

by differences in electron occupation of the molecular orbitals. Instead, the varying coordination geometries can be rationalized by the increase of d-orbital energies. An analogy can be made to the structures of $\text{Mo}(\text{bdt})_3$, $\text{Nb}(\text{bdt})_3^-$, and $\text{Zr}(\text{bdt})_3^{2-}$, which vary from trigonal prismatic to a distorted octahedron.²⁵⁻²⁷ The increase in the energies of the metal d orbitals is paralleled by a structural change. This can be related to the $4e'$ molecular orbital of Gray's scheme, which consists of metal and ligand character. As the d metal orbitals increase in energy, the $4e'$ orbital becomes more ligand in character and the ligands assume more dithiolate character. Thus, the relationship between coordination type and metal d-orbital energies is applicable to first-row transition-metal dithiolenes.

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Registry No. $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Mn}(\text{DDDT})_3]$, 124022-58-8; $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Nb}(\text{DDDT})_3]$, 124022-60-2; $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Ti}(\text{DDDT})_3]$, 124022-62-4; $[\text{Mn}(\text{DDDT})_3]^{3-}$, 124022-63-5; $[\text{Nb}(\text{DDDT})_3]^-$, 124022-64-6; $[\text{Nb}(\text{DDDT})_3]^{3-}$, 124022-65-7; $[\text{Nb}(\text{DDDT})_3]^{3-}$, 124022-66-8.

Supplementary Material Available: Tables SI-SV, listing crystallographic data, cation positional parameters, remaining bond angles, anisotropic thermal parameters, and hydrogen coordinates (9 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structures of Potassium Bis(μ -hydroxo)bis[dinitritoplatinate(II)] Sesquihydrate and Potassium *cyclo*-Tris(μ_3 -oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) Trihydrate

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The reaction of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ with dilute sulfuric acid has been investigated. At least two polynuclear complexes are formed in the reaction. The first, $\text{K}_2[\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$, is a hydroxo-bridged dimer of Pt(II). Crystal data are space group *Ibca*, $a = 11.879$ (6) Å, $b = 13.094$ (4) Å, $c = 32.060$ (11) Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4987$ (4) Å³, $Z = 16$, $R = 0.065$, and $R_w = 0.058$. The second, $\text{K}_5[\text{Pt}_4(\text{NO}_2)_9\text{O}_3] \cdot 3\text{H}_2\text{O}$, is a mixed-valence tetranuclear complex with a trinitritoplatinate(IV) unit oxo bridged to three *cyclo*-(μ_3 -oxo)dinitritoplatinate(II) units. Crystal data are space group *P* $\bar{1}$, $a = 9.940$ (2) Å, $b = 10.069$ (2) Å, $c = 15.206$ (3) Å, $\alpha = 72.15$ (1)°, $\beta = 74.69$ (1)°, $\gamma = 72.24$ (1)°, $V = 1354.9$ (4) Å³, $Z = 2$, $R = 0.032$, and $R_w = 0.032$.

Introduction

Recently, it has been demonstrated that $\text{K}_2\text{Pt}(\text{NO}_2)_4$ reacts with concentrated sulfuric or phosphoric acids to give respectively sulfate^{1,2} or phosphate^{2,3}-bridged dimeric metal-metal-bonded Pt(III) anionic complexes. This and other work has led to the recognition that there is a large class of relatively stable binuclear Pt(III) compounds with metal-metal bonds. It has been known for more than a century that $\text{K}_2\text{Pt}(\text{NO}_2)_4$ also reacts with dilute acids to give polynuclear products.⁴ These compounds have not been extensively investigated except that chemical studies of a red metallic appearing species have resulted in the suggestion that it is an ordered stacking of oxo-bridged trimeric molecules.⁵

Herein, we report the structures of two different polynuclear platinum complexes that result from the reaction of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ with dilute sulfuric acid.

Experimental Section

Preparation of Compounds. In a 5-mL round-bottom flask, 0.050 g of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ was dissolved in 1.0 mL of 0.22 M H_2SO_4 . The solution was stirred for 20 min at 85 °C, during which time the solution changed

Table I. Crystallographic Data

Potassium Bis(μ -hydroxo)bis[dinitritoplatinate(II)] Sesquihydrate	
$\text{K}_2[\text{Pt}(\text{NO}_2)_4(\text{OH})_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$	fw = 713.44
$a = 11.879$ (6) Å	space group <i>Ibca</i> (No. 73)
$b = 13.094$ (4) Å	$T = 24$ °C
$c = 32.060$ (11) Å	$\lambda = 0.71069$ Å (Mo K α)
$\alpha = \beta = \gamma = 90^\circ$	$\rho_{\text{calcd}} = 3.80$ g cm ⁻³
$V = 4987$ (4) Å ³	$\mu = 234$ cm ⁻¹ (Mo K α)
$Z = 16$	transm coeff = 0.06-0.59
$R(F_o) = 0.065$	$R_w(F_o) = 0.058$
Potassium	
<i>cyclo</i> -Tris(μ_3 -oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) Trihydrate	
$\text{K}_5[\text{Pt}_4(\text{NO}_2)_9\text{O}_3] \cdot 3\text{H}_2\text{O}$	fw = 1491.96
$a = 9.940$ (2) Å	space group <i>P</i> $\bar{1}$ (No. 2)
$b = 10.069$ (2) Å	$T = 24$ °C
$c = 15.206$ (3) Å	$\lambda = 0.71069$ Å (Mo K α)
$\alpha = 72.15$ (1)°	$\rho_{\text{calcd}} = 3.66$ g cm ⁻³
$\beta = 74.69$ (1)°	$\mu = 217$ cm ⁻¹ (Mo K α)
$\gamma = 72.24$ (1)°	transm coeff = 0.006-0.165
$V = 1354.9$ (4) Å ³	$R(F_o) = 0.032$
$Z = 2$	$R_w(F_o) = 0.032$

from colorless to blue to dark green. The solution was then evaporated to dryness by evacuation. The solid was dissolved in 0.5 mL of 0.22 M H_2SO_4 to form a red solution, the solution evaporated to dryness, the solid redissolved in 1 to 2 mL of water, and the new solution neutralized to pH 7.0 with K_2CO_3 . The resulting yellow solution was allowed to evaporate to dryness in a cold room, yielding solid material containing colorless and yellow crystals. The colorless crystals were presumed to

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Table II. $K_2[Pt_2(NO_2)_4(OH)_2] \cdot 1\frac{1}{2}H_2O$: Atom Coordinates and Isotropic Temperature Factors (\AA^2) with Standard Deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
Pt(1)	0.5117 (1)	0.1249 (1)	0.6098 (1)	0.019 (1) ^a
Pt(2)	0.2657 (1)	0.1370 (1)	0.6415 (1)	0.020 (1) ^a
O(1)	0.426 (1)	0.112 (1)	0.664 (1)	0.025 (4)
O(2)	0.351 (1)	0.124 (1)	0.587 (1)	0.024 (4)
N(1)	0.569 (2)	0.133 (2)	0.555 (1)	0.032 (5)
O(11)	0.648 (2)	0.193 (1)	0.542 (1)	0.033 (4)
O(12)	0.534 (2)	0.076 (2)	0.529 (1)	0.068 (7)
N(2)	0.658 (2)	0.114 (1)	0.640 (1)	0.027 (4)
O(21)	0.656 (2)	0.113 (1)	0.677 (1)	0.056 (6)
O(22)	0.750 (2)	0.110 (1)	0.619 (1)	0.047 (5)
N(3)	0.208 (2)	0.153 (1)	0.697 (1)	0.019 (4)
O(31)	0.252 (2)	0.109 (1)	0.726 (1)	0.045 (5)
O(32)	0.120 (2)	0.206 (1)	0.706 (1)	0.046 (5)
N(4)	0.120 (2)	0.152 (1)	0.610 (1)	0.028 (5)
O(41)	0.032 (2)	0.125 (1)	0.625 (1)	0.040 (5)
O(42)	0.119 (2)	0.183 (1)	0.575 (1)	0.050 (6)
O(3) ^b	0.5000	0.2500	0.721 (1)	0.027 (5)
O(4) ^b	0.535 (2)	0.0000	0.7500	0.041 (7)
O(5) ^b	0.2500	0.446 (2)	0.0000	0.070 (10)
K(1) ^b	0.3895 (4)	0.5866 (4)	0.1947 (3)	0.067 (3) ^a
K(2) ^b	0.1183 (5)	0.0981 (5)	0.0514 (3)	0.080 (3) ^a

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b The potassium and water oxygen atoms are not shown in Figure 1.

be simple potassium salts and were not studied further. Most of the yellow crystals were very thin plates, while a few thicker, darker yellow crystals were also present.

The crystals were separated from each other manually and recrystallized by cooling a saturated neutral aqueous solution from room temperature. Anal. Calcd for $H_6N_9O_{24}K_5Pt_4$: N, 8.4; Pt, 52.3. Found: N, 8.2; Pt, 50.8. X-ray structure determinations established that these were potassium salts of the dimeric and tetranuclear anions $[Pt_2(NO_2)_4(OH)_2]^{2-}$ and $[Pt_4(NO_2)_9O_3]^{5-}$, respectively.

Structure Determinations and Refinements. $K_2[Pt_2(NO_2)_4(OH)_2] \cdot 1\frac{1}{2}H_2O$. A thin plate-shaped pale yellow crystal (approximately $0.013 \times 0.36 \times 0.50$ mm) was mounted on a glass fiber for crystallographic data collection. Unit cell dimensions were obtained by least-squares refinement using 15 centered reflections for which $16^\circ < 2\theta < 28^\circ$ (graphite-monochromatized Mo $K\alpha$ radiation). Intensity data were taken on a Nicolet R3mE four-circle diffractometer. Three check reflections, monitored every 100 reflections, showed approximately 15% loss of intensity during the course of data collection, and the intensity data were scaled accordingly. Crystallographic data for this compound appear in Table I.

Data reduction,⁶ including corrections for Lorentz and polarization effects, gave 4540 independent reflections in the range $4^\circ < 2\theta < 65^\circ$, of which 1877 with $I > 3\sigma(I)$ were used for structure refinement. Axial photographs and diffraction data showed orthorhombic symmetry, and systematic absences uniquely determined the space group as *Ibca*. The platinum positions were determined from a Patterson synthesis, and the remaining non-hydrogen positions were located by difference syntheses. The small crystal volume resulted in too few observed data for anisotropic refinement of all atoms. Consequently, anisotropic thermal parameters were used for the platinum and potassium atoms, and isotropic refinement was used for nitrogen and oxygen positions. The structure was refined by block-cascade least squares, minimizing $\sum w\Delta^2$ with 101 parameters refined in each full-matrix block. Absorption corrections were calculated by Gaussian integration using measured crystal dimensions between indexed crystal faces. Atomic scattering factors, including terms for anomalous scattering, were taken from ref 7. The weighting scheme used was $w = k(\sigma^2(F_o) + 0.0001F_o^2)^{-1}$. No corrections for extinction were needed. Hydrogen positions could not be located on difference maps, and the final difference map was featureless except for the usual ripple near the platinum positions. Atom coordinates are given in Table II.

$K_5[Pt_4(NO_2)_9O_3] \cdot 3H_2O$. A yellow plate-shaped crystal (approximately $0.085 \times 0.34 \times 0.70$ mm) was mounted on a glass fiber. Unit cell

Table III. $K_5[Pt_4(NO_2)_9O_3] \cdot 3H_2O$: Atom Coordinates and Equivalent Isotropic Temperature Factors (\AA^2) with Standard Deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i> ^a
Pt(1)	0.0595 (1)	0.2004 (1)	0.3804 (1)	0.019 (1)
Pt(2)	0.3470 (1)	0.2656 (1)	0.2632 (1)	0.019 (1)
Pt(3)	0.0567 (1)	0.3895 (1)	0.1702 (1)	0.021 (1)
Pt(4)	0.2142 (1)	0.0715 (1)	0.2104 (1)	0.019 (1)
O(1)	0.0208 (5)	0.1977 (5)	0.2555 (4)	0.022 (2)
O(2)	0.2601 (5)	0.0920 (5)	0.3273 (3)	0.022 (2)
O(3)	0.2651 (5)	0.2652 (5)	0.1545 (3)	0.022 (2)
N(1a)	0.1197 (7)	0.1843 (7)	0.4976 (4)	0.027 (2)
O(11a)	0.0990 (7)	0.2879 (7)	0.5306 (4)	0.042 (3)
O(12a)	0.1876 (8)	0.0669 (7)	0.5370 (4)	0.050 (3)
N(1b)	-0.1353 (6)	0.3177 (7)	0.4201 (5)	0.029 (2)
O(11b)	-0.1522 (7)	0.4334 (8)	0.4379 (6)	0.055 (3)
O(12b)	-0.2441 (6)	0.2814 (8)	0.4236 (5)	0.044 (3)
N(2a)	0.4272 (6)	0.2470 (7)	0.3753 (4)	0.024 (2)
O(21a)	0.5086 (7)	0.1288 (7)	0.4046 (4)	0.040 (2)
O(22a)	0.3939 (7)	0.3417 (8)	0.4172 (5)	0.045 (3)
N(2b)	0.4210 (7)	0.4363 (7)	0.1885 (5)	0.031 (2)
O(21b)	0.4032 (8)	0.4510 (7)	0.2193 (5)	0.052 (3)
O(22b)	0.4782 (7)	0.4380 (8)	0.1050 (4)	0.047 (3)
N(3a)	-0.1514 (7)	0.4880 (7)	0.1818 (5)	0.031 (2)
O(31a)	-0.1948 (7)	0.6213 (7)	0.1554 (6)	0.050 (3)
O(32a)	-0.2400 (7)	0.4159 (8)	0.2103 (6)	0.058 (3)
N(3b)	0.1150 (7)	0.5662 (7)	0.0893 (5)	0.035 (3)
O(31b)	0.1705 (10)	0.5740 (8)	0.0065 (5)	0.063 (4)
O(32b)	0.1040 (8)	0.6665 (8)	0.1236 (6)	0.061 (4)
N(4a)	0.4176 (7)	-0.0449 (7)	0.1688 (5)	0.032 (2)
O(41a)	0.5182 (9)	-0.0252 (14)	0.1857 (10)	0.089 (7)
O(42a)	0.4337 (10)	-0.1332 (12)	0.1253 (9)	0.074 (5)
N(4b)	0.1551 (7)	-0.1150 (7)	0.2809 (5)	0.028 (2)
O(41b)	0.2281 (7)	-0.2031 (7)	0.3366 (5)	0.048 (3)
O(42b)	0.0438 (7)	-0.1367 (7)	0.2723 (5)	0.043 (3)
N(4c)	0.1623 (7)	0.0800 (7)	0.0880 (4)	0.029 (2)
O(41c)	0.2461 (9)	0.1192 (10)	0.0155 (5)	0.062 (4)
O(42c)	0.0519 (8)	0.0539 (10)	0.0867 (6)	0.068 (4)
O(4) ^b	0.2670 (8)	0.1887 (9)	0.6794 (5)	0.057 (3)
O(5) ^b	0.2707 (8)	0.8320 (9)	-0.1090 (6)	0.060 (3)
O(6) ^b	0.4381 (8)	0.3946 (9)	0.6353 (7)	0.068 (4)
K(1) ^b	0.5726 (2)	0.1415 (2)	0.5729 (1)	0.036 (1)
K(2) ^b	0.7771 (2)	0.1172 (2)	0.2889 (1)	0.038 (1)
K(3) ^b	0.1402 (3)	0.1202 (2)	-0.1333 (2)	0.045 (1)
K(4) ^b	0.1329 (2)	0.5445 (2)	0.3703 (2)	0.047 (1)
K(5) ^b	0.3934 (2)	0.3358 (2)	-0.0361 (2)	0.042 (1)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b The potassium and water oxygen atoms are not shown in Figure 2.

dimensions were obtained from 24 reflections with $28^\circ < 2\theta < 31^\circ$. Axial photographs showed triclinic symmetry, and the centrosymmetric space group was assumed and later confirmed by successful structure solution and refinement. Crystallographic data for this compound appear in Table I. Data reduction gave 9836 unique reflections in the range $4^\circ < 2\theta < 65^\circ$, of which 7753 with $I > 3\sigma(I)$ were used for structure refinement. The four platinum positions were obtained by direct methods, using agreement with a Patterson synthesis to identify the correct heavy-atom positions. Other non-hydrogen atoms were located by difference syntheses. Absorption corrections were made as above; extinction corrections were not needed. The structure was refined with anisotropic thermal parameters by using procedures described above. Atom coordinates are given in Table III.

During the last stages of structure refinement, one of the nitrite groups showed rather large thermal parameters for the oxygen atoms (O(41a) and O(42a)), indicating possible disorder. Small peaks on the final difference map suggested an alternative orientation of the nitrite group, rotated about 70° from the major orientation. The final difference map also showed possible hydrogen positions for the water molecules and the usual ripple near the platinum positions. No peaks were found near the bridging oxygen positions. Water hydrogen atoms were not included in the structure refinement.

Results and Discussion

$K_2[Pt_2(NO_2)_4(OH)_2] \cdot 1\frac{1}{2}H_2O$. The structure of the dimeric anion is shown in Figure 1. It has precedent in the analogous cation $[Pt_2(NH_3)_4(OH)_2]^{2+}$, for which X-ray structure determinations have been carried out on the nitrate⁸ and carbonate⁹

(6) All crystallographic calculations were performed on a Data General Eclipse computer using a SHELXTL program package by G. M. Sheldrick, Nicolet Instrument Corp., Madison, WI.

(7) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72-98, 149-150.

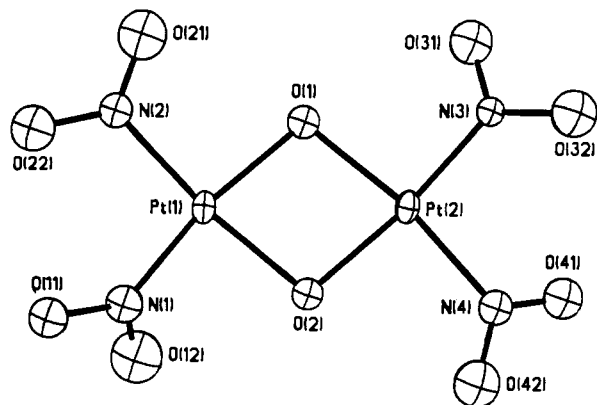


Figure 1. Thermal ellipsoid drawing (50% probability) of the Pt₂(NO₂)₄(OH)₂²⁻ anion. Platinum atoms were refined with anisotropic thermal parameters; nitrogen and oxygen atoms with isotropic thermals.

Table IV. K₂[Pt₂(NO₂)₄(OH)₂] \cdot 1 $\frac{1}{2}$ H₂O: Bond Lengths (Å) and Angles (deg) with Standard Deviations

Bond Lengths			
Pt(1)–O(1)	2.02 (2)	Pt(1)–O(2)	2.05 (2)
Pt(1)–N(1)	1.90 (3)	Pt(1)–N(2)	1.99 (2)
Pt(2)–O(1)	2.06 (2)	Pt(2)–O(2)	2.04 (2)
Pt(2)–N(3)	1.90 (2)	Pt(2)–N(4)	2.01 (2)
N(1)–O(11)	1.28 (3)	N(1)–O(12)	1.19 (4)
N(2)–O(21)	1.19 (4)	N(2)–O(22)	1.28 (3)
N(3)–O(31)	1.22 (4)	N(3)–O(32)	1.29 (3)
N(4)–O(41)	1.20 (3)	N(4)–O(42)	1.20 (4)

Bond Angles			
O(1)–Pt(1)–O(2)	81 (1)	O(1)–Pt(1)–N(1)	171 (1)
O(2)–Pt(1)–N(1)	90 (1)	O(1)–Pt(1)–N(2)	91 (1)
O(2)–Pt(1)–N(2)	171 (1)	N(1)–Pt(1)–N(2)	98 (1)
O(1)–Pt(2)–O(2)	80 (1)	O(1)–Pt(2)–N(3)	92 (1)
O(2)–Pt(2)–N(3)	171 (1)	O(1)–Pt(2)–N(4)	170 (1)
O(2)–Pt(2)–N(4)	90 (1)	N(3)–Pt(2)–N(4)	98 (1)
Pt(1)–O(1)–Pt(2)	99 (1)	Pt(1)–O(2)–Pt(2)	99 (1)
Pt(1)–N(1)–O(11)	127 (2)	Pt(1)–N(1)–O(12)	119 (2)
O(11)–N(1)–O(12)	114 (3)	Pt(1)–N(2)–O(21)	118 (2)
Pt(1)–N(2)–O(22)	120 (2)	O(21)–N(2)–O(22)	122 (3)
Pt(2)–N(3)–O(31)	121 (2)	Pt(2)–N(3)–O(32)	125 (2)
O(31)–N(3)–O(32)	115 (2)	Pt(2)–N(4)–O(41)	122 (2)
Pt(2)–N(4)–O(42)	121 (2)	O(41)–N(4)–O(42)	117 (3)

salts. As was done with the cationic dimer, we assign the valence of platinum as Pt(II) on the basis of the square-planar bonding geometry and the absence of any evidence of a Pt–Pt bond. The crystallographic data do not permit a determination of whether the bridging ligands are oxo or hydroxo groups. However, charge balance considerations indicate a hydroxo-bridged formulation, if the platinum oxidation state is Pt(II). The presence of an infrared band at 946 cm⁻¹, which can be assigned to the bridging O–H bending mode,⁸ supports the suggested formulation, as does the correspondence with the structure of the cationic dimer. Bond lengths and angles are given in Table IV.

A striking feature of the crystal structure of the dimeric compound is the pairing of anionic units by hydrogen bonding, giving a rather short nonbonded Pt–Pt separation of 3.29 (2) Å between paired dimers. The paired anions are related by a crystallographic 2-fold rotation axis, and the hydrogen bonding involves the protons of bridging hydroxo groups, a nitrito oxygen, and a lattice water molecule located on the 2-fold axis. The arrangement is illustrated in Figure 2.

The pairing is remarkably similar to that observed in the crystal structure of the carbonate salt of the [Pt₂(NH₃)₄(OH)₂]²⁺ cation, where the paired cations are related by an inversion center and the Pt–Pt separation is 3.17 Å.⁹ However, the nature of the hydrogen bonding is completely different. Hydrogen bonding

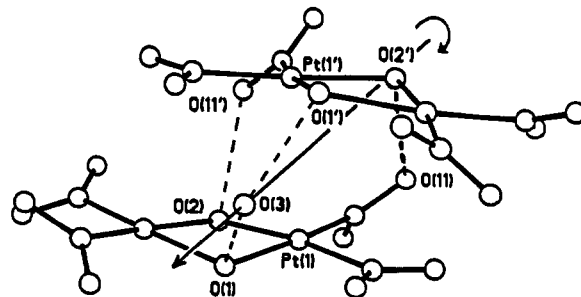


Figure 2. Paired dimer units related by a crystallographic 2-fold rotation axis (arrow). Hydrogen bonding between anionic units (dashed lines) involves a water molecule (O(3)) located on the 2-fold axis.

Table V. K₅[Pt₄(NO₂)₉O₃] \cdot 3H₂O: Bond Lengths (Å) and Angles (deg) with Standard Deviations

Bond Lengths			
Pt(1)–O(1)	2.045 (6)	Pt(1)–O(2)	2.045 (4)
Pt(1)–N(1a)	1.972 (7)	Pt(1)–N(1b)	1.983 (6)
Pt(2)–O(2)	2.045 (5)	Pt(2)–O(3)	2.028 (6)
Pt(2)–N(2a)	2.002 (7)	Pt(2)–N(2b)	1.979 (9)
Pt(3)–O(1)	2.044 (5)	Pt(3)–O(3)	2.063 (4)
Pt(3)–N(3a)	1.989 (6)	Pt(3)–N(3b)	1.982 (7)
Pt(4)–O(1)	2.032 (4)	Pt(4)–O(2)	2.030 (6)
Pt(4)–O(3)	2.035 (5)	Pt(4)–N(4a)	2.049 (6)
Pt(4)–N(4b)	2.031 (7)	Pt(4)–N(4c)	2.030 (8)
N(1a)–O(11a)	1.23 (1)	N(1a)–O(12a)	1.23 (1)
N(1b)–O(11b)	1.23 (1)	N(1b)–O(12b)	1.23 (1)
N(2a)–O(21a)	1.24 (1)	N(2a)–O(22a)	1.22 (1)
N(2b)–O(21b)	1.23 (1)	N(2b)–O(22b)	1.24 (1)
N(3a)–O(31a)	1.25 (1)	N(3a)–O(32a)	1.22 (1)
N(3b)–O(31b)	1.22 (1)	N(3b)–O(32b)	1.24 (1)
N(4a)–O(41a)	1.18 (2)	N(4a)–O(42a)	1.21 (2)
N(4b)–O(41b)	1.23 (1)	N(4b)–O(42b)	1.24 (1)
N(4c)–O(41c)	1.23 (1)	N(4c)–O(42c)	1.21 (1)

Bond Angles			
O(1)–Pt(1)–O(2)	81.3 (2)	O(1)–Pt(1)–N(1a)	172.7 (2)
O(2)–Pt(1)–N(1a)	91.6 (2)	O(1)–Pt(1)–N(1b)	94.8 (3)
O(2)–Pt(1)–N(1b)	174.7 (2)	N(1a)–Pt(1)–N(1b)	92.4 (3)
O(2)–Pt(2)–O(3)	81.9 (2)	O(2)–Pt(2)–N(2a)	93.2 (2)
O(3)–Pt(2)–N(2a)	174.7 (2)	O(2)–Pt(2)–N(2b)	173.3 (3)
O(3)–Pt(2)–N(2b)	91.5 (3)	N(2a)–Pt(2)–N(2b)	93.5 (3)
O(1)–Pt(3)–O(3)	81.0 (2)	O(1)–Pt(3)–N(3a)	93.9 (2)
O(3)–Pt(3)–N(3a)	172.2 (3)	O(1)–Pt(3)–N(3b)	173.4 (2)
O(3)–Pt(3)–N(3b)	92.7 (2)	N(3a)–Pt(3)–N(3b)	92.6 (3)
O(1)–Pt(4)–O(2)	82.0 (2)	O(1)–Pt(4)–O(3)	82.0 (2)
O(2)–Pt(4)–O(3)	82.1 (2)	O(1)–Pt(4)–N(4a)	174.8 (3)
O(2)–Pt(4)–N(4a)	93.9 (3)	O(3)–Pt(4)–N(4a)	94.3 (2)
O(1)–Pt(4)–N(4b)	93.9 (2)	O(2)–Pt(4)–N(4b)	92.1 (3)
O(3)–Pt(4)–N(4b)	173.3 (3)	N(4a)–Pt(4)–N(4b)	89.5 (3)
O(1)–Pt(4)–N(4c)	93.9 (2)	O(2)–Pt(4)–N(4c)	172.3 (2)
O(3)–Pt(4)–N(4c)	91.0 (3)	N(4a)–Pt(4)–N(4c)	89.8 (3)
N(4b)–Pt(4)–N(4c)	94.6 (3)	Pt(1)–O(1)–Pt(3)	102.2 (3)
Pt(1)–O(1)–Pt(4)	98.0 (2)	Pt(3)–O(1)–Pt(4)	97.0 (2)
Pt(1)–O(2)–Pt(2)	97.9 (2)	Pt(1)–O(2)–Pt(4)	98.1 (2)
Pt(2)–O(2)–Pt(4)	96.9 (2)	Pt(2)–O(3)–Pt(3)	106.6 (2)
Pt(2)–O(3)–Pt(4)	97.3 (2)	Pt(3)–O(3)–Pt(4)	96.3 (2)
Pt(1)–N(1a)–O(11a)	123.2 (5)	Pt(1)–N(1a)–O(12a)	118.4 (6)
O(11a)–N(1a)–O(12a)	118.3 (8)	Pt(4)–N(1b)–O(11b)	121.3 (6)
Pt(1)–N(1b)–O(12b)	121.5 (6)	O(11b)–N(1b)–O(12b)	117.1 (6)
Pt(2)–N(2a)–O(21a)	116.3 (6)	Pt(2)–N(2a)–O(22a)	123.2 (5)
O(21a)–N(2a)–O(22a)	120.4 (7)	Pt(2)–N(2b)–O(21b)	122.8 (5)
Pt(2)–N(2b)–O(22b)	116.5 (7)	O(21b)–N(2b)–O(22b)	120.5 (7)
Pt(3)–N(3a)–O(31a)	122.3 (6)	Pt(3)–N(3a)–O(32a)	119.2 (5)
O(31a)–N(3a)–O(32a)	118.3 (7)	Pt(3)–N(3b)–O(31b)	120.6 (7)
Pt(3)–N(3b)–O(32b)	120.1 (6)	O(31b)–N(3b)–O(32b)	119.1 (8)
Pt(4)–N(4a)–O(41a)	120.6 (8)	Pt(4)–N(4a)–O(42a)	119.1 (7)
O(41a)–N(4a)–O(42a)	120.3 (9)	Pt(4)–N(4b)–O(41b)	118.5 (6)
Pt(4)–N(4b)–O(42b)	121.2 (5)	O(41b)–N(4b)–O(42b)	120.2 (7)
Pt(4)–N(4c)–O(41c)	116.2 (7)	Pt(4)–N(4c)–O(42c)	121.5 (5)
O(41c)–N(4c)–O(42c)	122.3 (9)		

between cation pairs involves the protons of coordinated NH₃ groups and the oxygen atoms of the bridging hydroxo groups. There is also hydrogen bonding between the hydroxo and NH₃ protons and the carbonate anions. Hydrogen bonding between the paired cations involves a proton and two ligand atoms (Pt–N–H...O–Pt), while in the paired anions of K₂[Pt₂(NO₂)₄–

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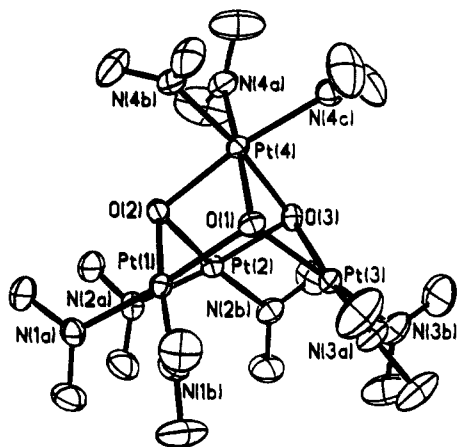


Figure 3. Thermal ellipsoid drawing (50% probability) of the $\text{Pt}_4(\text{NO}_2)_9\text{O}_3^{5-}$ anion.

$(\text{OH})_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$, there is an additional atom involved ($\text{Pt}-\text{N}-\text{O} \cdots \text{H}-\text{O}-\text{Pt}$ and $\text{Pt}-\text{O}-\text{H} \cdots \text{O} \cdots \text{H}-\text{O}-\text{Pt}$). This allows for shorter hydrogen bonds in the anion pair, $\text{O}-\text{H} \cdots \text{O} = 2.72 \text{ \AA}$ (OH to water) and $\text{O}-\text{H} \cdots \text{O} = 2.81 \text{ \AA}$ (OH to nitrito oxygen), than in the cation pair, $\text{N}-\text{H} \cdots \text{O} = 2.86$ and 3.09 \AA , even though the Pt–Pt distance is shorter in the cation pair. It has been proposed that in the carbonate salt there is a charge repulsion between the platinum atoms of the paired dimer units, resulting in a small displacement (0.09 \AA) of the platinum atoms from their ligand planes.⁹ No significant displacement is seen for the analogous platinum atoms in the anion pair we have studied or for the platinum atoms of the nitrate salt of $[\text{Pt}_2(\text{NH}_3)_4(\text{OH})_2]^{2+}$. The latter displays chaining of cation complexes by hydrogen bonding in the crystal structure,⁸ rather than pairing as described above.

$\text{K}_5[\text{Pt}_4(\text{NO}_2)_9\text{O}_3] \cdot 3\text{H}_2\text{O}$. The structure of the tetranuclear anion $[\text{Pt}_4(\text{NO}_2)_9\text{O}_3]^{5-}$ is shown in Figure 3. It features a six-coordinate platinum ion oxo bridged to three four-coordinate platinum ions,

which form a triangle bridged by the same three oxygen atoms. There are three nitrito ligands on the unique platinum and two on each of the other three platinum giving the anionic complex approximate C_{3v} symmetry. The coordination geometries and overall charge balance lead to the conclusion that the unique platinum is Pt(IV) and the others are Pt(II). No band is observed in the infrared spectrum that could be assigned to a bridging OH bending mode, in contrast to what is observed for the dimer reported above. Bond lengths and angle are given in Table V.

The Pt(II) part of this complex is analogous to the *cyclo-tris*(μ -hydroxo)tris[*cis*-diammineplatinum(II)] cation whose molecular structure has been reported as the carbonate salt.⁹ In this complex, three diammineplatinum(II) units form a ring with bridging by hydroxo groups. In our complex, the hydroxo protons have been replaced by a trinitritoplatinate(IV) group. Interestingly, a second conformation has been reported for the trimer. As the nitrate salt, one hydroxo oxygen is below the plane of the platinum(II) ions.¹⁰

The observation of a mixed-valence species in these reaction mixtures is of interest because in more acidic solutions $\text{Pt}(\text{III})_2^{6+}$ units are formed. Such units could be formed from the reverse disproportionation wherein Pt(IV) reacts with Pt(II) in a mixed-valence compound like the one described above.

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Supplementary Material Available: Listings of crystal data and structure refinement information, thermal parameters, least-squares planes, and nonbonded distances and packing diagrams (7 pages); listings of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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Detection of Covalency in Cyclopentadienyl Complexes of the Alkaline-Earth and f Elements: Statistical Evaluation of Structural Data

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Evidence for covalent bonding in cyclopentadienyl complexes of the alkaline-earth and f elements was sought by determining the strength of the linear relationship between metal radii and metal–Cp distances in over 200 structurally characterized compounds. Regression analysis indicates that the metal radius alone is a strong predictor of metal–Cp distances in divalent complexes but that the ligand environment around the metal markedly influences the “effective ionic radius” of the Cp ligand in trivalent and tetravalent compounds. Such steric effects need to be considered before inferences about the presence or absence of covalent bonding are drawn. Revised estimates for the Cp radius in several classes of cyclopentadienyl complexes are presented.

Introduction

Investigation of the degree of covalent bonding in cyclooctatetraenyl and cyclopentadienyl compounds of the pretransition and f elements has been a subject of recurrent interest ever since the isolation of uranocene ($(\text{C}_8\text{H}_8)_2\text{U}$) over 20 years ago.¹ Spectroscopic and physical evidence increasingly suggest that substantial covalent metal–ligand character exists in many organolanthanide and -actinide complexes, especially those in high oxidation states (≥ 3).²

Nevertheless, definitive *structural* evidence for covalency in complexes of the pretransition and f elements has remained more

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