disordered between two sites on either side of the mirror.[11] Such a model results in reasonable W(1)–W(2) distances and was adopted.

All calculations were done by using programs of the CRYM X-ray computing system,[12] plus ORTEP.[13] Atomic parameters are given in Table II. Hydrogen atoms were ignored in the calculations. A drawing of the structure is shown in Figure 1.

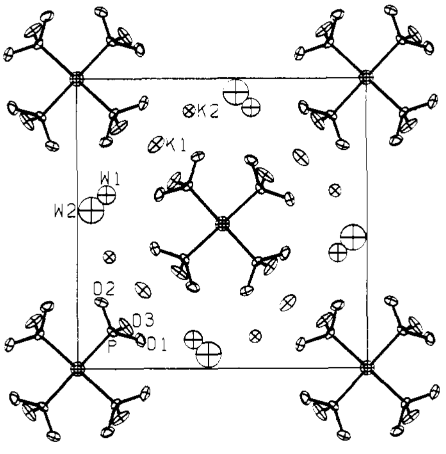

Figure 1. An ORTEP[13] drawing of "Pt_2Br" projected down the c axis. Only half of each $Pt_2(pop)_4$ group is shown.

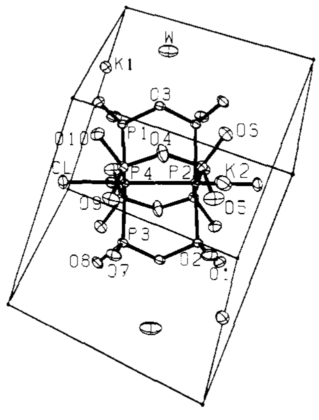

Figure 2. An ORTEP[13] drawing of "Pt_2Cl_2" with the unit cell outlined.

(b) "Pt_2Cl_2". Preliminary photographs indicated a triclinic cell. Space group $P\bar{1}$ (no. 2) was indicated by intensity statistics and confirmed by the successful solution. A crystal 0.14 × 0.08 × 0.29 mm was carefully centered on the diffractometer; cell dimensions (Table I) and the orientation matrix were determined from the setting angles of 15 reflections with $23° < 2\theta < 30°$. Data were collected as with the bromine compound; 3939 reflections were scanned in the 2θ range 3°–45° and merged to give 2981 independent reflections, of which 2946 had $I > 0$. Four check reflections were collected every 96 reflections and showed no significant variations. Variances were assigned as for the bromine compound, and Lp and absorption corrections were made (μ = 128.6 cm^{-1}; crystal faces {100], {110}, {001}). The structure was solved and refined as before to a final R of 0.038 for the 2946 reflections with $F_o^2 > 0$ and

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(11) Whichever site is occupied by W(1), the occupancy factory of W(2) can be no larger than 0.25 without requiring unacceptably short O···O distances. The final parameters (Table II), which include isotropic B's for W(1) and W(2), require at least one W(1)···W(2) distance of 2.47 (3) Å; this suspiciously short distance and the large B of W(2) suggest that our model is an oversimplication.

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Table III. Parameters (Coordinates ×10^4) for $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$

atom	x	y	z	B_{eq}[a]
Pt	3916.0 (3)	3405.4 (3)	4951.1 (3)	0.911 (3)
Cl	2007 (3)	541 (2)	4840 (2)	2.12 (3)
K(1)	7227 (2)	278 (2)	1841 (2)	2.10 (3)
K(2)	450 (3)	7619 (3)	1464 (2)	2.56 (3)
P(1)	4543 (3)	2307 (2)	2769 (2)	1.31 (3)
P(2)	6018 (2)	3405 (2)	6924 (2)	1.30 (3)
P(3)	3143 (3)	4319 (2)	7117 (2)	1.25 (3)
P(4)	1646 (2)	3181 (2)	2991 (2)	1.28 (3)
O(1)	2901 (8)	939 (7)	1328 (7)	1.99 (9)
O(2)	5708 (8)	1668 (7)	3192 (7)	2.18 (10)
O(3)	5425 (7)	3748 (6)	1892 (6)	1.60 (8)
O(4)	7680 (8)	5285 (7)	7787 (7)	2.31 (10)
O(5)	6773 (9)	2413 (8)	6238 (7)	2.66 (12)
O(6)	5492 (8)	2860 (7)	8346 (7)	1.88 (9)
O(7)	1424 (7)	4168 (7)	6676 (7)	1.95 (9)
O(8)	3169 (8)	3455 (7)	8502 (7)	1.86 (9)
O(9)	281 (7)	3236 (8)	3684 (7)	2.16 (10)
O(10)	716 (7)	1637 (7)	1501 (7)	1.95 (9)
W(1)	8123 (9)	3134 (9)	646 (8)	3.02 (13)

[a] $B_{eq} = (8\pi^2/3)(\Sigma_i\Sigma_j U_{ij}(a_i^*a_j^*)a_ia_j)$; $\sigma(B_{eq}) = 1/(6)^{1/2}\langle\sigma(U_{ii})/U_{ii}\rangle B_{eq}$.

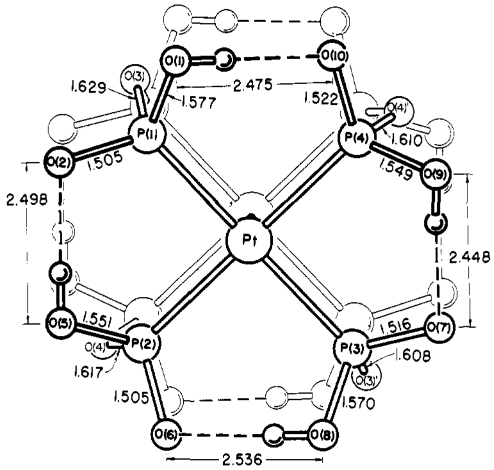

Figure 3. The $Pt_2(pop)_4$ unit. Distances and numbering are shown for "Pt_2Cl_2"; the unit is essentially unchanged in "Pt_2" and "Pt_2Br".

a goodness of fit of 2.18 ($n = 2981$, $p = 172$). Final parameters are given in Table III, and a drawing of the molecule is shown in Figure 2. A view of the $Pt_2(pop)_4$ unit is shown in Figure 3.

(c) "Pt_2". The limited information given here and in Table I was taken from ref 4 and 8 and is for comparison purposes only. Cu Kα radiation on a Nonius CAD-4 diffractometer was used. The linear absorption coefficient is 287.1 cm^{-1}. The structure was refined to an R of 0.036 for 1055 reflections with $I > 2.5\sigma(I)$.

The correct space group for this crystal is probably $P4/mbm$[8] and not $P\bar{4}b2$.[4] Although the changes in the overall structure are minor, the correction points up the very close relation between the crystal structures of "Pt_2" and "Pt_2Br". The revised atomic coordinates for "Pt_2" are given in Table IV.

Spectroscopic Measurements. Absorption spectra in the visible and ultraviolet regions were measured on a Cary 17. The resonance Raman spectrum of an aqueous solution of $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ (~10^{-2} M) at room temperature was measured by using a Spex Industries model 14018 double monochromator (2400 lines/millimeter-holographic gratings) and a Hamamatsu R455 photomultiplier tube. Argon ion laser (Spectra-Physics Model 170) excitation (514.5 nm) was employed. Vibrational frequencies were referenced to CCl_4 (estimated error ±1 cm^{-1}).

Table IV. "Pt_2": Revised Atomic Coordinates (×10^4)[a]

atom	no. in cell	x	y	z
Pt	4	0	0	3169 (0)
K(1)	4	2755 (2)	$^1/_2 + x$	0
K(2)	4	3865 (2)	$^1/_2 + x$	$^1/_2$
P	16	1153 (2)	1303 (2)	3135 (4)
O(1)	16	2150 (6)	1055 (7)	2152 (9)
O(2)	16	802 (6)	2323 (6)	2526 (12)
O(3)	8	1596 (5)	1493 (6)	$^1/_2$
W(1)	4	1013 (6)	$^1/_2 + x$	$^1/_2$

[a] Reference 8.

Table V. Selected Bond Distances and Angles

	"Pt_2"	"Pt_2Br"	"Pt_2Cl_2"
	Bond (Å)		
Pt–Pt	2.925 (1)	2.793 (1)	2.695 (1)
Pt–P	2.320 (5)	2.334 (1)	2.350 [1] (2)[a]
P–O(H)	1.579 (9)	1.562 (4)	1.557 [8] (7)[a]
P=O	1.519 (9)	1.505 (4)	1.512 [7] (7)[a]
P–O(bridging)	1.623 (6)	1.618 (3)	1.616 [8] (7)[a]
Pt–X	...	2.699 (1)	2.407 (2)
P···P	2.980 (6)	2.935 (2)	2.873 [20] (3)
O(H)···O	2.505 (19)	2.487 (5)	2.486 [32] (9)[a]
	Angle (deg)		
Pt–Pt–P	90.67 (10)	91.74 (2)	92.17 [46] (5)[a]
Pt–P–O(H)	114.0 (5)	113.4 (1)	113.9 [9] (3)[a]
Pt–P=O	118.0 (5)	117.3 (2)	115.7 [10] (3)[a]
Pt–P–O(bridge)	110.3 (4)	110.4 (2)	110.2 [10] (3)
P–O–P	133.3 (9)	130.2 (3)	125.5 [19] (4)[a]
Pt–Pt–X	...	180.00	179.00 (5)

[a] Numbers in square brackets are root-mean-square deviations of the individual values (either 2 or 4 in number) from their mean; numbers in parentheses are esd's in the individual values.

Results and Discussion

All three halides "Pt_2X" (X = Cl, Br, I) form golden or copper-bronze metallic appearing crystals that are strongly dichroic when viewed under a polarizing microscope. The electronic absorption spectrum of a polycrystalline sample of each "Pt_2X" in a KX disk exhibits a broad band that peaks at around 600 nm. The position of this band, which is completely absent in the corresponding "Pt_2X" aqueous solution spectrum, is nearly the same as that of a prominent system exhibited by a number of "platinum blue" species.[14]

Both electronic absorption and resonance Raman spectra show that "Pt_2Br" disproportionates to "Pt_2" and "Pt_2Br_2" in aqueous solution (RR peaks peaks (Pt-Pt) attributable to "Pt_2" and "Pt_2Br_2" are observed at 117 and 113 cm^{-1}, respectively). The solution disproportionation reaction is reversed during the formation of solid compounds, because $K_4[Pt_2(pop)_4X]$ can be prepared by reacting stoichiometric amounts of $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4X_2]$ in water. There is no suggestion of discrete "Pt_2" and "Pt_2Br_2" units in crystals of "Pt_2Br", because the bromine atom is located (by symmetry) exactly midway between two "Pt_2" units and its moderate $U(33)$ value (0.0382 Å^2) does not even hint at any disorder.

Surprisingly, the structures of the starting, unoxidized material "Pt_2" and of the partially oxidized bromine compound "Pt_2Br" are strikingly similar, despite the fact that "Pt_2Br" is a conductor and "Pt_2" is not. Both compounds crystallize in the tetragonal space group $P4/mbm$, with the $Pt_2(pop)_4$ units lying on fourfold axes so as to form infinite columns along c; the potassium ions and water molecules occupy the spaces between these columns. The bromine atom in "Pt_2Br" connects adjacent $Pt_2(pop)_4$ units, thereby forming a conducting chain (Pt–Br–Pt–Pt–Br), whereas "Pt_2", which lacks the connecting atom, is an insulator. The structure of the fully oxidized compound "Pt_2Cl_2" is quite different, consisting of isolated binuclear units.

Important interatomic distances and angles in the three compounds are given in Table V. The Pt–Pt distance within the $Pt_2(pop)_4$ units decreases from 2.925 (1) Å in "Pt_2" to 2.695 (1) Å in "Pt_2Cl_2", consistent with the depopulation of the dσ* level in the Pt(III) complex ("Pt_2" is (dσ)^2(dσ*)^2, "Pt_2Cl_2" is (dσ)^2.[6] It

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Table VI. K···O and K···Cl Distances (Å) in the Three Compounds

	atoms	"Pt_2" K···O	"Pt_2Br" K···O	"Pt_2Cl_2" atom	"Pt_2Cl_2" K···atom
K(1)	4 O(2)	2.847 (13)	2.912 (6)	O(2)	2.689 (7)
	4 O(1)	2.848 (14)	2.915 (5)	O(9)	2.770 (7)
				O(1)	2.785 (7)
				O(6)	2.793 (7)
				W	2.872 (8)
				O(10)	2.996 (7)
				Cl	3.157 (3)
				O(8)	3.351 (7)
K(2)	2 W	2.869 (8)	2.835 (2)	W	2.692 (8)
	4 O(2)	2.886 (13)	2.875 (5)	O(7)	2.791 (7)
	2 O(3)	3.222 (8)	3.272 (7)	O(1)	2.920 (7)
				O(10)	2.935 (7)
				O(5)	2.976 (8)
				O(8)	3.059 (7)
				Cl	3.213 (3)
				O(4)	3.281 (7)

has been noted[15] that the Pt–Pt distance in several highly conducting platinum complexes varies linearly with the formal oxidation state of Pt, and we find that the Pt–Pt distance in "Pt_2Br", with formal oxidation state +2.5 (and orbital configuration $(d\sigma)^2(d\sigma^*)^1$), is approximately midway between those in "Pt_2" and "Pt_2Cl_2". The Pt–Pt distance in "Pt_2" is shorter than in some other Pt(II) compounds,[16] suggesting appreciable metal–metal bonding; however, the distance in "Pt_2Cl_2" is longer than in the following three binuclear Pt(III) complexes: $Pt_2(SO_4)_4(H_2O_2)^{2-}$ (2.466 (?) Å);[17] $Pt_2(H_2PO_4)_4(H_2O)_2{}^{2-}$ (2.486 (2) Å);[18] and $Pt_2(SO_4)_4(OSMe)_2{}^{2-}$ (2.471 (1) Å).[19] The constraining effect of the bridging sulfato or phosphato ligands likely is one reason for the shorter Pt–Pt distances in the latter complexes; in analogous Rh(II) species, the Rh–Rh distances range from 2.3 to 2.8 Å (depending on the nature of the bridging ligands),[20] and we can expect a similar range in binuclear Pt(III) units.

The Pt–Cl distance in "Pt_2Cl_2" (2.407 (2) Å) is somewhat longer than a normal single bond (~2.33 Å),[21-23] suggesting that a Pt–Pt structural trans effect is operative. Evidence that a Pt–Pt kinetic trans effect also is important in this binuclear complex has come from studies in which we have found that the coordinated chloride is relatively substitution labile.[24]

Aside from the variations in the Pt–Pt distances, the $Pt_2(pop)_4$ units (see Figure 3) are remarkably similar in the three compounds. Thus, as the Pt–Pt distance shrinks by 0.23 Å in going from "Pt_2" to "Pt_2Cl_2", the P···P distance decreases by only 0.11 Å (Table V), the P–O–P angle closes by about 8°, and the Pt–P bonds lengthen only slightly. Other dimensions remain nearly constant. The rigidity of the $Pt_2(pop)_4$ cluster is no doubt due, in part, to pairs of very strong O–H···O hydrogen bonds between adjacent $H_2O_5P_2$ units (Figure 3). Although we have not located the hydrogen atoms in any of the structures, the P—O distances (Table V) indicate the atoms to which the protons are attached; the average values of the bond lengths P—O(H), 1.564 (3) Å, P=O, 1.508 (3) Å, and P—O(bridging), 1.618 (2) Å, are all in good agreement with standard values. Thus, although the O···O distance is in the range where symmetric hydrogen bonds may be found, the bonds are clearly asymmetric. In all three compounds the OH groups occupy the same relative positions in the $Pt_2(pop)_4$ unit (Figure 3).

The potassium ions are very important to the stabilities of all three compounds. In all cases they have eight neighboring oxygen atoms, at distances ranging from 2.69 to 3.35 Å (see Table VI). The most regular array of neighbors is seen by atoms K(1) of the tetragonal compounds "Pt_2" and "Pt_2Br"; coordination about the other potassium ions is very irregular. A chlorine atom is included in the coordination group about each potassium ion in the fully oxidized compound "Pt_2Cl_2".

The water molecule in "Pt_2Cl_2" is hydrogen bonded to diphosphite ions (O···O = 2.73 and 2.96 Å). Surprisingly, the water molecules in the other two compounds form no such bonds; other than occupying coordination sites about the potassium ions, they seem to serve little purpose. We note in particular that the increase in length of the *c* axis in "Pt_2Br" relative to "Pt_2" (required by the insertion of the Br atoms into the Pt chain) enlarges the cavity occupied by water molecules and results in disorder and an additional, partially occupied water site W(2).

The structure of these three platinum diphosphite complexes can be described on the basis of roughly cylindrical $Pt_2(pop)_4$ "barrels" held together by strong K^+–O interactions. In "Pt_2" and "Pt_2Br" the barrels stack end-to-end, forming columns along the direction of the *c* axis. End-to-end stacking does not occur in "Pt_2Cl_2", presumably because of the Cl···Cl repulsions that would result. Within the barrels in each complex, the Pt–Pt distance adjusts according to the oxidation state of the platinum. In "Pt_2Br", where Pt has a formal oxidation state of 2.5, the bromine atom serves to connect adjacent barrels within each column so as to form a conducting pathway along *c*; "Pt_2" (oxidation state 2) is nonconducting.

It is easy to imagine that species other than bromine might occupy the gap between adjacent barrels of partially oxidized materials and similarly provide a pathway for conduction. Indeed, we have isolated "Pt_2Cl" and "Pt_2I" compounds that exhibit significant conductivities. Controlled incorporation of varying amounts of halogen and uncharged bridging groups such as pyrazine might well lead to interesting conducting materials in which the average oxidation state of Pt could be varied from 2 to 2.5.

The –Pt_2–Br–Pt_2–chain observed in $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ is the first example of a symmetric Pt–X–Pt unit in a crystal. The relatively small changes in the structures of the barrels from "Pt_2" to "Pt_2Cl_2" suggest that atom-transfer reactions between "Pt_2" and "Pt_2X_2" species should be relatively facile in solution.

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Registry No. "Pt_2", 80011-26-3; "Pt_2Br", 85553-24-8; "Pt_2I", 85553-25-9; "Pt_2Cl", 85553-26-0; "Pt_2Cl_2", 82135-56-6.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters for "Pt_2Br" and "Pt_2Cl_2" (37 pages). Ordering information is given on any current masthead page.

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