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Reaction of α-Pyridone with Diaquo(ethylenediamine)platinum(II). Synthesis and Structure of the Head-to-Head Isomer of Bis(μ-2-pyridonato-*N*,*O*)bis[(ethylenediamine)platinum(II)] Nitrate

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The head-to-head isomer of the dimeric compound $[Pt_2(en)_2(C_5H_4NO)_2](NO_3)_2$ has been synthesized in the reaction of $[Pt(en)(H_2O)_2]^{2+}$ with α-pyridone (C_5H_4NHO). An X-ray structural study of this compound shows that, like its *cis*-diammineplatinum(II) analogue, it forms a dimer of dimers in the solid state. The Pt–Pt distances of 2.992 (1) Å for the α-pyridonate-bridged binuclear unit and 3.236 (1) Å for the interdimer separation are each ~0.1 Å longer than the corresponding values in the *cis*-diammineplatinum(II) complex. This increase in the Pt–Pt distances is attributed to steric repulsion between adjacent in-plane ligands, which is greater in the ethylenediamine complex. The steric interaction also affects the chemical reactivity of the $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ cation, which preliminary work shows to isomerize more readily and to be more stable toward oxidation to the Pt(III) dimer with nitric acid than the diammine analogue. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 12.169$ (2) Å, $b = 10.860$ (1) Å, $c = 17.282$ (3) Å, $\beta = 103.11$ (2)°, $V = 2224$ Å^3, and $Z = 4$. Refinement converged at $R_1 = 0.033$.

Introduction

Studies of the reactions of *cis*-diammineplatinum(II) complexes with α-pyridone have been instrumental in elucidating the chemistry of platinum blues.[1-5] For a number of years, the nature of the blue products produced from the reactions of *cis*-diaquodiammineplatinum(II) with a variety of multifunctional amide ligands, such as uracil and thymine, remained unknown.[6] An understanding of this chemistry, which is complicated by large product distributions and product instability,[1,6,7] began to emerge in 1977, when the first crystalline platinum blue was isolated from the reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with α-pyridone.[2] X-ray structural studies of the complex, *cis*-diammineplatinum α-pyridone blue (PPB), showed this anomalously colored platinum compound to be a mixed-valent tetramer, formally comprised of one Pt(III) and three Pt(II) centers (Figure 1). The tetranuclear chain of PPB, which contains one unpaired electron delocalized over the four platinum atoms, is composed of two dimeric *cis*-$Pt(NH_3)_2$ units bridged in a head-to-head fashion by α-pyridonate ligands. Comparative chemical and spectroscopic studies, which show that PPB is similar to the blue platinum products obtained in the related reactions of uracil and thymine, provided a basis for understanding these latter materials.[3,9]

Recent ^{195}Pt NMR and X-ray crystallographic work[4] revealed that both head-to-head and head-to-tail α-pyridonate-bridged dimers of *cis*-diammineplatinum(II) are also produced in the reaction that leads to PPB. The structure of the head-to-head platinum(II) dimer, $[(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2](NO_3)_2$, is very similar to that of PPB. Two of the head-to-head binuclear units are associated through intermolecular hydrogen bonds, resulting in a tetranuclear platinum(II) species that has a similar geometry but with longer (~0.1–0.2 Å) Pt–Pt distances than found in PPB. Chemical and electrochemical studies showed that the head-to-head platinum(II) complex can be oxidized to the mixed-valent tetramer PPB through a net loss of one electron per two dimeric units or to the diplatinum(III) complex $[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(H_2O)]^{3+}$ through the loss of two electrons per dimer.[5] Studies of this oxidation process, which involves the formation of partial metal–metal bonds in PPB and a single Pt–Pt bond in the head-to-head platinum(III) dimer, provided valuable insight into the chemistry that leads to formation of the platinum blues.

In this report we examine the reaction of α-pyridone with a related diaquoplatinum(II) complex, $[Pt(en)(H_2O)_2]^{2+}$, to study the effect of the nonbridging ligand on the structure and reactivity of the α-pyridonate-bridged complexes. In previous structural investigations[4,5,10] of the α-pyridonate-bridged complexes of *cis*-diammineplatinum, nonbonded repulsions between the ammine ligands in adjacent platinum coordination planes induced structural changes in the binuclear cations, which varied with the Pt–Pt distance. For example, as the Pt–Pt distance decreases in going from the Pt(II) to Pt(III) dimers, the ammine ligands assume a more staggered orientation through a rotation of the adjacent platinum coordination planes about the Pt–Pt vector. It was also suggested[5,10] that the interaction between the adjacent ammine ligands could be partly responsible for the longer (~0.1 Å) Pt–Pt distances in these diplatinum(III) complexes, when compared to those of symmetrically bridged diplatinum(III) complexes, such as $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$,[11] which lack this feature. Here we show, through studies of the ethylenediamine analogue, that the Pt–Pt distances and the chemical reactivity of the head-to-head α-pyridonate-bridged platinum(II) complexes are influenced by the steric properties of the adjacent in-plane ligand. This effect could prove useful in studying other systems that lead to platinum blue complexes.

Experimental Section

Preparation of Compounds. The starting material, $[Pt(en)I_2]$, was prepared from $K_2[PtCl_4]$ (Engelhard) by using a modification of the

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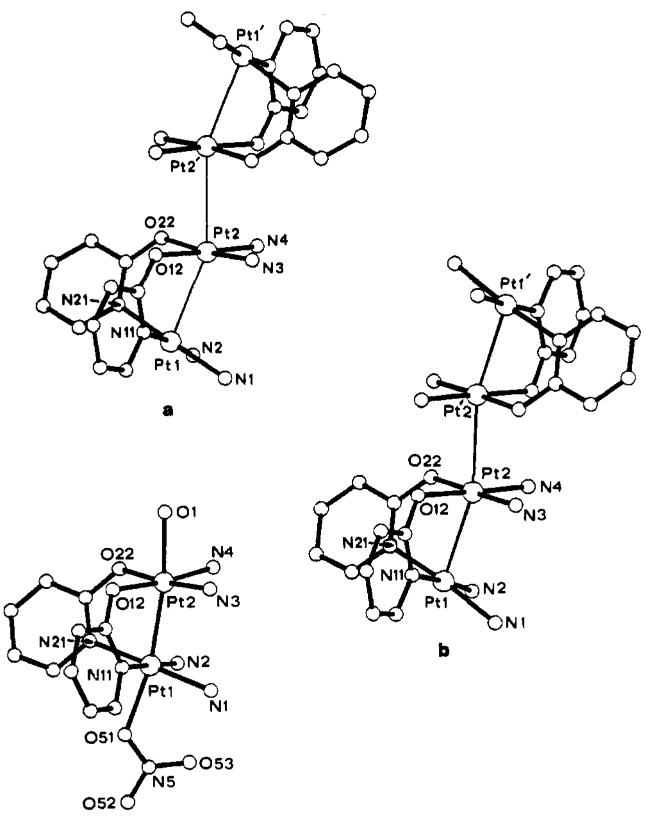

Figure 1. Structures of the head-to-head α-pyridonate-bridged complexes of *cis*-diammineplatinum: (a) the platinum(II) dimer of dimers, $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2^{4+}$; (b) the mixed-valent ($Pt^{2.25+}$) tetramer, *cis*-diammineplatinum α-pyridone blue, $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2^{5+}$; (c) the platinum(III) dimer, $[Pt_2(NH_3)_4(C_5H_4NO)_2(H_2O)(NO_3)]^{3+}$.

method of Dhara.[12] A solution of 16.8 g (40 mmol) of $K_2[PtCl_4]$ in 168 mL of water was warmed to 40 °C with stirring while a solution of KI (27.7 g/25 mL of water) (167 mmol) was added dropwise. After 12 min at 40 °C, 3.75 mL of ethylenediamine (Aldrich) was slowly added over a period of 5 min to the dark solution of $K_2[PtI_4]$. The resulting ochre precipitate was stirred for an additional 15 min at 40 °C and then cooled to 0 °C for 1 h. The $[Pt(en)I_2]$ was removed by filtration and washed two times with 100 mL of warm water, two times with 100 mL of ethanol, and once with 250 mL of diethyl ether. The yield was 20.2 g (98%), after drying. The $[Pt(en)I_2]$ prepared in this fashion can be used directly, or it can be converted to $[Pt(en)Cl_2]$,[12] which may also be used as a starting material in the reaction described below.

Bis(μ-2-pyridonato-*N*,*O*)bis[(ethylenediamine)platinum(II)] Nitrate, $[Pt_2(en)_2(C_5H_4NO)_2]_2(NO_3)_4$ (1): Head-to-Head Isomer. Compound **1** was obtained from the reaction of $[Pt(en)(H_2O)_2]^{2+}$ with α-pyridone as follows. An aqueous solution of $[Pt(en)(H_2O)_2](NO_3)_2$ was prepared by adding 2.04 g of $AgNO_3$ to a suspension of 6.13 g (12 mmol) of $[Pt(en)I_2]$ in 60 mL of water. After the suspension was stirred for 2 h at 60 °C, the temperature was lowered to 0 °C for 2 h and the resulting AgI precipitate was removed by filtration. A solution of 1.15 g of α-pyridone in 10 mL of water was added to the filtrate, and the pH of the resulting solution was adjusted to 6 with 1 M NaOH. The solution was kept at 40 °C for 20 h and then allowed to evaporate in air for 1 day. Large (up to several mm^3) yellow crystals of **1** were collected from this solution (4.9 g). A second crop (1.8 g) was obtained from further evaporation of the filtrate, providing a total yield of 68%. Anal. Calcd for $Pt_2C_{14}H_{24}N_8O_8$ (**1**): C, 20.44; H, 2.94; N, 13.62. Found: C, 20.29; H, 2.93; N, 13.53. UV–visible spectrum of **1** in water: λ 298 (ε 5800 cm^{-1} M^{-1}), 365 nm (sh, ε <170 cm^{-1} M^{-1}).

Collection and Reduction of X-ray Data for $[Pt_2(en)_2(C_5H_4NO)_2]_2(NO_3)_4$ (1). A small, equidimensional (0.1 mm × 0.1 mm × 0.1 mm), yellow crystal, nearly spherical in shape, was chosen for the diffraction study. The quality of the crystal was examined by taking open-counter ω scans of several strong low-angle (<10° in θ) reflections and judged to be acceptable for data collection ($\Delta\bar{\omega}_{1/2} \sim 0.1°$). The unit cell parameters, space group,[13] and data collection procedures[14] are summarized in Table I.

Table I. Experimental Details of the X-ray Diffraction Study of $[Pt_2(en)_2(C_5H_4NO)_2](NO_3)_2$ (1)

(A) Crystal Parameters[a] at 23 °C

a, Å	12.169 (2)	space group	$P2_1/c$
b, Å	10.860 (1)	*Z*	4
c, Å	17.282 (3)	ρ(calcd), g cm^{-3}	2.456
β, deg	103.11 (2)	ρ(obsd), g cm^{-3}	2.45 (2)[b]
V, $Å^3$	2224.4	mol wt	822.57

(B) Measurement of Intensity Data[c]

instrument	Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized
stds,[d] measd every 1 h of X-ray exposure time	$(1\bar{7}6)$, $(\bar{3}\bar{4}3)$, $(\bar{4}\bar{2}5)$
no. of reflcns collcd (non-space group extinguished)	5623 [$3 \leqslant 2\theta \leqslant 55°$ $(+h, +k, \pm l)$; $3 \leqslant 2\theta \leqslant 20°$ $(-h, -k, \pm l)$]

(C) Treatment of Intensity Data[c]

μ,[e] cm^{-1}	128.7
averaging, R_{av}	0.014
no. of reflcns after averaging	5103
obsd unique data [$F_o > 4\sigma(F_o)$]	3876

[a] From a least-squares fit of the setting angles of 25 reflections with $2\theta > 30°$. [b] By suspension in a mixture of $CHBr_3$ and $CHCl_3$. [c] See ref 14 for typical procedures used in our laboratory. [d] Showed no decay during data collection. [e] Since the crystal was small and nearly spherical in shape, an absorption correction was not performed. ψ scans of several reflections showed only small (<10%) variation in intensity as a function of ψ.

Structure Solution and Refinement. The structure was solved by the usual Patterson and Fourier methods and refined[15] with anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors and anomalous dispersion corrections for all non-hydrogen atoms were obtained from ref 16, and hydrogen atom scattering factors, from ref 17. The positions of all C–H and N–H hydrogen atoms were refined with constraints by using isotropic thermal parameters. The hydrogen atoms of the α-pyridonate rings and of the ethylenediamine carbon atoms were placed at calculated positions [*d*(C–H) = 0.95 Å] and constrained to "ride" on the carbon atoms to which they are attached.[15] The hydrogen atoms of the amine groups were also placed at calculated positions [*d*(N–H) = 0.87 Å] and refined as rigid groups. The hydrogen atoms of each α-pyridonate ring were given an independent set of common thermal parameters in the refinement. The hydrogen atoms of each carbon atom in the two ethylenediamine ligands were also given a set of independent thermal parameters. All hydrogen atoms attached to the nitrogen atoms of the amine groups were refined with fixed thermal parameters (U_{iso} = 0.06 $Å^2$).

Full-matrix least-squares refinement of the structure using 318 parameters converged at $R_1 = 0.033$ and $R_2 = 0.041$.[18] The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.000/[\sigma^2(F_o) + 0.000625F_o^2]$. The maximum parameter shift in the final cycle of refinement was 0.08σ, and the only residual peaks of significant height (<1.9 e $Å^{-3}$) observed in the final difference Fourier

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

Table II. Final Positional Parameters for $[Pt_2(en)_2(C_5H_4NO)_2]_2(NO_3)_4$ (1)[a]

ATOM	X	Y	Z
Pt1	0.19002(2)	0.80261(3)	0.35718(2)
Pt2	0.37506(2)	0.95551(3)	0.45476(2)
N1	0.1446(6)	0.8849(6)	0.2488(4)
H1N1	0.1535(13)	0.8314(15)	0.2136(3)
H2N1	0.1887(9)	0.9475(14)	0.2491(8)
C1	0.0252(7)	0.9247(10)	0.2347(5)
H1C1	0.0103(7)	0.9862(10)	0.1945(5)
H2C1	-0.0236(7)	0.8565(10)	0.2189(5)
C2	0.0079(8)	0.9778(8)	0.3139(5)
H1C2	-0.0693(8)	0.9970(8)	0.3098(5)
H2C2	0.0523(8)	1.0498(8)	0.3278(5)
N2	0.0450(5)	0.8795(7)	0.3744(4)
H1N2	0.0590(11)	0.9095(15)	0.4221(5)
H2N2	-0.0052(6)	0.8214(10)	0.3694(11)
N3	0.3661(6)	1.1319(6)	0.4161(4)
H1N3	0.3238(18)	1.1371(8)	0.3679(5)
H2N3	0.4342(12)	1.1590(7)	0.4150(12)
C3	0.3179(13)	1.2144(10)	0.4702(8)
H1C3	0.2667(13)	1.2703(10)	0.4385(8)
H2C3	0.3778(13)	1.2590(10)	0.5031(8)
C4	0.2608(13)	1.1499(11)	0.5184(8)
H1C4	0.2605(13)	1.1980(11)	0.5643(8)
H2C4	0.1854(13)	1.1364(11)	0.4898(8)
N4	0.3143(7)	1.0268(7)	0.5446(4)
H1N4	0.3690(13)	1.0382(17)	0.5868(4)
H2N4	0.2637(15)	0.9785(11)	0.5569(10)
012	0.4427(5)	0.8938(5)	0.3628(3)
N11	0.3268(5)	0.7254(6)	0.3296(4)
C12	0.4248(7)	0.7853(7)	0.3327(5)
C13	0.5092(8)	0.7284(8)	0.3003(5)
H13	0.5767(8)	0.7720(8)	0.2999(5)
C14	0.4949(8)	0.6119(9)	0.2695(6)
H14	0.5508(8)	0.5750(9)	0.2465(6)
C15	0.3975(8)	0.5491(8)	0.2728(6)
H15	0.3880(8)	0.4662(8)	0.2551(6)
C16	0.3142(7)	0.6063(8)	0.3015(5)
H16	0.2465(7)	0.5629(8)	0.3019(5)
022	0.4018(5)	0.7872(5)	0.5078(4)
N21	0.2254(6)	0.7001(6)	0.4594(4)
C22	0.3276(7)	0.7016(7)	0.5112(5)
C23	0.3543(9)	0.6066(9)	0.5676(6)
H23	0.4264(9)	0.6048(9)	0.6030(6)
C24	0.2766(10)	0.5162(10)	0.5719(6)
H24	0.2944(10)	0.4530(10)	0.6107(6)
C25	0.1728(9)	0.5181(10)	0.5192(7)
H25	0.1188(9)	0.4554(10)	0.5204(7)
C26	0.1495(7)	0.6096(8)	0.4665(5)
H26	0.0767(7)	0.6122(8)	0.4321(5)
N5	0.1970(6)	0.2122(8)	0.2152(5)
051	0.2492(7)	0.1261(7)	0.2543(4)
052	0.1217(7)	0.1840(8)	0.1557(5)
053	0.2210(8)	0.3153(8)	0.2308(8)
N6	0.0966(7)	-0.1742(8)	0.5883(4)
061	0.0902(8)	-0.0833(8)	0.5450(4)
062	0.1852(7)	-0.1981(7)	0.6348(4)
063	0.0138(7)	-0.2383(10)	0.5848(6)

[a] Atoms are labeled as shown in Figure 2. The atoms of the α-pyridonate rings are labeled according to their ring number followed by their ring position (e.g., ring 1 contains N11 and C12–C16). Hydrogen atoms are labeled according to the atom to which they are attached (H16 is bound to C16, etc.). Estimated standard deviations in the least significant digit(s) are given in parentheses.

Table III. Interatomic Distances (Å) and Angles (deg) for $[Pt_2(en)_2(C_5H_4NO)_2]_2$ (1)[a]

Coordination Sphere			
Pt1-Pt2	2.9915(4)	Pt2-Pt2'	3.2355(5)
Pt1-N1	2.035(6)	Pt2-N3	2.024(7)
Pt1-N2	2.034(6)	Pt2-N4	2.019(7)
Pt1-N11	2.015(6)	Pt2-012	2.060(6)
Pt1-N21	2.050(6)	Pt2-022	2.038(6)
Pt1-Pt2-Pt2'	160.58(2)	N3-Pt2-N4	83.6(3)
N1-Pt1-N2	83.7(3)	N3-Pt2-012	93.1(2)
N1-Pt1-N11	91.8(3)	N3-Pt2-022	171.4(2)
N1-Pt1-N21	172.7(3)	N4-Pt2-012	176.1(3)
N2-Pt1-N11	174.8(2)	N4-Pt2-022	92.7(3)
N2-Pt1-N21	96.7(3)	012-Pt2-022	90.3(2)
N11-Pt1-N21	87.4(3)		
Ligand Geometry			
012-C12	1.287(9)	022-C22	1.306(10)
N11-C12	1.349(10)	N21-C22	1.358(10)
C12-C13	1.418(11)	C22-C23	1.405(12)
C13-C14	1.368(12)	C23-C24	1.376(14)
C14-C15	1.379(13)	C24-C25	1.381(15)
C15-C16	1.374(12)	C25-C26	1.333(13)
C16-N11	1.378(10)	C26-N21	1.373(10)
012-N11	2.302(9)	022-N21	2.321(9)
N1-C1	1.481(10)	N3-C3	1.507(11)
C1-C2	1.543(12)	C3-C4	1.389(16)
C2-N2	1.491(9)	C4-N4	1.511(12)
Pt1-N11-C12	124.1(5)	Pt1-N21-C22	122.9(5)
Pt1-N11-C16	116.3(5)	Pt1-N21-C26	116.9(6)
Pt2-012-C12	123.3(5)	Pt2-022-C22	128.1(5)
C12-N11-C16	119.6(7)	C22-N21-C26	118.9(7)
012-C12-N11	121.6(7)	022-C22-N21	121.2(7)
012-C12-C13	119.2(7)	022-C22-C23	120.0(8)
N11-C12-C13	119.2(7)	N21-C22-C23	118.8(8)
C12-C13-C14	121.2(8)	C22-C23-C24	120.5(9)
C13-C14-C15	118.4(8)	C23-C24-C25	119.3(9)
C14-C15-C16	120.2(8)	C24-C25-C26	118.9(9)
C15-C16-N11	121.3(8)	C25-C26-N21	123.5(9)
Pt1-N1-C1	109.4(5)	Pt2-N3-C3	110.9(5)
Pt1-N2-C2	109.0(5)	Pt2-N4-C4	108.5(6)
N1-C1-C2	106.8(7)	N3-C3-C4	113.0(9)
C1-C2-N2	105.9(7)	C3-C4-N4	112.7(10)
Anion Geometry			
N5-051	1.241(10)	N6-061	1.230(10)
N5-052	1.251(11)	N6-062	1.217(10)
N5-053	1.173(10)	N6-063	1.215(11)
051-N5-052	116.9(8)	061-N6-062	119.8(10)
051-N5-053	121.6(10)	061-N6-063	119.5(9)
052-N5-053	121.3(10)	062-N6-063	120.7(10)
Hydrogen Bonds			
Inter-cation			
H2N3-022'	2.21(1)	N3-H2N3-022'	143(3)
H1N4-012'	2.38(2)	N4-H1N4-012'	145(1)
Nitrate Anions			
051-H2N1	2.07(2)	051-H2N1-N1	162(1)
051-H1N3	1.97(1)	051-H1N3-N3	169(2)
052-H2N2'	2.04(1)	052-H2N2'-N2'	174(2)
061-H1N2	2.07(1)	061-H1N2-N2	160(1)
061-H2N4	2.18(2)	061-H2N4-N4	152(2)
062-H1N1'	2.08(1)	062-H1N1'-N1'	176(1)

[a] For atom-labeling scheme, see Figure 2. Distances have not been corrected for thermal motion.

map were within 1.0 Å of the platinum atoms. 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 function was found to be acceptable.

The final atomic positional parameters together with their estimated standard deviations are reported in Table II. The interatomic distances and angles with estimated standard deviations are presented in Table III. A complete listing of atomic positional and thermal parameters for compound 1 (Table S1) and a listing of final observed an calculated structure factors (Table S2) are available as supplementary material.

Results and Discussion

The head-to-head α-pyridonate-bridged compound crystallizes with four dimeric units per unit cell. Each unique binuclear cation is symmetry related to a neighboring cation through a crystallographic inversion center that lies midway between the two cations, on the Pt2–Pt2′ vector (Figure 2). The halves of the resulting tetranuclear unit are linked through hydrogen bonds formed between the exocyclic oxygen atoms of the α-pyridonate ligands and the hydrogen atoms of the amine nitrogens of the ethylenediamine ligands (H2N3–O22′, H1N4–O12′; see Table III). The Pt2–Pt2′ distance [3.236 (1) Å] is considerably longer (0.244 Å) than the distance [2.992 (1) Å] within the bridged, binuclear unit. The angle between the Pt1–Pt2 and Pt2–Pt2′ vectors in the tetranuclear chain is 160.58 (2)°.

The bond lengths and angles between the platinum and its donor atoms are typical of those found in other ethylenediamine[19] and amidate-bridged[20] complexes of platinum(II). The bond lengths and angles within the the ethylenediamine ligands also compare favorably with those found in related platinum(II) complexes. The geometry of the ethylenediamine

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(19) (a) Faggiani, R.; Lippert, B.; Lock, C. J. L. *Inorg. Chem.* **1980**, *19*, 295. (b) Gellert, R. W.; Bau, R. *J. Am. Chem. Soc.* **1975**, *97*, 7380. (c) Neidle, S.; Taylor, G. L.; Robins, A. B. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1838.

(20) (a) Lock, C. J. L.; Peresie, H. J.; Rosenberg, B.; Turner, G. *J. Am. Chem. Soc.* **1978**, *100*, 3371. (b) Faggiani, R.; Lock, C. J. L.; Pollock, R. J.; Rosenberg, B.; Turner, G. *Inorg. Chem.* **1981**, *20*, 804.

Table IV. Comparison of Geometric Properties of Head-to-Head α-Pyridonate-Bridged Platinum Complexes

compd	formal Pt oxidn state	Pt-Pt dist, Å	dihedral angle,[a] deg τ	dihedral angle,[a] deg ω	Pt-Pt-Pt angle, deg	ref
$[Pt_2(en)_2(C_5H_4NO)_2]_2(NO_3)_4$ (1)	2.0	2.992 (1) 3.236 (1)	39.6	24.9	160.58 (2)	*b*
$[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ (2)	2.0	2.877 (1) 3.129 (1)	30.0	20.3	158.40 (3)	4
$[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_5\cdot H_2O$ (3)	2.25	2.775 (1) 2.877 (1)	27.4	22.8	164.60 (2)	2
$[Pt_2(NH_3)_4(C_5H_4NO)_2(H_2O)(NO_3)](NO_3)_3\cdot 2H_2O$ (4)	3.0	2.540 (1)	20.0	23.2		5

[a] τ is the tilt angle between adjacent platinum coordination planes in the bridged unit, and ω is the average torsion angle (or twist) about the Pt-Pt vector. [b] This work.

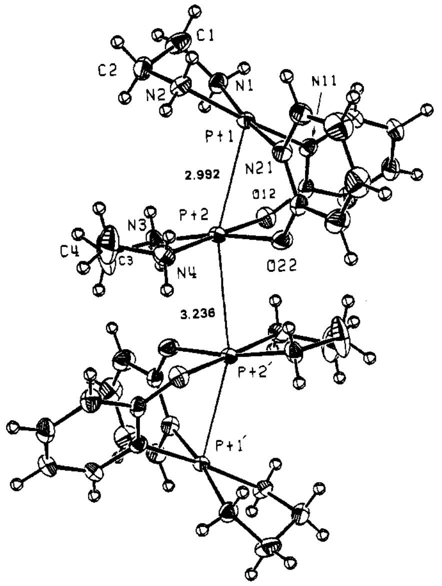

Figure 2. ORTEP illustration of the structure of the head-to-head α-pyridonate-bridged cation $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ (**1**), showing the 40% probability thermal ellipsoids and the Pt–Pt distances in Å. For clarity, the hydrogen atoms are depicted as spheres with *B* set to 1 $Å^2$. The two dimeric cations of the tetranuclear unit are related to one another by a crystallographic inversion center that lies at the center of the Pt2–Pt2′ vector.

ligand attached to Pt2 is, however, significantly different from the geometry of the corresponding ligand bound to Pt1. The N3–C3–C4 and C3–C4–N4 bond angles of 113.0 (9) and 112.7 (10)°, respectively, are an average of 6.5° (5.4σ)[21] larger, and the C3–C4 bond distance is 0.15 Å (7.7σ) smaller than the corresponding values in the Pt1 ethylenediamine ligand. While the bond lengths and angles in both ethylenediamine ligands are within the range (C–C–N angles 109–119° and C–C distances 1.29–1.54 Å)[19] found in other ethylenediamine–platinum(II) complexes, the distortion of the geometry of the Pt2 ethylenediamine ligand may be a result of a static or dynamic disorder of the C3 and C4 carbon atoms. Although distinct positions of disorder for C3 and C4 were not observed in the electron density map in this region, static disorder over two closely spaced positions could be responsible for the distorted ring conformation in the Pt2 ethylenediamine ligand. Alternatively, the increased amplitude of the thermal motion of these carbon atoms, which lies in a direction perpendicular to the vector defined by nitrogen atoms N3 and N4 (Figure 2), could account for the observed geometry. The increased thermal motion of the C3 and C4 atoms may result from a dynamic process that involves movement of the intercation hydrogen bonds. To maximize the hydrogen bond interaction between the hydrogen atoms of N3 and N4 and the exocyclic oxygen atoms of the adjacent cation, the amine hydrogen atoms must both assume axial positions in the five-membered PtN_2C_2 chelate ring. This conformation, which allows both amine hydrogen atoms to point in the same direction, can be obtained by reducing the N3–C3–C4–N4 torsion angle, and as expected, the torsion angle about the C3–C4 bond (35.3°) is 19.3° smaller than the C1–C2 torsion angle (54.6°). Similar changes in ring conformations, induced by the rotation of NH_2 or NH groups to maximize hydrogen-bonding interactions, have also been observed in the diethylenetriamine complexes *fac*-$[Pt(dien)Cl_3]Cl\cdot H_2O$[22a] and $[Co(dien)_2]^{3+}$.[22b] Fluctuations in the positions of the axial hydrogen atoms (H2N3 and H1N4; see Table III) could be responsible for changing the ring conformation in a fashion that leads to the increased amplitude of vibration for carbon atoms C3 and C4 and produces an averaged geometry that appears distorted.

Both platinum coordination spheres in the head-to-head dimer are planar, with a rms deviation of 0.039 Å for the four ligands from the least-squares plane of Pt1 and 0.049 Å for the plane of Pt2. As observed in the α-pyridonate-bridged complexes of *cis*-diammineplatinum(II),[4] the platinum atoms are slightly displaced out of the plane toward one another (0.091 Å for Pt1 and 0.090 Å for Pt2). The tilt angle between the two platinum coordination planes is 39.6°, and the average torsion angle about the Pt1–Pt2 vector is 24.9°. The α-pyridonate rings are also planar with a seven-atom rms deviation of 0.028 Å for ring 1 and 0.010 Å for ring 2. The platinum atoms Pt1 and Pt2 are displaced out of the plane of ring 1 by 0.310 and 0.932 Å and out of the plane of ring 2 by 0.497 and 0.502 Å, respectively. The dihedral angles between the platinum coordination planes and the planes of the α-pyridonate rings are, for the Pt1 plane, 79.6° (ring 1) and 61.9° (ring 2) and, for the Pt2 plane, 57.0° (ring 1) and 89.0° (ring 2).

A comparison of the bond lengths and angles within the α-pyridonate ligands shows that both rings have equivalent geometries. Both of the α-pyridonate rings also have similar ligand bite distances (N1–O2 = 2.302 (9) Å in ring 1 and 2.321 (9) Å in ring 2). A comparison of the geometry of the α-pyridonate rings in compound **1** to that of free α-pyridone[23] shows the usual[4] changes to occur upon platinum coordination. Discussion of the unit cell packing of compound **1** may be found in ref 24.

A comparison of selected geometric features of a number of related α-pyridonate-bridged platinum complexes is presented in Table IV. The structure of compound **1** is similar to that of the head-to-head α-pyridonate-bridged dimer of *cis*-diammineplatinum(II), $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ (**2**). This compound (Figure 1a) also forms a hydrogen-bonded tetranuclear unit in the crystal lattice. The intra- and inter-

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[21] The esd is calculated with $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$, where σ_1 and σ_2 are the errors in the bond lengths or angles being compared.

[22] (a) Britten, J. F.; Lock, C. J. L. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2958. (b) Keene, F. R.; Searle, G. H. *Inorg. Chem.* **1974**, *13*, 2173.

[23] (a) Almlöf, J.; Kvick, Å.; Olovsson, I. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1201. (b) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591.

[24] Hollis, L. S., Ph.D. Dissertation, Columbia University, 1982.

molecular Pt–Pt distances within the tetranuclear unit of the ethylenediamine analogue **1** are 0.115 (1) and 0.106 (1) Å longer, respectively, and the Pt1–Pt2–Pt2′ angle is 2.2 (3)° larger than the corresponding values in the diammine complex **2**.

The relationship between the Pt–Pt distances and the two geometric parameters τ and ω in a number of α-pyridonate-bridged complexes of *cis*-diammineplatinum has been examined previously.[4,5,10] When the head-to-head α-pyridonate-bridged platinum(II) complex **2** is oxidized by removing one electron from the tetranuclear unit, the paramagnetic complex *cis*-diammineplatinum α-pyridone blue (PPB) is produced (Figure 1b).[2–5] This mixed-valent species, $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2^{5+}$ (**3**), also retains the basic structural geometry that is found in the platinum(II) analogue **2**. The main structural differences between these two complexes are (1) a decrease in the Pt–Pt distances [0.102 (1) Å between Pt1–Pt2 and 0.252 (1) Å between Pt2–Pt2′], (2) a decrease in the tilt angle τ (from 30.0 to 27.4°), and (3) an increase in the torsion angle ω (from 20.3 to 22.8°). When the mixed-valent ($Pt^{2.25+}$) complex PPB is oxidized by removing three additional electrons per tetranuclear unit, the head-to-head platinum(III) dimer is produced.[5] This complex (Figure 1c), $[(H_2O)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_3\cdot 2H_2O$ (**4**), contains a Pt–Pt single bond and axial water and nitrate ligands. The Pt–Pt distance in the diplatinum(III) complex is 0.235 (1) Å shorter than the corresponding distance in PPB, and accompanying this decrease, the tilt angle (τ) again decreases from 27.4 to 20.0° and the twist angle increases from 22.8 to 23.2°. This relationship is also found in the structures of the head-to-tail α-pyridonate-bridged dimers of platinum(II)[4] $[(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2](NO_3)_2\cdot 2H_2O$ (**5**) and platinum(III)[5] $[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_2\cdot {}^1/_2H_2O$ (**6**). As the Pt–Pt distance decreases from 2.898 (1) Å in **5** to 2.547 (1) Å in the nitrate-capped diplatinum(III) complex **6**, τ decreases from 28.8 to 20.3° and ω increases from 20.3 to 26.3°.

The reason that the interplanar tilt angle (τ) is coupled to the Pt–Pt distance in these compounds is related to the α-pyridonate ligand bite distance, which remains constant (~2.3 Å) in each case, and to the platinum coordination geometry, which remains planar in each complex. The decrease in the Pt–Pt distance that accompanies metal–metal bond formation in both head-to-head and head-to-tail bridged complexes requires the platinum coordination planes to move closer together. The decrease in the interplanar separation is accomplished by decreasing the Pt–O2–C2 and Pt–N1–C2 angles in a motion that can be viewed as a pivoting of the platinum coordination planes at their points of attachment. The result of this change is a decrease in the interplanar tilt angle. As the Pt–Pt distance decreases, the average torsion angle (ω) about the Pt–Pt vector increases. Since the van der Waals radius of the NH_3 group is approximately that of a methyl group (2 Å),[25] the increase in the interplanar twist angle serves to minimize the nonbonded repulsions between the ammine ligands in adjacent platinum coordination planes.

The elongated Pt–Pt distance in the ethylenediamine complex **1** is also related to the steric interaction between the adjacent in-plane ligands. The large interplanar tilt angle, 9.6° greater than the tilt angle in the diammine analogue **2**, is consistent with the long Pt–Pt distance, but the large twist angle (24.9°) is not. While ω decreases with an increase in the Pt–Pt distance in the diammine complexes **2**, **3**, and **4**, the opposite effect is found in the ethylenediamine complex. The large twist angle, which is even greater than that found in the head-to-head platinum(III) dimer **4**, reflects the increased interplanar steric repulsion associated with the relatively bulky ethylenediamine ligands. The increase in the Pt–Pt distance presumably occurs to relieve the enhanced nonbonded repulsive interactions. Further structural studies of α-pyridonate-bridged complexes containing in-plane ligands with different steric properties are required to determine the limitations of this effect.

The relationship between the steric properties of the in-plane ligands and the geometric properties of the α-pyridonate-bridged compounds may prove useful in designing complexes having specific chemical properties. Preliminary studies of the ethylenediamine complex **1** indicate it to be more difficult to oxidize than the diammine analogue **2**. Treatment of the diammine complex **2** with 1 M HNO_3 results in the immediate formation of PPB (**3**), whereas the ethylenediamine complex is stable in 1 M HNO_3. Further addition of nitric acid (to ~3 M) does, however, produce a transient blue species, which presumably is a mixed-valent complex similar to PPB. The steric properties of the in-plane ligands, which lead to an increase in the Pt–Pt distances, also attenuate the redox potential of the complex. With the proper choice of the in-plane ligand, it may be possible to tune the redox potential in these binuclear platinum complexes. This prospect is of particular interest since, in the case of the head-to-tail α-pyridonate-bridged complex **5**, the redox reaction, which converts the platinum(II) dimer **5** to the diplatinum(III) complex **6**, proceeds through a concerted two-electron charge-transfer process.[5] Assuming that the in-plane ligands are capable of influencing the redox properties of the head-to-tail isomer in a fashion similar to that found in the head-to-head dimer, it may be possible to prepare a tunable two-electron redox couple. Moreover, ^{195}Pt NMR studies of **1** reveal that it undergoes a head-to-head to head-to-tail isomerization more readily than the less sterically strained analogue.[26] Further studies of this system are currently in progress.[26]

Conclusion

The structure of the head-to-head α-pyridonate-bridged dimer of (ethylenediamine)platinum(II) is similar to that of the analogous complex of *cis*-diammineplatinum(II). The intercation Pt–Pt distance in the ethylenediamine complex is ~0.1 Å longer than the corresponding distance in the diammine analogue, however. The increase in the Pt–Pt distance is attributed to steric repulsions between adjacent in-plane ligands, which are greater in the ethylenediamine complex. This steric effect influences the chemical reactivity of the complex by stabilizing the platinum(II) dimer toward oxidation with nitric acid and accelerating its rate of isomerization to the head-to-tail isomer.

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Registry No. 1, 86372-66-9; $[Pt(en)(H_2O)_2](NO_3)_2$, 52241-27-7.

Supplementary Material Available: Atomic positional and thermal parameters for compound **1** (Table S1) and final observed and calculated structure factors (Table S2) (18 pages). Ordering information is given on any current masthead page.

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