Novel Crystal Structure of a Tetranuclear Platinum Complex: Bis(μ_4-carbonato-*O,O,O′,O′*)-tetrakis(diammineplatinum(II)) Tetranitrate Trihydrate

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The antitumor drug *cis*-dichlorodiammineplatinum(II) (*cis*-DDP) continues to attract attention because of its success in the treatment of certain human cancers.[3] Hydrolysis of *cis*-DDP, typically initiated by the addition of 2 equiv of silver nitrate, produces a composition of species that shows marked sensitivity to pH. Compounds, analyzed by X-ray crystallography, include *cis*-dinitratodiammineplatinum(II),[4a] nitrate[4b,c] and carbonate[4d] salts of bis(μ-hydroxo)-bridged diammineplatinum(II) dimers, and nitrate[4e] and sulfate[4f] salts of cyclic hydroxy-bridged diammineplatinum(II) trimers. Measurements by NMR spectroscopies[5] of aqueous solutions also admit the presence of diaqua and aquahydroxo species where the former prevails in acidic medium (pH ~2) and is believed the active agent for the antitumor activity of the *cis*-$Pt(NH_3)_2^{2+}$ system.[6]

During an investigation of *cis*-DDP with 2′-deoxyuridine, we observed a minor product, consisting of a few thin plates in a blue precipitate. An X-ray diffraction study, which is the subject of this paper, revealed to our surprise that the crystals contained a novel *cyclo* tetranuclear platinum cation, formulated as $[\{cis\text{-}Pt(NH_3)_2\}_4(\mu_4\text{-}CO_3)_2]^{4+}$. Carbonato coordination with hydrolysis products of *cis*-DDP has been evidenced by vibrational spectroscopy of precipitates from neutral or basic solutions, following dissolution of CO_2.[4d] (Carbonato)(amine)platinum(II) complexes have been reported as being formed from silver carbonate instead of silver nitrate.[7] However, these materials have not been crystallographically characterized.

Experimental Section

cis-DDP, prepared from K_2PtCl_4 (Engelhard) using a modified version of the Dhara method,[8] was treated with silver nitrate. After 24 h AgCl was removed. Typically, 1 equiv of 2′-deoxyuridine (Aldrich) was added to the solution and the mixture was heated for several hours at ~40 °C under aerobic conditions. The blue solution (pH ~2.0) was stored for several weeks. The resulting solutions became intensely blue. When the solutions were stored at 0 °C, noncrystalline blue and green precipitates formed as long as no base was added. A similar observation was reported by Lippert et al. for solutions containing *cis*-$Pt(NH_3)_2^{2+}$ products and 1-methyluracil.[9]

On one occasion, several transparent crystals were separated microscopically from the blue precipitate. We chose a crystal with dimensions about 0.2 × 0.15 × 0.04 mm for study. The crystal was found to be triclinic, belonging to the space group $P\bar{1}$. Information relating to data collection and structure refinement is summarized in Table I. Data collection was performed at room temperature using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The cell dimensions were obtained from a least-squares fit of sin θ values for 25 reflections (16.5° ≤ θ ≤ 19.0°), accurately centered at four equivalent positions. The data were corrected for Lorentz and polarization effects. Absorption corrections were performed using the ψ-scan method. Of the 7794 reflections which were collected, 7787 were unique ($R_{int} = 0.014$). The structure was solved by Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and no attempt was made to include the hydrogen atoms. Full-matrix least-squares refinement of the structure using 353 parameters, including a secondary extinction parameter ($g = 1.20678e^{-0.7}$), converged at $R = 0.039$ and $R_w = 0.041$.[10] Final atomic positional and isotropic equivalent displacement parameters are listed in Table II.

Results and Discussion

An ORTEP[11] drawing of the tetranuclear platinum cation is shown in Figure 1. The four platinum atoms, which define the corners of a nearly planar square (mean unweighted deviation of 0.034 Å) with sides of 3.279(1), 3.2296(8), 3.2405(8), and 3.184(1) Å, do not form metal–metal bonds, in contrast to the tetranuclear platinum carboxylate complexes with Pt–Pt distances of 2.49–2.50 Å.[12] The cation can be described as consisting of four fused six-membered rings. The platinum–oxygen backbone may be visualized as an eight-membered-ring system having approximately S_4 symmetry, where the bridging oxygen atoms lie above and below the platinum plane. Pt–O distances vary from 2.03 to 2.08 Å, and the Pt–O–Pt angles maintain a narrow range between 101.1(5) and 105.8(5)° (see Table III). Similar ring structures have been observed for dimethylgold(III) hydroxide,[13] $[(CH_3)_2AuOH]_4$, and (ethylenediamine)platinum(II) hydroxide,[14] $[Pt(en)OH]_4^{4+}$.

Platinum(II) coordination, PtN_2O_2, is best described as square planar, having mean deviations of 0.0190, 0.0294, 0.0112, and 0.0271 Å from the plane. The Pt–N distances are within the normal range observed for platinum(II) ammine complexes (see Table III). The PtN_2O_2 planes are inclined with respect to the platinum plane, subtending dihedral angles of 54.52, 55.50, 54.48, and 57.03°. Consequently, negligible overlap between juxtaposed Pt $5d_{z^2}$ orbitals is expected in this case and may relate to the crystals' apparent lack of hue. The crystal, formulated as $[Pt_4(NH_3)_8(\mu_4\text{-}CO_3)_2](NO_3)_4{\cdot}3H_2O$ (**1**), is held together by a hydrogen-bonding system involving three lattice water molecules and four nitrate ions. The cation of **1** hydrogen-bonds with water (2.88–2.90 Å) and with nitrate (2.85 Å); however, the shortest hydrogen-bond distance (2.73 Å) occurs between water and nitrate.[15]

Compound **1** features a novel cation with $\eta^1,\eta^1,\eta^1,\eta^1$-carbonato coordination, such that two oxygen atoms each form a single-

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Table I. Crystallographic Data for 1

formula: $Pt_4O_{21}C_2N_{12}H_{30}$
fw = 1338.69
a = 11.324(1) Å
b = 12.151(1) Å
c = 10.926(1) Å
α = 103.792(8)°
β = 111.266(8)°
γ = 75.845(8)°
V = 1339.7(2) Å^3
Z = 2
takeoff angle = 2.8°
F_{000} = 1212
space group: $P\bar{1}$ (No. 2)
$2\theta_{max}$ = 60.0°
ρ_{calcd} = 3.318 g/cm^3
μ = 208.40 cm^{-1}
$R(F_o)$ = 0.039
$R_w(F_o^2)$ = 0.041
4485 refl with $I > 3.00\sigma(I)$
goodness of fit = 1.60

Table II. Atomic Positional and Isotropic Equivalent Thermal Parameters[a] for 1

atom	x	y	z	B_{eq}, Å^2
Pt1	0.28100(5)	0.16982(5)	0.19016(7)	1.69(1)
Pt2	0.15128(5)	0.01312(4)	–0.09590(7)	1.62(1)
Pt3	0.09214(5)	0.23494(4)	–0.23844(6)	1.62(1)
Pt4	0.20687(5)	0.38928(4)	0.04162(6)	1.54(1)
C1	0.017(1)	0.242(1)	0.000(2)	1.9(3)
C2	0.346(1)	0.153(1)	–0.054(2)	2.2(3)
O11	0.124(1)	0.2850(9)	0.097(1)	2.7(2)
O12	0.034(1)	0.1697(8)	–0.114(1)	2.8(3)
O13	–0.086(1)	0.2652(10)	0.017(1)	3.1(3)
O21	0.310(1)	0.0886(9)	0.013(1)	2.7(3)
O22	0.266(1)	0.2577(9)	–0.091(1)	3.1(3)
O23	0.451(1)	0.1211(9)	–0.077(1)	2.7(3)
N1	0.256(1)	0.245(1)	0.369(1)	2.5(3)
N2	0.439(1)	0.063(1)	0.290(2)	3.1(3)
N3	0.266(1)	–0.1457(10)	–0.088(2)	3.0(3)
N4	–0.005(1)	–0.065(1)	–0.198(2)	2.6(3)
N5	–0.078(1)	0.211(1)	–0.394(1)	2.8(3)
N6	0.146(1)	0.297(1)	–0.364(1)	2.5(3)
N7	0.295(1)	0.4981(9)	–0.002(1)	2.0(3)
N8	0.146(1)	0.525(1)	0.170(2)	2.6(3)
N31	–0.449(2)	0.369(1)	0.211(2)	4.4(5)
N41	0.305(1)	–0.196(1)	0.239(2)	3.5(4)
N51	–0.071(1)	0.396(1)	0.331(2)	3.0(3)
N61	–0.237(2)	–0.018(1)	0.457(2)	3.9(4)
O31	–0.440(2)	0.371(1)	0.107(2)	5.2(4)
O32	–0.420(2)	0.280(1)	0.259(2)	6.4(5)
O33	–0.485(1)	0.464(1)	0.278(2)	4.8(4)
O41	0.388(1)	–0.184(1)	0.198(2)	5.5(4)
O42	0.228(1)	–0.1093(10)	0.264(2)	3.8(3)
O43	0.301(1)	–0.2923(10)	0.256(2)	4.4(4)
O51	0.002(2)	0.436(1)	0.304(2)	6.0(5)
O52	–0.178(2)	0.451(2)	0.320(3)	9.7(8)
O53	–0.043(1)	0.296(1)	0.354(2)	5.0(4)
O61	–0.275(2)	0.064(1)	0.396(2)	6.7(5)
O62	–0.318(1)	–0.074(1)	0.453(2)	4.6(4)
O63	–0.122(1)	–0.045(1)	0.518(1)	4.7(3)
OW1	–0.401(1)	–0.3543(10)	0.226(2)	4.0(3)
OW2	0.504(2)	0.316(2)	0.486(2)	7.6(6)
OW3	0.282(2)	–0.478(2)	0.449(2)	8.1(6)

[a] $B_{eq} = {}^8/_3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

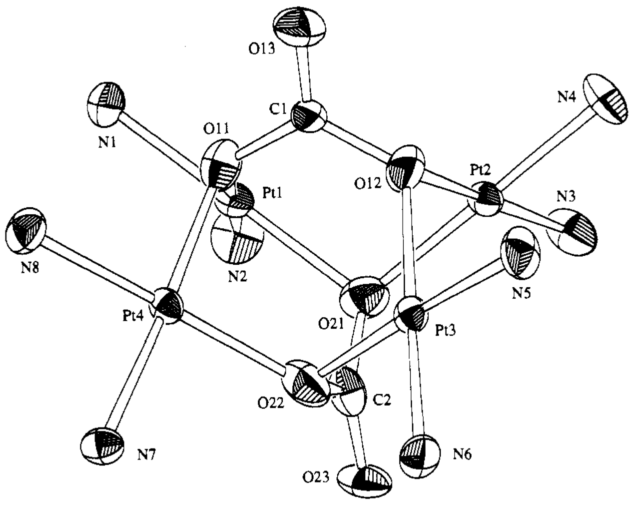

Figure 1. ORTEP drawing of $[\{cis\text{-}Pt(NH_3)_2\}_4(\mu_4\text{-}CO_3)_2]^{4+}$ (cation of 1). Hydrogen atoms are not included (see Experimental Section). FTIR bands of 1, obtained using a Digilab FTS-60 instrument with a UMA 300-Å microscopic attachment, reported between 800 and 1850 cm^{-1}: 1826 (vw), 1758 (w), 1693 (w), 1538 (m), 1426 (vw), 1269 (m), 1021 (m), 853 (s).

Table III. Selected Bond Distances (Å) and Angles (deg) for 1

	Distances		
Pt1–N1	2.03(1)	Pt3–N5	2.08(1)
Pt1–N2	2.05(1)	Pt3–N6	2.03(1)
Pt1–O11	2.07(1)	Pt3–O12	2.08(1)
Pt1–O21	2.06(1)	Pt3–O22	2.07(1)
Pt2–N3	2.05(1)	Pt4–N7	2.06(1)
Pt2–N4	2.04(1)	Pt4–N8	2.05(1)
Pt2–O12	2.05(1)	Pt4–O11	2.05(1)
Pt2–O21	2.05(1)	Pt4–O22	2.04(1)
C1–O11	1.41(2)	C2–O21	1.40(2)
C1–O12	1.38(2)	C2–O22	1.42(2)
C1–O13	1.20(2)	C2–O23	1.24(2)
	Angles		
N1–Pt1–N2	88.0(6)	N1–Pt1–O11	89.7(5)
N3–Pt2–N4	89.3(5)	N2–Pt1–O21	90.1(5)
N5–Pt3–N6	87.7(6)	N3–Pt2–O21	89.7(5)
N7–Pt4–N8	88.2(5)	N4–Pt2–O12	89.2(5)
O11–Pt1–O21	92.2(5)	N5–Pt3–O12	91.0(5)
O21–Pt2–O12	91.9(4)	N6–Pt3–O22	89.8(5)
O12–Pt3–O22	91.5(5)	N7–Pt4–O22	90.4(4)
O11–Pt4–O22	92.0(4)	N8–Pt4–O11	89.5(5)
Pt1–O11–Pt4	103.1(5)	Pt1–O21–Pt2	105.8(5)
Pt1–O11–C1	118.8(8)	Pt1–O21–C2	117.0(9)
Pt4–O11–C1	117.2(9)	Pt2–O21–C2	116.1(9)
Pt3–O22–Pt4	101.5(5)	Pt3–O12–Pt2	103.4(5)
Pt3–O22–C2	113.6(9)	Pt3–O12–C1	118.0(8)
Pt4–O22–C2	123.0(10)	Pt2–O12–C1	118.8(10)
O11–C1–O12	118.0(10)	O21–C2–O22	119.0(10)
O11–C1–O13	120.0(10)	O21–C2–O23	120.0(10)
O12–C1–O13	120.0(10)	O22–C2–O23	120.0(10)

atom bridge between two platinum atoms and the terminal oxygen atom (O_t) remains noncoordinated.[16] X-ray structural analysis has revealed numerous modes of carbonate coordination in monodentate and polydentate complexes.[17] However, this is the first example of carbonate coordination, of which we are aware, in which four metal atoms link with just two oxygens. Chelated[18] and bridging bidentate[19] carbonate complexes have been observed with platinum. As shown in Table III, the bridging C–O distances (1.38–1.42 Å) are longer and the terminal distances (1.20–1.24 Å) are shorter than the C–O distance (1.294 Å) in the free carbonate ion (e.g. calcite[20]). Bridging bidentate C–O distances are usually found between 1.29 and 1.34 Å, but longer bonds (1.36–1.41 Å)[21] are known. Each carbonate ligand is planar within experimental error (mean deviations from the plane are 0.003 and 0.007 Å). Elongation of C–O is attributed to effective metal competition for the carbonate p_π electrons with a con-

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(15) (a) The closest intermolecular contacts occur between OW1 and O41 (2.73 Å), OW1 and O33 (2.85 Å), OW2 and O32 (2.81 Å), and OW2 and O43 (2.91 Å). Other possible hydrogen bonds occur between OW2 and N1 (2.88 Å), OW1 and N6 (2.90 Å), OW3 and N8 (2.89 Å), and N4 and O42 (2.85 Å). (b) The N–O distances and O–N–O angles are normal for free nitrate ions. Distances (Å): 1.19(2), 1.24(2), 1.26(2) for N1; 1.24(2), 1.24(2), 1.24(2) for N2; 1.21(2), 1.21(2), 1.24(2) for N3; 1.23(2), 1.25(2), 1.23(2) for N4. Free nitrate ion (e.g. $NaNO_3$) has N–O distances of 1.245 Å (Addison, C. C.; Logan, N.; Wallwork, S. C. *Quart. Rev.*, **1971**, *25*, 289).

(16) Carbonate coordination is favored over that of nitrate. The four counterions are seen to have bond distances typical of the nitrate ion (see ref 15b) rather than carbonate (see text). The presence of two carbonate ligands satisfies the requisite charge balance with +2 oxidation for the platinum atoms. Ammine displacement, while possible, is not generally known to occur except with ligands having a strong *trans* influence (Norman, R. E.; Ranford, J. D.; Sadler, P. J. *Inorg. Chem.* **1992**, *31*, 877–888). An alternate crystallographic refinement was performed by replacing C1 and C2 with N, which converged to R = 0.041 and R_w = 0.043; a similar result was reported for the interchange of N and O in $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ (see ref 4b).

comitant reduction in C–O π bonding, and C–O_t takes on double-bond character. The Pt atoms are displaced from the carbonate C1 plane by 1.617 Å and from C2 plane by 1.610 Å, indicating that the dative bonds could involve both the σ and π orbitals of the carbonate groups. The carbonate ligands are perpendicular to each other (87.93°) and to the platinum plane (89.05 and 85.60°). The symmetry of the cation can be reasonably described in the D_{2d} point group.

In conclusion, crystallographic measurements showing unprecedented carbonate bonding in a platinum complex are reported. The 2′-deoxyuridine platinum blue solutions, which derive their color from species with Pt oxidation >2 and weak Pt–Pt bonds[22] and are related to the "platinum blues",[23] contain non-blue Pt species as well.[24] The formation of **1**, occurring in an acidic medium (pH <2), might reasonably involve an initial reaction step with CO_2 (aq) rather than its associated ions (HCO_3^- and CO_3^{2-}). It is well-known that carbonate or bicarbonate metal complexes can form in solution via the absorption of CO_2.[25] A rational synthesis of **1** is currently in progress.[26]

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Supplementary Material Available: A table of anisotropic temperature factors (2 pages). Ordering information is given on any current masthead page.

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(26) In this regard, a reviewer of our paper suggested that compound **1** results from the reaction of CO_2 with a Pt–OH species such as $[Pt(NH_3)_2OH]_4^{4+}$, which might exist at low pH. We currently favor the reaction of CO_2 with a species such as $[Pt(NH_3)_2OH]_2^{2+}$ to form a bis(bicarbonato)-bridged Pt dimer such as $[Pt(NH_3)_2(O_2COH)]_2^{2+}$ or $[(NH_3)_2Pt(O_2COH)(\mu\text{-}OCO_2H)Pt(NH_3)_2]^{2+}$, which can yield the cation of **1** by addition of 2 equiv of *cis*-$Pt(NH_3)_2^{2+}$.