triphenylphosphine or thiourea. As expected, the coordinated thiolato sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is not as good a nucleophile as the noncoordinated thiolato sulfur atom of $C_2H_5S^-$, coordination to cobalt(III) reducing the nucleophilicity by about a factor of 10. However, this coordination-induced decrease in nucleophilicity toward hydroxylamine-*O*-sulfonic acid is much less than the comparable decrease in nucleophilicity towards CH_3I.[4] This observation implies that, for soft nucleophiles, cleavage of hydroxylamine-*O*-sulfonic acid is relatively insensitive to the nature of the attacking nucleophile. This implication is further supported by the small range of activation parameters observed for nucleophilic cleavage of hydroxylamine-*O*-sulfonic acid (Table V), indicating that for these soft nucleophiles it is primarily the energetics of N–O bond cleavage that dominate the activation process.

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Registry No. $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_3$, 87434-58-0; $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$, 87434-62-6; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5; $[(en)_2Co(S(NHCH_3)CH_2CH_2NH_2)](ClO_4)_3$, 87434-60-4; $HSCH_2CH_2NH_2$, 60-23-1; NH_3OSO_3, 2950-43-8; $CH_3NH_2OSO_3$, 3400-11-1.

Supplementary Material Available: Listings of $10|F_o|$ and $10|F_c|$ values (Table A), observed first-order rate parameters (Table B), bond lengths, bond angles, and torsion angles (Table C), anisotropic temperature factors (Table D), hydrogen-bond contact distances (Table E), and hydrogen atom coordinates and temperature factors (Table F) (18 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Columbia University, New York, New York 10027, and Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Synthesis and Structures of Platinum(III) Complexes of α-Pyridone, $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2\cdot nH_2O$ ($X^- = Cl^-, NO_2^-, Br^-$)

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Oxidative addition of the head-to-tail platinum(II) dimer *cis*-$[Pt(NH_3)_2(C_5H_4NO)]_2^{2+}$, where C_5H_4NO is the α-pyridonate anion, with nitric acid in the presence of an excess of NO_2^-, Cl^-, or Br^- leads to crystalline platinum(III) dimers of general formula $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2\cdot nH_2O$ (**1**, **2**, and **6**, respectively). The structures of all three cations are composed of two *cis*-diammineplatinum(III) units linked in a head-to-tail fashion by two bridging α-pyridonate groups and capped on the Pt–Pt bond axis by the anionic X^- ligand. The Pt–Pt bond lengths [2.582 (1)–2.547 (1) Å] vary as $X^- = Br^- \sim NO_2^- > Cl^- > NO_3^-$, a statistically valid (30σ) trend that parallels the known trans-influence series for these ligands. The axial ligand–platinum bonds are elongated by ~0.15 Å from "normal" values, revealing the metal–metal bond itself to have a strong trans influence. Compound **1** ($X^- = NO_2^-$) is monoclinic, space group $C2/c$, with $a = 32.184$ (5) Å, $b = 8.712$ (2) Å, $c = 18.500$ (4) Å, $\beta = 124.20$ (2)°, $V = 4290$ Å^3, and $Z = 8$; **2** ($X^- = Cl^-$) is monoclinic, space group $P2_1/n$, with $a = 8.656$ (1) Å, $b = 25.728$ (3) Å, $c = 10.203$ (2) Å, $\beta = 113.45$ (2)°, $V = 2084$ Å^3, and $Z = 4$; **6** ($X^- = Br^-$) is monoclinic, space group $I2/c$, with $a = 27.059$ (5) Å, $b = 8.597$ (3) Å, $c = 18.789$ (3) Å, $\beta = 90.48$ (1)°, $V = 4371$ Å^3, and $Z = 8$.

Introduction

Until recently there have been only a few reports of binuclear compounds of platinum(III) that contain metal–metal bonds.[1-7] Consequently, the chemistry of platinum(III) complexes remains largely unexplored. Among the more thoroughly investigated examples of these compounds are the binuclear *cis*-diammineplatinum(III) complexes of α-pyridone, $[(X)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(X)]^{n+}$.[3,4] These compounds, which contain α-pyridonate ligands that bridge the Pt–Pt bond in either a head-to-head or a head-to-tail fashion, can be prepared from chemical or electrochemical oxidation of the corresponding platinum(II) dimer, $[(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2]^{2+}$.[3] Structural studies have shown that the Pt–Pt distance in the α-pyridonate-bridged complexes decreases by an average of 0.3 Å upon metal–metal bond formation. Electrochemical studies of this process show that, in the case of the head-to-tail isomer, the platinum–platinum bond is formed through a concerted two-electron charge-transfer process.[3] Metal–metal bond formation in the corresponding head-to-head isomer has also been studied in detail.[3,8] In both cases, the binuclear platinum(III) complexes contain neutral or anionic ligands (X) that occupy positions trans to the Pt–Pt bond, and consequently these complexes are structurally similar to a variety of isoelectronic rhodium(II) dimers.[9]

In a preliminary structural report,[4] it was shown that the axial ligands, X ($X = NO_2^-, NO_3^-$), in the head-to-tail α-pyridonate-bridged platinum(III) complexes are capable of influencing the platinum–platinum bond distance. While this effect has been the subject of numerous structural and theoretical studies in the case of the tetrakis(μ-carboxylato)dirhodium(II) complexes $[Rh_2(O_2CR)_4L_2]$,[9,10] the details of the

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Table I. Experimental Details of the X-ray Diffraction Studies of $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2\cdot{}^1/_2H_2O$ (1), $[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2), and $[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2\cdot{}^1/_2H_2O$ (6)

(A) Crystal Parameters[a] at 23 °C

	1	2	6		1	2	6[b]
a, Å	32.184 (5)	8.656 (1)	27.059 (5)	space group	*C*2/*c*	*P*2$_1$/*n*	*I*2/*c*
b, Å	8.712 (2)	25.728 (3)	8.597 (3)	*Z*	8	4	8
c, Å	18.500 (4)	10.203 (2)	18.789 (3)	ρ(calcd), g cm^{-3}	2.70	2.69	2.85
β, deg	124.20 (2)	113.45 (2)	90.48 (1)	ρ(obsd), g cm^{-3}	2.72 (2)[c]	2.70 (2)[c]	2.83 (2)[c]
V, Å^3	4290.0	2084.4	4370.7	mol wt	871.5	844.4	939.3

(B) Measurement of Intensity Data[d]

	1	2	3
instrument	Enraf-Nonius CAD-4F κ-geometry diffractometer		
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized		
takeoff angle, deg	2.0	5.0	5.0
stds, measd every 1 h of X-ray exposure time	($\overline{15}$,3,$\bar{1}$), ($\overline{18}$,2,3), ($\overline{18}$,$\bar{2}$,5)	(3,6,$\bar{6}$), (2,5,2), ($\bar{2}$,2,5)	($\overline{11}$,2,5), ($\overline{16}$,0,2), ($\bar{6}$,$\bar{4}$,2)
no. of reflcns collected (excluding systematic absences)	5412 [3 $\leqslant 2\theta \leqslant$ 55° ($\pm h,+k,+l$)]	5175 [3 $\leqslant 2\theta \leqslant$ 55° ($\pm h,+k,+l$)]	5516 [3 $\leqslant 2\theta \leqslant$ 55° ($\pm h,+k,+l$)]

(C) Treatment of Intensity Data[e]

	1	2	6
μ, cm^{-1}	132.5	138.7	166.0
transmissn factor range[f]	0.07–0.20	0.21–0.58	0.16–0.31
averaging, R_{av}[c]	0.039	0.034	0.037
no. of reflcns after averaging	4926	4790	5020
obsd unique data [$F_o > n\sigma(F_o)$]	3335, *n* = 4	3653, *n* = 4	3599, *n* = 4

[a] From a least-squares fit of the setting angles of 25 reflections with $2\theta > 30°$. [b] Although data were collected in *C*2/*c* (see text), all parameters in this table refer to the *I*2/*c* cell used in the final refinement. [c] By suspension in a mixture of $CHBr_3$ and $CHCl_3$. [d] See ref 12 for more details. [e] F_o and $\sigma(F_o)$ were corrected for background, attenuator, and Lorentz-polarization of X radiation as described previously (see ref 12). [f] Absorption corrections were performed with the Wehe-Busing-Levey ORABS program.

metal–metal and metal–ligand interactions have not been extensively examined in the binuclear complexes of platinum(III). In this paper we provide information on the structural trans influence in diplatinum(III) complexes through synthetic and X-ray crystallographic studies of the head-to-tail α-pyridonate-bridged platinum(III) complexes, $[(X)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(X)]^{2+}$ (X^- = NO_2^-, NO_3^-, Cl^-, Br^-). The relationship between the Pt–Pt distance and the structural trans influence of the axial ligands in the complexes is correlated with the existing structural information on other binuclear platinum(III) complexes.

Experimental Section and Results

Preparation of Compounds. The starting material, the head-to-tail α-pyridonate-bridged platinum(II) dimer $[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2\cdot2H_2O$ (3), was prepared by using previously described methods.[8a,b] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Bis(*μ*-*α*-pyridonato-*N*,*O*)bis(*cis*-diamminenitroplatinum(III))(*Pt*-*Pt*) Nitrate Hemihydrate, $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2\cdot{}^1/_2H_2O$ (1). The nitrite-capped platinum(III) dimer (1) was prepared by oxidizing the head-to-tail platinum(II) complex (3) with nitrous acid as follows. The pH of a solution containing 150 mg of 3 and 150 mg of $NaNO_2$ in 25 mL of water was adjusted to 1 with concentrated nitric acid. The yellow precipitate (1) that formed after HNO_3 addition was separated by filtration, and the filtrate was evaporated in air. After 2 days, a second crop of well-formed crystals of compound 1 were collected by filtration. Combined yields of 100 mg (60%) were typically obtained. Anal. Calcd for $Pt_2C_{10}H_{21}N_{10}O_{12.5}$ (1): C, 13.78; H, 2.43; N, 16.07. Found: C, 13.72; H, 2.46; N, 16.00.

Bis(*μ*-*α*-pyridonato-*N*,*O*)bis(*cis*-diamminechloroplatinum(III))(*Pt*-*Pt*) Nitrate, $[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2). The chloride-capped platinum(III) dimer was prepared by oxidizing the head-to-tail platinum(II) dimer (3) with nitric acid in the presence of chloride. A solution of 150 mg of 3 and 87 mg of NaCl (8 equiv) in 15 mL of water was treated with 5 mL of concentrated nitric acid. Air evaporation of the resulting orange solution provided a 50–60% yield of compound 2 as yellow-orange crystals. Anal. Calcd for $Pt_2C_{10}H_{20}N_8O_8Cl_2$: C, 14.22; H, 2.40; N, 13.32. Found: C, 14.05; H, 2.40; N, 13.13.

Bis(*μ*-*α*-pyridonato-*N*,*O*)bis(*cis*-diamminebromoplatinum(III))(*Pt*-*Pt*) Nitrate Hemihydrate, $[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2\cdot{}^1/_2H_2O$ (6). This bromide-capped platinum(III) dimer was obtained in a manner analogous to that reported for the chloride-capped compound 2 by addition of 5 mL of concentrated nitric acid to 150 mg of 3 and 153 mg of NaBr (8 equiv) dissolved in a solution of 4 mL of concentrated nitric acid and 12 mL of H_2O. The resulting orange precipitate was collected and washed with cold ethanol. Evaporation of the filtrate yielded additional crops of the crystals. The composition of the product was confirmed crystallographically (vide infra).

Collection and Reduction of X-ray Data. $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2\cdot{}^1/_2H_2O$ (1). The yellow crystal used in the X-ray diffraction study was tabular in shape with dimensions of 0.14 mm × 0.15 mm × 0.30 mm and was bounded by the following faces: (100), ($\bar{1}$00), (10$\bar{1}$), ($\bar{1}$01), (0$\bar{1}$1), (010). The quality of the crystal was examined by taking open-counter ω scans of several low-angle reflections and was found to be acceptable ($\Delta\bar{\omega}_{1/2} \sim 0.1°$). The intensity data and the unit cell parameters were measured with a single-crystal diffractometer as described in Table I. The space group was suggested to be either *C*2/*c* (C_{2h}^6, No. 15) or *Cc* (C_s^4, No. 9)[11] from the systematic absences, and the former choice was justified by the successful solution and refinement of the structure.

$[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2). The crystal used for data collection was a yellow plate with dimensions of 0.21 mm × 0.11 mm × 0.04 mm bounded by the following faces: (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (100), ($\bar{1}$01). Inspection of several low-angle ω scans indicated the crystal to be acceptable for data collection ($\Delta\bar{\omega}_{1/2}$ = 0.1°). The space group was determined to be *P*2$_1$/*n* (C_{2h}^5, No. 14; in a nonstandard setting)[13] from the systematic absences. Further details of the data collection are given in Table I.

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Table II. Final Positional Parameters for $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2 \cdot {}^1/_2H_2O$ (1)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pt1	0.37695 (2)	0.42235 (5)	0.52025 (2)	N5	0.3551 (5)	0.6410 (12)	0.5458 (7)
Pt2	0.38897 (2)	0.15977 (5)	0.47038 (3)	O51	0.3878 (5)	0.7378 (13)	0.5838 (8)
N1	0.4120 (4)	0.5492 (12)	0.4759 (7)	O52	0.3118 (5)	0.6661 (12)	0.5188 (7)
N2	0.4411 (4)	0.4254 (12)	0.6441 (6)	N6	0.3907 (6)	−0.0681 (12)	0.4250 (9)
N3	0.4530 (4)	0.1996 (11)	0.4758 (7)	O61	0.4320 (5)	−0.1333 (12)	0.4611 (10)
N4	0.4294 (4)	0.0581 (11)	0.5912 (6)	O62	0.3535 (5)	−0.1374 (12)	0.3725 (8)
O12	0.3137 (3)	0.4306 (9)	0.4007 (5)	N7	0.0523 (6)	0.415 (2)	0.2092 (11)
N11	0.3442 (4)	0.2506 (10)	0.3481 (6)	O71	0.0327 (7)	0.290 (2)	0.2113 (15)
C12	0.3106 (4)	0.3616 (12)	0.3342 (7)	O72	0.0337 (6)	0.499 (3)	0.1413 (9)
C13	0.2724 (6)	0.4023 (16)	0.2489 (8)	O73	0.0924 (6)	0.450 (3)	0.2727 (9)
H13	0.2477 (6)	0.4753 (16)	0.2386 (8)	N8	0.4498 (6)	0.470 (3)	0.3352 (11)
C14	0.2706 (7)	0.3368 (19)	0.1816 (8)	O81	0.4618 (7)	0.388 (3)	0.2955 (13)
H14	0.2440 (7)	0.3621 (19)	0.1235 (8)	O82	0.4062 (5)	0.470 (2)	0.3115 (9)
C15	0.3063 (7)	0.2369 (17)	0.1952 (9)	O83	0.4821 (6)	0.498 (3)	0.4115 (10)
H15	0.3062 (7)	0.1964 (17)	0.1474 (9)	O1	0.0000	0.687 (4)	0.2500
C16	0.3424 (6)	0.1946 (14)	0.2791 (8)	H1N1	0.4416 (12)	0.511 (5)	0.495 (4)
H16	0.3671 (6)	0.1223 (14)	0.2889 (8)	H2N1	0.3942 (15)	0.550 (7)	0.4187 (9)
O22	0.3266 (3)	0.1068 (8)	0.4640 (4)	H3N1	0.416 (3)	0.644 (2)	0.494 (4)
N21	0.3403 (3)	0.2957 (10)	0.5616 (5)	H1N2	0.4395 (13)	0.357 (6)	0.6773 (14)
C22	0.3202 (4)	0.1578 (12)	0.5228 (6)	H2N2	0.4674 (5)	0.403 (8)	0.6433 (12)
C23	0.2918 (4)	0.0818 (14)	0.5451 (7)	H3N2	0.4457 (15)	0.515 (3)	0.6683 (18)
H23	0.2753 (4)	−0.0105 (14)	0.5153 (7)	H1N3	0.4504 (11)	0.282 (5)	0.446 (4)
C24	0.2867 (5)	0.1354 (15)	0.6091 (8)	H2N3	0.4790 (6)	0.212 (8)	0.5297 (11)
H24	0.2675 (5)	0.0786 (15)	0.6244 (8)	H3N3	0.4599 (16)	0.123 (4)	0.453 (4)
C25	0.3096 (5)	0.2726 (14)	0.6519 (7)	H1N4	0.4617 (4)	0.067 (7)	0.615 (2)
H25	0.3062 (5)	0.3118 (14)	0.6963 (7)	H2N4	0.423 (2)	0.101 (6)	0.6263 (16)
C26	0.3362 (5)	0.3483 (13)	0.6282 (7)	H3N4	0.422 (2)	−0.040 (2)	0.5871 (12)
H26	0.3529 (5)	0.4404 (13)	0.6577 (7)				

[a] Atoms are labeled as shown in Figure 1. Estimated standard deviations in the last significant digit(s) are given in parentheses.

$[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2 \cdot {}^1/_2H_2O$ (6). The orange crystal used for the diffraction study was a parallelepiped with approximate dimensions of 0.09 mm × 0.13 mm × 0.16 mm bounded by the following faces: (100), ($\bar{1}00$), ($1\bar{1}\bar{1}$), ($\bar{1}11$), ($11\bar{1}$), ($\bar{1}\bar{1}1$). Its quality was checked on the diffractometer by taking open-counter ω scans of several strong low-angle reflections and was judged to be acceptable ($\Delta\omega_{1/2} \sim 0.2°$). Study on the diffractometer showed the crystal to have space group either $C2/c$ (C_{2h}^6, No. 15) or Cc (C_s^4, No. 9)[11] and unit cell parameters $a = 32.813$ (5) Å, $b = 8.597$ (3) Å, $c = 18.789$ (3) Å, and $\beta = 124.45$ (1)°. Owing to the large β angle, the data were transformed before final refinement to the nonstandard setting $I2/c$, parameters for which are reported, together with further details of the data collection procedures, in Table I.

Structure Solution and Refinement. $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2 \cdot {}^1/_2H_2O$ (1). The structure was solved by standard Patterson and Fourier methods and refined[14] by using anisotropic thermal parameters for all non-hydrogen atoms, except for the atoms of the apparently disordered nitrate anion N8, which was refined as a rigid group with isotropic thermal parameters. The temperature factor of the nitrate oxygen atom O81 was fixed in the final cycle of refinement. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were obtained from ref 15, and hydrogen atom scattering factors were taken from ref 16. The positions of all hydrogen atoms were refined with constraints using isotropic thermal parameters. The hydrogen atoms of the α-pyridonate rings were placed at calculated positions [d(C–H) = 0.95 Å] and constrained to "ride" on the carbon atoms to which they are attached.[14] The hydrogen atoms of the ammine ligands were refined as rigid groups by fixing[14] the following interatomic distances: N–H = 0.87 (1) Å, H–H = 1.42 (1) Å, and Pt–H = 2.50 (1) Å, for each hydrogen in the group. The hydrogen atoms of each α-pyridonate ring were given an independent set of common thermal parameters. The thermal parameters of the hydrogen atoms of the ammine ligands were fixed with U set to 0.05 Å^2. The hydrogen atoms of the water molecule of hydration O1, which lies on a crystallographic twofold symmetry axis, were not located.

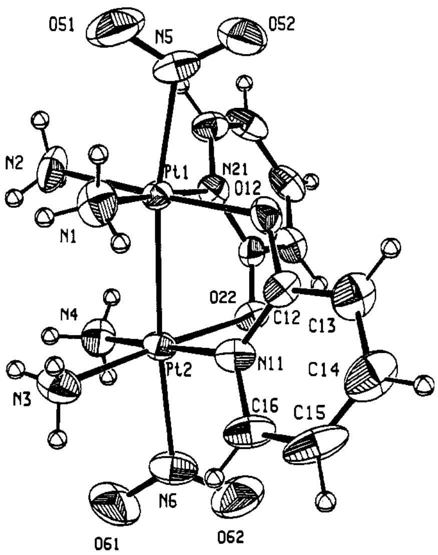

Figure 1. ORTEP illustration of the structure of the head-to-tail α-pyridonate-bridged cation $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2]^{2+}$ (1) showing the 40% probability thermal ellipsoids. For clarity the hydrogen atoms are depicted as spheres with B set to 1 Å^2. The hydrogen atom labels (not shown) are assigned according to the atoms to which they are attached (e.g. H1N2 is attached to N2, etc.).

Full-matrix least-squares refinement of the structure using 333 parameters converged at $R_1 = 0.039$ and $R_2 = 0.048$.[17] The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.9955/[\sigma^2(F_o) + 0.000625F_o^2]$. The maximum parameter shift in the final cycle of refinement was 0.1σ, and the largest peaks on the final difference map (≤2.3 e Å^{-3}) were in the vicinity of the Pt atoms (≤0.9 Å). The largest peak (1.1 e Å^{-3}) away from the Pt atoms was 0.4 Å from atom N8. The average $w\Delta^2$ values for groups of data sectioned according to parity group, $(\sin\theta)/\lambda$, $|F_o|$, $|h|$, $|k|$, or $|l|$ showed good consistency, and the weighting scheme was considered acceptable.

The final atomic positional parameters together with their estimated standard deviations are reported in Table II. The interatomic distances

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(17) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Table III. Final Positional Parameters for $[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pt1	0.48764 (3)	0.140400 (10)	0.65258 (3)	H14	0.8374 (10)	0.0193 (4)	1.2076 (9)
Pt2	0.28651 (3)	0.125290 (10)	0.77809 (3)	C15	0.6278 (11)	0.0624 (4)	1.1720 (9)
Cl1	0.6822 (3)	0.14592 (10)	0.5332 (2)	H15	0.6308 (11)	0.0592 (4)	1.2657 (9)
Cl2	0.0974 (2)	0.10011 (9)	0.8903 (2)	C16	0.5027 (10)	0.0894 (3)	1.0715 (8)
N1	0.6548 (8)	0.1879 (3)	0.8049 (6)	H16	0.4189 (10)	0.1055 (3)	1.0958 (8)
N2	0.3673 (8)	0.2029 (2)	0.5295 (6)	N5	0.4572 (9)	0.2314 (3)	0.2319 (7)
N3	0.3166 (8)	0.1945 (3)	0.8844 (6)	O51	0.4832 (7)	0.2633 (3)	0.3316 (7)
N4	0.0741 (7)	0.1540 (3)	0.6174 (6)	O52	0.5464 (8)	0.2333 (3)	0.1617 (6)
O22	0.2451 (7)	0.0564 (2)	0.6770 (5)	O53	0.3435 (10)	0.1988 (4)	0.2028 (8)
N21	0.3383 (7)	0.0886 (3)	0.5079 (6)	N6	0.4437 (9)	0.3211 (3)	0.7472 (8)
C22	0.2588 (9)	0.0512 (3)	0.5551 (7)	O61	0.5001 (8)	0.2822 (3)	0.8278 (7)
C23	0.1929 (10)	0.0068 (3)	0.4714 (8)	O62	0.3549 (10)	0.3140 (4)	0.6215 (7)
H23	0.1449 (10)	−0.0202 (3)	0.5066 (8)	O63	0.4785 (12)	0.3640 (3)	0.8008 (8)
C24	0.1977 (10)	0.0022 (4)	0.3397 (10)	H1N1	0.620 (4)	0.2201 (5)	0.792 (4)
H24	0.1553 (10)	−0.0281 (4)	0.2836 (10)	H2N1	0.666 (6)	0.1783 (16)	0.8905 (10)
C25	0.2659 (12)	0.0427 (4)	0.2887 (9)	H3N1	0.754 (2)	0.1866 (20)	0.801 (5)
H25	0.2648 (12)	0.0410 (4)	0.1953 (9)	H1N2	0.264 (3)	0.1949 (9)	0.474 (5)
C26	0.3343 (10)	0.0848 (4)	0.3735 (8)	H2N2	0.365 (7)	0.2291 (9)	0.5835 (17)
H26	0.3802 (10)	0.1122 (4)	0.3379 (8)	H3N2	0.420 (5)	0.2131 (16)	0.476 (5)
O12	0.6135 (6)	0.0800 (2)	0.7724 (5)	H1N3	0.390 (6)	0.1916 (8)	0.973 (2)
N11	0.4944 (7)	0.0941 (3)	0.9357 (6)	H2N3	0.352 (7)	0.2188 (7)	0.843 (4)
C12	0.6154 (9)	0.0742 (3)	0.8933 (7)	H3N3	0.221 (2)	0.2050 (12)	0.886 (6)
C13	0.7468 (10)	0.0460 (3)	1.0021 (9)	H1N4	0.079 (4)	0.1879 (5)	0.613 (5)
H13	0.8331 (10)	0.0314 (3)	0.9782 (9)	H2N4	0.062 (5)	0.1409 (20)	0.5349 (13)
C14	0.7510 (10)	0.0394 (4)	1.1386 (9)	H3N4	−0.0156 (13)	0.146 (2)	0.633 (4)

[a] Atoms are labeled as shown in Figure 2. Estimated standard deviations in the last significant digit(s) are given in parentheses.

and angles are contained with their estimated standard deviations in Table V. A complete listing of atomic positional and thermal parameters for compound **1** (Table S1) and a listing of observed and calculated structure factors (Table S2) are available as supplementary material. Figure 1 depicts the coordination geometry and atom-labeling scheme for the $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2]^{2+}$ cation.

$[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2). The structure was solved and refined as above for the nitrite derivative. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms of the α-pyridonate rings and ammine ligands were refined with constraints. The hydrogen atoms of each α-pyridonate ring were given an independent set of common isotropic thermal parameters, and the hydrogen atoms of the ammine ligands were given fixed thermal parameters ($U_{iso} = 0.05$ Å^2) during the refinement.

Full-matrix least-squares refinement of the structure using 313 parameters converged at $R_1 = 0.029$ and $R_2 = 0.035$.[17] The weighting function used in the refinement was $w = 0.7395/[\sigma^2(F_o) + 0.000625F_o^2]$, and the maximum parameter shift in the final cycle of refinement was 0.01σ. The only residual peaks of significant height (<1.8 e Å^{-3}) that were observed in the final difference Fourier map were located near the Pt atoms (<1.5 Å). The $w\Delta^2$ value for groups of data sectioned as above showed good consistency, and the weighting function was found acceptable.

The final atomic positional parameters with their estimated standard deviations are reported in Table III. The interatomic distances and angles with estimated standard deviations are presented in Table VI. A complete listing of atomic positional and thermal parameters for compound **2** (Table S3) and a listing of final observed and calculated structure factors (Table S4) are available as supplementary material. Figure 2 shows the coordination geometry and atom-labeling scheme for the $[Pt_2(NH_3)_4(C_5H_4NO)_2)Cl_2]^{2+}$ cation.

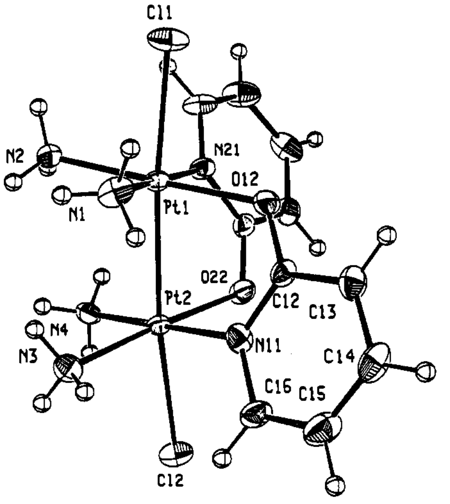

Figure 2. ORTEP illustration of the structure of the head-to-tail α-pyridonate-bridged cation $[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2]^{2+}$ (**2**) showing the 40% probability thermal ellipsoids. See caption to Figure 1.

$[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2\cdot{}^1/_2H_2O$ (6). The structure was solved and refined as described above for compounds **1** and **2**. In **6**, the two ionic nitrate groups were found to be disordered about two hinging oxygen atoms O51 and O52 of nitrate N51–O53B and O61 and O62 of nitrate N61–O63B. Thus, the nitrate atom group of O51, O52, N51, and O53B is related through disorder to the atom group O51, O52, N52, and O53A, with the occupancy of both summing to an average of one per asymmetric unit. A similar situation occurs with atom groups O61, O62, N61, O63A and O61, O62, N62, O63B. All the oxygen atoms of the nitrates were located in the difference Fourier map, but individual peaks corresponding to the two disordered nitrogen atom positions could not be resolved. The nitrogen atoms were therefore placed in calculated positions, and the nitrates were refined as rigid groups.[14] Here the N–O and O···O distances were fixed at 1.23 and 2.13 Å, respectively. Atoms O51, O52, O61, and O62 were refined with anisotropic temperature factors. The remaining atoms of the nitrates were refined with isotropic temperature and variable occupancy factors. All other non-hydrogen atoms were refined anisotropically. Ammine hydrogen atoms were set up and refined as rigid groups (N–H = 0.87 Å, H–N–H = 109.5°), pivoting on their respective nitrogen atoms, with a common isotropic temperature factor that converged toward $U = 0.079$ Å^2. The hydrogen atoms of the α-pyridonate rings were refined with constraints as described above.

Full-matrix least-squares refinement of 284 variables converged to final residual indices[17] of $R_1 = 0.038$ and $R_2 = 0.048$. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.9025/[\sigma^2(F_o) + 0.000625F_o^2]$. In the final cycle of refinement, no parameter shifted by more than 0.107 of its estimated standard deviation. The final difference Fourier map showed no peaks ≥1.70 e Å^{-3}, the largest of which was located near the nitrate atoms. This peak may be associated with the presence of a disordered water molecule, assumed to be present in the lattice. The close proximity of this peak to atom O51 (2.02 Å), however, did not permit an accurate placement of the water oxygen, so it was omitted. All remaining peaks were <1.36 e Å^{-3}, located around the Pt atoms. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin\theta)/\lambda$, $|h|$, $|k|$, or $|l|$ showed good consistency, and the weighting scheme was considered to be satisfactory.

Final non-hydrogen atom positional parameters, together with their

Table IV. Final Positional Parameters for the Non-Hydrogen Atoms of $[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2 \cdot {}^1/_2H_2O$ (6)[a,b]

atom	*x*	*y*	*z*
Pt1	0.37892 −0.378920 (10)	0.40195 −0.09805 (5)	0.53189 −0.15297 (2)
Pt2	0.38334 −0.383340 (10)	0.14205 −0.35795 (5)	0.46779 −0.08445 (2)
Br1	0.36038 −0.36038 (7)	0.66261 0.16261 (16)	0.57493 −0.21455 (8)
Br2	0.37450 −0.37450 (6)	−0.11701 −0.61701 (15)	0.39265 −0.01815 (8)
N1	0.4129 −0.4129 (3)	0.5346 0.0346 (10)	0.4905 −0.0776 (5)
N2	0.4430 −0.4430 (3)	0.3819 −0.1181 (11)	0.6549 −0.2119 (5)
N3	0.4470 −0.4470 (3)	0.1805 −0.3195 (11)	0.4745 −0.0275 (5)
N4	0.4207 −0.4207 (3)	0.0164 −0.4836 (11)	0.5821 −0.1614 (5)
O12	0.3156 −0.3156 (3)	0.4297 −0.0703 (9)	0.4129 −0.0973 (4)
N11	0.3410 −0.3410 (3)	0.2582 −0.2418 (10)	0.3511 −0.0101 (5)
C12	0.3113 −0.3113 (4)	0.3704 −0.1296 (13)	0.3441 −0.0334 (6)
C13	0.2737 −0.2737 (5)	0.4258 −0.0742 (18)	0.2634 0.0103 (7)
H13	0.2515 −0.2515 (5)	0.5028 0.0028 (18)	0.2582 −0.0067 (7)
C14	0.2686 −0.2686 (5)	0.3686 −0.1314 (17)	0.1902 0.0784 (7)
H14	0.2416 −0.2416 (5)	0.3997 −0.1003 (17)	0.1338 0.1078 (7)
C15	0.3032 −0.3032 (5)	0.2650 −0.2350 (15)	0.2002 0.1030 (7)
H15	0.3027 −0.3027 (5)	0.2336 −0.2664 (15)	0.1512 0.1515 (6)
C16	0.3384 −0.3384 (5)	0.2076 −0.2924 (14)	0.2806 0.0578 (6)
H16	0.3613 −0.3613 (5)	0.1320 −0.3680 (14)	0.2872 0.0741 (6)
O22	0.3208 −0.3208 (3)	0.0954 −0.4046 (9)	0.4598 −0.1390 (4)
N21	0.3415 −0.3415 (3)	0.2752 −0.2248 (11)	0.5680 −0.2265 (5)
C22	0.3172 −0.3172 (4)	0.1477 −0.3523 (13)	0.5219 −0.2047 (5)
C23	0.2876 −0.2876 (4)	0.0633 −0.4367 (14)	0.5397 −0.2521 (6)
H23	0.2701 −0.2701 (4)	−0.0265 −0.5265 (14)	0.5078 −0.2368 (6)
C24	0.2849 −0.2849 (4)	0.1129 −0.3871 (16)	0.6041 −0.3192 (7)
H24	0.2642 −0.2642 (4)	0.0584 −0.4416 (16)	0.6156 −0.3514 (7)
C25	0.3110 −0.3110 (5)	0.2417 −0.2583 (16)	0.6548 −0.3438 (6)
H25	0.3088 −0.3088 (5)	0.2744 −0.2256 (16)	0.7008 −0.3920 (6)
C26	0.3405 −0.3405 (5)	0.3213 −0.1787 (16)	0.6360 −0.2955 (6)
H26	0.3598 −0.3598 (5)	0.4074 −0.0926 (16)	0.6706 −0.3108 (6)
N51[c]	0.4568 −0.4568 (3)	0.0310 −0.4690 (11)	0.7932 −0.3364 (4)
N52[c]	0.4510 −0.4510 (3)	0.0670 −0.4330 (11)	0.8022 −0.3512 (4)
O51	0.4743 −0.4743 (3)	−0.0154 −0.5154 (11)	0.8674 −0.3931 (4)
O52	0.4121 −0.4121 (3)	0.0193 −0.4807 (11)	0.7368 −0.3247 (4)
O53A[c]	0.4652 −0.4652 (3)	0.2002 −0.2998 (11)	0.8039 −0.3387 (4)
O53B[c]	0.4834 −0.4834 (3)	0.0966 −0.4034 (11)	0.7764 −0.2930 (4)
N61[c]	0.4546 −0.4546 (3)	0.4801 −0.0199 (15)	0.8671 −0.4125 (6)
N62[c]	0.4523 −0.4523 (3)	0.5534 0.0534 (15)	0.8497 −0.3974 (6)
O61	0.4105 −0.4105 (3)	0.5141 0.0141 (15)	0.8258 −0.4153 (6)
O62	0.4855 −0.4855 (3)	0.5628 0.0628 (15)	0.9278 −0.4423 (6)
O63A[c]	0.4679 −0.4679 (3)	0.3683 −0.1317 (15)	0.8445 −0.3766 (6)
O63B[c]	0.4602 −0.4602 (3)	0.5912 0.0912 (15)	0.7956 −0.3354 (6)
H1N1	0.4450 −0.4550 (5)	0.533 0.033 (9)	0.528 −0.083 (3)
H2N1	0.403 −0.403 (3)	0.632 0.132 (2)	0.483 −0.080 (3)
H3N1	0.406 −0.406 (3)	0.501 0.001 (7)	0.4406 −0.0346 (5)
H1N2	0.459 −0.459 (2)	0.470 −0.030 (4)	0.671 −0.212 (4)
H2N2	0.462 −0.462 (2)	0.310 −0.190 (8)	0.656 −0.194 (3)
H3N2	0.4363 −0.4363 (7)	0.357 −0.143 (11)	0.6923 −0.256 (1)
H1N3	0.4724 −0.4724 (6)	0.185 −0.315 (12)	0.5284 −0.056 (1)
H2N3	0.445 −0.445 (2)	0.269 −0.231 (6)	0.450 −0.005 (4)
H3N3	0.451 −0.451 (2)	0.106 −0.394 (7)	0.447 0.004 (4)
H1N4	0.448 −0.448 (2)	−0.023 −0.523 (10)	0.592 −0.144 (2)
H2N4	0.402 −0.402 (2)	−0.059 −0.559 (7)	0.579 −0.177 (4)
H3N4	0.428 −0.428 (3)	0.076 −0.423 (3)	0.625 −0.197 (2)

[a] Atoms are labeled as shown in Figure 3. [b] Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter. The atomic coordinates listed without esd's are those transformed through the operation $X' = -X$, $Y' = {}^1/_2 + Y$, $Z' = -X - Z$ in order to facilitate comparison with Table II. The corresponding transformed *C*2/*c* cell has the parameters a = 33.072 (5) Å, b = 8.597 (3) Å, c = 18.789 (3) Å, and β = 125.10 (1)° and is related to the original *C*2/*c* setting by the transformation $a' = a + 2c$, $b' = -b$, $c' = -c$. The atomic coordinates listed on the second line for each atom are those from the final stage of the *I*2/*c* refinement. [c] These atoms are disordered and have the following population parameters: N51, O53B = 0.53; N52, O53A = 0.47; N61, O63A = 0.47; N62, O63B = 0.53.

estimated standard deviations, appear in Table IV. To facilitate comparison with compound 1, atom coordinates are also reported for the *C*2/*c* crystal setting in Table IV. Interatomic distances and angles are given in Table VII. A listing of final observed and calculated structure factor amplitudes, anisotropic thermal parameters, and hydrogen and rigid-group atom positional and thermal parameters is available as supplementary material in Tables S5–S7, respectively. Figure 3 shows the geometry of the cation and the atom-labeling scheme.

Discussion

The series of α-pyridonate-bridged, metal–metal-bonded, ligand(X)-capped diplatinum(III) cations $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X]^{2+}$ (X^- = NO_3^-, Cl^-, NO_2^-, Br^-) has been prepared from the corresponding platinum(II) dimer by oxidation with nitric or nitrous acid in the presence of excess capping ligand X^-. The structures of all four cations (Figures 1–3 and ref 3) are very similar. Each consists of two *cis*-diammineplatinum(III) units bridged by two α-pyridonate ligands in a head-to-tail arrangement. The axial site of each platinum atom is occupied by a donor atom from the capping ligand, and including the metal–metal bond, each platinum is six-coordinate.

The Pt–N distances (Table V–VII) for both equatorial ammine and α-pyridonate nitrogen atoms are within the range (2.00–2.08 Å) normally found in related platinum(II) and platinum(III) compounds.[3,8,18] The equatorial Pt–O bond

Table V. Interatomic Distances (Å) and Angles (deg) for $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2\cdot{}^1/_2H_2O$ (**1**)[a]

Coordination Sphere			
Pt1-Pt2	2.5759 (7)	Pt2-N3	2.035 (9)
Pt1-N1	2.050 (9)	Pt2-N4	2.051 (9)
Pt1-N2	2.048 (7)	Pt2-N11	2.039 (8)
Pt1-N21	2.051 (9)	Pt2-O22	1.999 (7)
Pt1-O12	1.995 (7)	Pt2-N6	2.168 (11)
Pt1-N5	2.172 (10)		
Pt2-Pt1-N5	171.4 (3)	Pt1-Pt2-N6	173.5 (4)
N1-Pt1-N2	90.3 (4)	N3-Pt2-N4	90.9 (4)
N1-Pt1-N21	178.6 (4)	N4-Pt2-N11	175.6 (4)
N1-Pt1-O12	89.2 (4)	N4-Pt2-O22	88.0 (3)
N2-Pt1-N21	91.1 (4)	N3-Pt2-N11	93.0 (4)
N2-Pt1-O12	177.0 (4)	N3-Pt2-O22	176.4 (3)
N21-Pt1-O12	89.4 (3)	N11-Pt2-O22	88.0 (3)
N5-Pt1-N1	86.1 (4)	N6-Pt2-N4	83.6 (4)
N5-Pt1-N2	89.5 (4)	N6-Pt2-N3	86.0 (4)
N5-Pt1-N21	93.8 (4)	N6-Pt2-N11	94.7 (4)
N5-Pt1-O12	87.5 (4)	N6-Pt2-O22	90.5 (4)
Ligand Geometry			
O12-C12	1.322 (12)	O22-C22	1.294 (12)
N11-C12	1.364 (14)	N21-C22	1.362 (13)
C12-C13	1.395 (16)	C22-C23	1.368 (15)
C13-C14	1.340 (18)	C23-C24	1.366 (16)
C14-C15	1.348 (22)	C24-C25	1.394 (18)
C15-C16	1.367 (19)	C25-C26	1.335 (16)
C16-N11	1.336 (13)	C26-N21	1.389 (12)
O12-N11	2.332 (15)	O22-N21	2.293 (12)
N5-O51	1.218 (14)	N6-O61	1.241 (16)
N5-O52	1.208 (15)	N6-O62	1.198 (16)
Pt1-N11-C12	118.4 (7)	Pt1-N21-C22	118.7 (7)
Pt2-N11-C16	122.6 (8)	Pt1-N21-C26	121.0 (8)
Pt1-O12-C12	120.7 (7)	Pt2-O22-C22	119.9 (6)
C12-N11-C16	118.3 (10)	C22-N21-C26	120.3 (9)
O12-C12-N11	120.7 (9)	O22-C22-N21	119.6 (9)
O12-C12-C13	119.7 (11)	O22-C22-C23	122.4 (10)
N11-C12-C13	119.6 (10)	N21-C22-C23	118.0 (10)
C12-C13-C14	119.6 (14)	C22-C23-C24	121.5 (12)
C13-C14-C15	121.0 (13)	C23-C24-C25	120.2 (11)
C14-C15-C16	118.4 (11)	C24-C25-C26	117.9 (10)
C15-C16-N11	122.7 (13)	C25-C26-N21	122.4 (11)
Pt1-N5-O51	116.9 (10)	Pt2-N6-O61	117.7 (11)
Pt1-N5-O52	120.6 (9)	Pt2-N6-O62	122.9 (10)
O51-N5-O52	122.4 (12)	O61-N6-O62	119.1 (12)
Anion Geometry			
N7-O71	1.264 (21)	N8-O81	1.232 (9)
N7-O72	1.275 (20)	N8-O82	1.213 (9)
N7-O73	1.199 (19)	N8-O83	1.218 (9)
O71-N7-O72	123.9 (20)	O81-N8-O82	118.1 (12)
O71-N7-O73	117.9 (22)	O81-N8-O83	117.3 (12)
O72-N7-O73	118.0 (22)	O82-N8-O83	118.5 (12)

[a] See footnote *a* of Table II. Distances have not been corrected for thermal motion.

lengths are also in the normal range (1.99–2.07 Å).[3,8,18] The equatorial ligands of each platinum atom define a plane with a four-atom rms deviation that does not exceed 0.025 Å for any of the three structures. The two platinum atoms are slightly displaced out of these planes toward one another by 0.027 Å for Pt1 and 0.047 Å for Pt2 where $X^- = NO_2^-$, 0.036 and 0.037 Å, respectively, for $X^- = Cl^-$, and 0.032 and 0.030 Å, respectively, for $X^- = Br^-$. The tilt angles (τ) between the adjacent equatorial coordination planes are 20 ± 1°, and the average torsion angle (or twist) about the Pt–Pt vector is 27.1 and 27.4° for the nitrite- and chloride-capped dimers, respectively, and slightly larger (29.4°) for the bromide analogue.

Table VI. Interatomic Distances (Å) and Angles (deg) for $[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (**2**)[a]

Coordination Sphere			
Pt1-Pt2	2.5684 (5)	Pt2-N3	2.047 (6)
Pt1-N1	2.052 (6)	Pt2-N4	2.053 (6)
Pt1-N2	2.051 (6)	Pt2-N11	2.041 (6)
Pt1-N21	2.027 (6)	Pt2-O22	2.009 (5)
Pt1-O12	2.009 (5)	Pt2-Cl2	2.429 (2)
Pt1-Cl1	2.444 (2)		
Pt2-Pt1-Cl1	174.6 (1)	Pt1-Pt2-Cl2	173.2 (1)
N1-Pt1-N2	91.7 (3)	N3-Pt2-N4	89.7 (2)
N1-Pt1-N21	174.9 (3)	N4-Pt2-N11	177.9 (3)
N1-Pt1-O12	87.2 (3)	N4-Pt2-O22	89.3 (2)
N2-Pt1-N21	92.8 (2)	N3-Pt2-N11	92.2 (2)
N2-Pt1-O12	177.9 (2)	N3-Pt2-O22	176.5 (2)
N21-Pt1-O12	88.2 (2)	N11-Pt2-O22	88.8 (2)
Cl1-Pt1-N1	85.7 (2)	Cl2-Pt2-N4	85.1 (2)
Cl1-Pt1-N2	86.1 (2)	Cl2-Pt2-N3	87.1 (2)
Cl1-Pt1-N21	92.4 (2)	Cl2-Pt2-N11	94.1 (2)
Cl1-Pt1-O12	91.9 (2)	Cl2-Pt2-O22	89.5 (2)
Ligand Geometry			
O12-C12	1.297 (9)	O22-C22	1.302 (9)
N11-C12	1.344 (10)	N21-C22	1.375 (9)
C12-C13	1.403 (9)	C22-C23	1.405 (10)
C13-C14	1.389 (12)	C23-C24	1.366 (12)
C14-C15	1.375 (13)	C24-C25	1.397 (13)
C15-C16	1.351 (11)	C25-C26	1.365 (12)
C16-N11	1.363 (9)	C26-N21	1.361 (9)
O12-N11	2.310 (10)	O22-N21	2.327 (9)
Pt2-N11-C12	118.1 (5)	Pt1-N21-C22	117.9 (5)
Pt2-N11-C16	120.6 (5)	Pt1-N21-C26	122.2 (5)
Pt1-O12-C12	119.1 (7)	Pt2-O22-C22	121.1 (5)
C12-N11-C16	121.0 (6)	C22-N21-C26	119.2 (7)
O12-C12-N11	122.0 (6)	O22-C22-N21	120.7 (7)
O12-C12-C13	119.4 (7)	O22-C22-C23	119.7 (7)
N11-C12-C13	118.6 (7)	N21-C22-C23	119.7 (7)
C12-C13-C14	120.2 (8)	C22-C23-C24	120.2 (8)
C13-C14-C15	118.8 (7)	C23-C24-C25	119.0 (8)
C14-C15-C16	120.0 (9)	C24-C25-C26	119.8 (8)
C15-C16-N11	121.2 (8)	C25-C26-N21	121.7 (8)
Anion Geometry			
N5-O51	1.256 (9)	N6-O61	1.263 (10)
N5-O52	1.245 (10)	N6-O62	1.218 (9)
N5-O53	1.236 (9)	N6-O63	1.216 (10)
O51-N5-O52	119.2 (7)	O61-N6-O62	119.1 (9)
O51-N5-O53	120.4 (8)	O61-N6-O63	117.6 (8)
O52-N5-O53	120.3 (8)	O62-N6-O63	123.3 (9)

[a] See footnote *a* of Table III. Distances have not been corrected for thermal motion.

The bond lengths and angles within the α-pyridonate ligands are similar to those found in related structure determinations and show the usual changes[8] from the geometry of the free ligand.[19] The axial nitrite ligands in **1** have nearly equivalent geometries. As observed in other platinum nitrite complexes,[20] the average O–N–O angle is 5° larger than that found in the free nitrite ion. The plane of the nitrite ligand N5 roughly bisects the N1–Pt1–N2 angle, with the dihedral angle between the nitrite plane and the plane defined by N1, Pt1, N21, N5 being 48.6°. The same orientation is found for the other nitrite ligand where the corresponding dihedral angle is 51.4° (Figure 1). The nitrate ion geometry in all three structures is unexceptional. Packing diagrams and a complete list of hydrogen-bonding interactions may be found in the tables and ref 21.

A comparison of metal–metal and metal–axial ligand distances for a number of binuclear platinum(III) complexes

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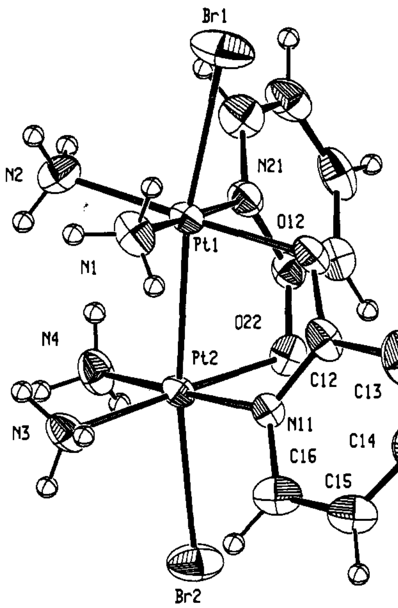

Figure 3. ORTEP illustration of the structure of the head-to-tail α-pyridonate-bridged cation $[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2]^{2+}$ (**6**) showing the 40% probability thermal ellipsoids. See caption to Figure 1.

Table VII. Interatomic Distances (Å) and Angles (deg) for $[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2\cdot{}^1/_2H_2O$ (**6**)[a]

	Coordination Sphere		
Pt1-Pt2	2.5820 (6)	Pt2-Br2	2.562 (1)
Pt1-Br1	2.573 (1)	Pt2-N3	2.061 (8)
Pt1-N1	2.044 (8)	Pt2-N4	2.063 (8)
Pt1-N2	2.057 (9)	Pt2-N11	2.058 (8)
Pt1-N21	2.035 (9)	Pt2-O22	2.026 (7)
Pt1-O12	2.013 (7)		
Pt2-Pt1-Br1	171.04 (4)	Pt1-Pt2-Br2	171.95 (4)
N1-Pt1-Br1	85.2 (3)	N3-Pt2-Br2	87.8 (3)
N1-Pt1-N2	92.2 (4)	N3-Pt2-N4	92.3 (3)
N1-Pt1-N21	176.9 (4)	N3-Pt2-O22	177.7 (3)
N1-Pt1-O12	87.7 (3)	N3-Pt2-N11	91.9 (3)
N2-Pt1-Br1	89.9 (3)	N4-Pt2-Br2	85.9 (3)
N2-Pt1-N21	90.6 (4)	N4-Pt2-O22	87.0 (3)
N2-Pt1-O12	177.7 (3)	N4-Pt2-N11	175.4 (3)
N21-Pt1-Br1	93.5 (3)	O22-Pt2-Br2	89.9 (2)
N21-Pt1-O12	89.5 (3)	O22-Pt2-N11	88.7 (3)
O12-Pt1-Br1	87.8 (2)	N11-Pt2-Br2	92.4 (2)
	Ligand Geometry		
O22-C22	1.318 (12)	O12-C12	1.308 (13)
N21-C22	1.341 (14)	N11-C12	1.331 (14)
C22-C23	1.404 (14)	C12-C13	1.388 (17)
C23-C24	1.334 (17)	C13-C14	1.377 (19)
C24-C25	1.391 (19)	C14-C15	1.376 (20)
C25-C26	1.393 (16)	C15-C16	1.364 (18)
C26-N21	1.357 (14)	C16-N11	1.349 (14)
O22-N21	2.321 (12)	O12-N11	2.312 (11)
Pt1-N21-C22	118.5 (7)	Pt2-N11-C12	117.5 (7)
Pt1-N21-C26	120.5 (8)	Pt2-N11-C16	120.6 (8)
Pt2-O22-C22	118.3 (6)	Pt1-O12-C12	119.9 (6)
C22-N21-C26	121.1 (10)	C12-N11-C16	121.3 (10)
O22-C22-N21	121.7 (9)	O12-C12-N11	122.4 (9)
O22-C22-C23	117.7 (10)	O12-C12-C13	117.9 (10)
N21-C22-C23	120.7 (10)	N11-C12-C13	119.7 (11)
C22-C23-C24	118.1 (12)	C12-C13-C14	119.7 (13)
C23-C24-C25	122.5 (11)	C13-C14-C15	118.7 (12)
C24-C25-C26	117.8 (11)	C14-C15-C16	120.0 (12)
C25-C26-N21	119.8 (13)	C15-C16-N11	120.2 (12)
	Hydrogen Bonds <2.36 Å		
O51-H1N4	2.23 (5)	O61-H3N1	2.25 (2)
O51-H3N3	2.19 (7)	O62-H1N1	1.96 (2)
O53A-H2N2	2.27 (5)	O62-H2N3	2.17 (6)
O53A-H3N2	2.20 (6)		
O53B-H2N2	2.36 (6)		
O53B-H3N4	2.33 (7)		
O51-H1N4-N4	155 (7)	O61-H3N1-N1	157 (6)
O51-H3N3-N3	153 (6)	O62-H1N1-N1	158 (6)
O53A-H2N2-N2	156 (5)	O62-H2N3-N3	144 (4)
O53A-H3N2-N2	138 (5)		
O53B-H2N2-N2	152 (5)		
O53B-H3N4-N4	142 (5)		

[a] See footnote *a* of Table IV. Distances have not been corrected for thermal motion.

including **1**, **2**, and **6** is presented in Table VIII.[3,5,6,18,22] In addition to **1**, **2**, and **6**, the structure of the nitrate-capped head-to-tail α-pyridonate-bridged platinum(III) dimer has been determined (**4**).[3b] With the exception of differences in the axial ligands, all four complexes have basically the same geometry. The Pt–Pt distances in the cations $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X]^{2+}$ increase in the series $X^- = NO_3^- < Cl^- < NO_2^- < Br^-$. The magnitude of the change in Pt–Pt distance is 0.035 Å, and, while this difference is small, it represents a significant change (30σ)[23] in metal–metal distance. Differences of this magnitude are also found in the tetrakis(μ-carboxylato)dirhodium(II) complexes, $Rh_2(O_2CR)_4L_2$, where the Rh–Rh bond lengths increase as the donor strength of the axial ligand L increases.[9,10] The change in the Rh–Rh bond length is a result of electronic effects that depend upon overlap populations and energetic differences between the interacting metal and ligand orbitals.[10] The Pt–Pt bond lengths in the diplatinum(III) complexes also increase with the increasing ligand donor strength. On the basis of the structural trans-influence series in mononuclear platinum(II) complexes,[24] the ordering of the ligands in this study, according to their ability to weaken a trans-ligand bond, follows the series found above: $Br^- \sim NO_2^- > Cl^- > NO_3^-$. The Pt–Pt distance in a related α-pyridonate-bridged complex, the head-to-head *cis*-diammineplatinum(III) dimer $[(H_2O)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)]^{3+}$ (**5**), is 0.007 Å shorter than the nitrate-capped head-to-tail dimer **4**. While this decrease would also be consistent with the structural trans-influence ability of the axial ligands ($NO_3^- > H_2O$), the decrease in the platinum–platinum distance may also result from electronic and steric differences associated with the opposite orientation of the α-pyridonate ligands.

The mutual nature of the structural trans-influence can be seen by examining the platinum–axial ligand bond distances. In each of the α-pyridonate-bridged platinum(III) complexes, the axial Pt–ligand bond is longer than normally found in complexes where the ligand is not trans to a Pt–Pt bond. In **1** the axial Pt–N bond lengths are ~0.15 Å longer than normally found in platinum nitrite complexes,[20] in **2** the Pt–Cl distances are ~0.13 Å larger than typically found in mononuclear platinum(II) complexes (range 2.27–2.33 Å),[25] and in **6** the Pt–Br bonds are ~0.1 Å larger than the values of 2.44–2.48 Å found in platinum(II) amine bromide structures.[26] An increase in the metal–axial ligand distance is also observed in many other metal–metal-bonded transition-metal complexes.[9,10] The large magnitude of this effect suggests that metal atoms can be considered among the strongest trans-influencing ligands. This point is illustrated by the fact that the Pt–Br bond trans to hydride ion, one of the best known trans

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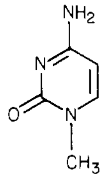
Table VIII. Comparison of Geometric Properties of Related Platinum(III) Complexes

	distance, Å			
compd	Pt-Pt	Pt-L(axial)		ref
$[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2](NO_3)_2\cdot{}^1/_2H_2O$ (1)	2.576 (1)	2.172 (10) (NO_2^-)	2.168 (11) (NO_2^-)	*a*
$[Pt_2(NH_3)_4(C_5H_4NO)_2Cl_2](NO_3)_2$ (2)	2.568 (1)	2.444 (2) (Cl^-)	2.429 (4) (Cl^-)	*a*
$[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_3)_2](NO_3)_2\cdot{}^1/_2H_2O$ (4)	2.547 (1)	2.170 (10) (NO_3^-)	2.165 (10) (NO_3^-)	3b
$[Pt_2(NH_3)_4(C_5H_4NO)_2(H_2O)(NO_3)](NO_3)_3\cdot 2H_2O$ (5)	2.540 (1)	2.122 (6) (H_2O)	2.193 (7) (NO_3^-)	3b
$[Pt_2(NH_3)_4(C_5H_4NO)_2Br_2](NO_3)_2\cdot{}^1/_2H_2O$ (6)	2.582 (1)	2.573 (1) (Br^-)	2.562 (1) (Br^-)	*a*
$(H_5O_2)[Pt_2(NH_3)_4(C_5H_6N_3O)_2(NO_2)_2](NO_3)_2$ (7)	2.584 (1)	2.12 (3) (NO_2^-)	2.13 (2) (NO_2^-)	18a
$K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ (8)	2.695 (1)	2.407 (2) (Cl^-)	*b*	6, 22
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ (9)	2.486 (2)[c]	2.151 (11) (H_2O)[c]		5b
$K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$ (10)	2.471 (1)	2.1226 (6) ($OSMe_2$)	*b*	5a

[a] This work. [b] Both Pt-L(axial) distances are symmetry equivalent. [c] Average values.

labilizers, in *trans*-$[PtHBr(PEt_3)_2]$ is 2.56 Å,[27] comparable to the values found in **6**.

The structure of the nitrite-capped platinum(III) dimer **1** is very similar to that of the head-to-tail dimer of 1-methylcytosine, $[(NO_2)(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)]^+$ (**7**).[18a] This binuclear complex of *cis*-diammineplatinum is bridged by 1-methylcytosinate ligands through the annular nitrogen atom N3 and a deprotonated exocyclic amine (4-NH_2) group. The complex contains a Pt–Pt distance of 2.584 (1) Å and axial nitrite ligands that are attached to the platinum atoms through elongated Pt–N bonds. The overall geometry of the cation is also comparable to that of compound **1**. The axial nitrite ligands assume similar orientations relative to the ligands in the equatorial platinum coordination plane. The tilt angle between adjacent platinum coordination planes (21°) and the average torsion angle about the Pt–Pt vector (25°) in compound **7** are also close to those values (20.4 and 27.1°, respectively) in the α-pyridonate-bridged complex **1**. As discussed previously,[3a] the oxidation state of platinum in **7** is probably +3 rather than +2.5 as originally believed.[18a] This reassignment is supported by the known correlation between bond order and bond length in metal–metal-bonded platinum complexes.[3b,28] Thus, a change in bond order from 0.5 to 1.0 should produce a significant change in the Pt–Pt distance, whereas the metal–metal bond lengths in **1** and **7** are very similar (Table VIII). With the synthetic route to the nitrite-capped dimer **1** described here, it may be possible to repeat the preparation of the 1-methylcytosinate-bridged dimer **7** so that further studies can be performed to verify the assigned oxidation state.



1-methylcytosine

The structure of the chloride-capped α-pyridonate dimer **2** can be compared to the structure of the binuclear platinum(III) octaphosphite complex, $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ (**8**).[6,22] While this complex contains a Pt–Pt single bond and axial chloride ligands, the geometry of the binuclear anion is quite different from that of the chloride-capped α-pyridonate-bridged dimer. The platinum coordination planes in the phosphite-bridged dimer are parallel to one another, and the platinum atoms in the complex are related to each other by a crystallographic inversion center. The Pt–Pt distance in compound **8** [2.695 (1) Å] is 0.127 Å longer and the average Pt–Cl distance is 0.030 Å shorter than the corresponding distances in compound **2**. The Pt–Pt bond in the phosphite-bridged dimer is considerably longer than that found in other symmetrically bridged diplatinum(III) complexes. For example, the Pt–Pt distances in the tetrakis(μ-phosphato)diplatinum(III) complex, $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ (**9**),[5b] and the tetrakis(μ-sulfato)diplatinum(III) complex, $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$ (**10**),[5a] are 2.486 (2) and 2.471 (1) (Å), respectively. This large difference (~0.22 Å) in Pt–Pt distance may be due in part to the structural trans influence of the axial chloride ligand, which is greater than that of a weak oxygen donor [H_2O in **9** and $OSMe_2$ in **10**]. The influence of the bridging ligands may also be a contributing factor, however. The ligand bite distance (P–P) in the phosphite-bridged dimer is very long (2.87 Å) compared to the bite distance (~2.5 Å) in the phosphate- (**9**) and sulfate- (**10**) bridged dimers. While the average ligand bite distance (2.3 Å) in the α-pyridonate-bridged diplatinum(III) complexes is shorter than those found in **9** and **10**, the presence of nonbonded repulsions between the in-plane ligands (NH_3) in the α-pyridonate dimers may contribute to the longer metal–metal distance in these compounds.[3b] Further studies are required to determine the relative importance of electronic and steric factors in determining the Pt–Pt distance in diplatinum(III) complexes.

Conclusion

cis-Diammineplatinum(III) α-pyridonate-bridged dimers are readily synthesized from the platinum(II) analogues by oxidative addition to the bimetallic center accompanied by metal–metal bond formation. The Pt–Pt bond distances in the head-to-tail α-pyridonate-bridged diplatinum(III) complexes $[(X)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(X)]^{2+}$ increase as a function of the axial ligand (X) in the series $NO_3^- < Cl^- < NO_2^- < Br^-$. The Pt–Pt distance lengthens with increasing axial ligand donor strength in a fashion consistent with the established structural trans influence series in mononuclear platinum complexes. Electronic and steric effects associated with the in-plane ligands also influence the Pt–Pt bond distances in diplatinum(III) complexes.

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Registry No. 1, 87420-62-0; **2**, 87352-14-5; **3**, 76775-76-3; **6**, 87352-17-8; Pt, 7440-06-4.

Supplementary Material Available: Atomic positional and thermal parameters (Tables S1 and S3, for **1** and **2**, respectively), final observed and calculated structure factors (Tables S2 and S4, for **1** and **2**, respectively), and final structure factors, anisotropic thermal parameters, and hydrogen and rigid-group atom positional and thermal parameters (Tables S5–S7, for **6**) (51 pages). Ordering information is given on any current masthead page.

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