

Contribution from the Institute for Materials Research, McMaster University, Hamilton, Ontario, L8S 4M1, Canada, and the Department of Biophysics, Michigan State University, East Lansing, Michigan 48823

Hydroxo-Bridged Platinum(II) Complexes. 4. Crystal Structure and Vibrational Spectra of Di- μ -hydroxo-bis[diammineplatinum(II)] Carbonate Dihydrate, $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$

B. LIPPERT,^{1a} C. J. L. LOCK,*^{1b} B. ROSENBERG,^{1a} and M. ZVAGULIS^{1b}

Received October 21, 1977

The crystal structure of the complex di- μ -hydroxo-bis[diammineplatinum(II)] carbonate dihydrate, $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$, has been determined by X-ray diffraction. The monoclinic crystal, space group $P2_1/c$, has cell dimensions $a = 7.127$ (2) Å, $b = 11.416$ (3) Å, $c = 15.379$ (4) Å, and $\beta = 119.15$ (2)° and has four formula units per unit cell. Data were collected using Mo $K\alpha$ radiation and a Syntex $P2_1$ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0521$, $R_2 = 0.0554$. The cation is composed of two dimeric units, with hydrogen bonding between one dimer and its centrosymmetrically related unit holding the pair together. The Pt-Pt interdimer distance is 3.167 (1) Å. Distances within the dimer (Pt-N range 2.02 (2)–2.05 (2) Å, Pt-O range 2.02 (1)–2.07 (1) Å) are normal. Infrared and Raman spectra are discussed.

With the recent identification of several hydroxo-bridged platinum(II) complexes²⁻⁵ that are formed from a primary hydrolysis product of the cancerostatically active compounds *cis*-Pt(NH₃)₂Cl₂ and (en)PtCl₂, respectively, the question concerning the stability of such OH bridges emerged. It had been shown that, in the (en)Pt system, these hydroxo bridges are stable at rather low concentration.⁵ On the other hand, our studies in the *cis*-Pt(NH₃)₂ system indicated that such OH bridges are also stable over a wide range of pH. For example, we could isolate a hydroxo-bridged species even from a concentrated aqueous solution of pH 2,⁶ and the compound described here was isolated from an aqueous solution of pH 10–11. Stability of OH bridges, even toward the good nucleophile OH⁻, parallels findings on the stability of similar hydroxo-bridged phosphine complexes of platinum when treated with excess tertiary phosphines.⁷

Di- μ -hydroxo-bis[diammineplatinum(II)] carbonate dihydrate, $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$, was formed when the dimeric complex di- μ -hydroxo-bis[diammineplatinum(II)] nitrate, $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$,³ was treated with sodium hydroxide in the presence of carbon dioxide.

The formulation of the title compound presented a problem. Between pairs of dimeric cations there was a relatively short Pt-Pt distance of 3.164 Å. Platinum-platinum distances in the range 3.1–3.4 Å are well-known in platinum complexes containing planar units stacked vertically, the best known being Magnus' green salt with a Pt-Pt distance of 3.25 (1) Å.⁸ Another example is μ -pyrophosphato-bis[diammineplatinum(II)] with an intermolecular Pt-Pt distance of 3.11 Å and an intramolecular Pt-Pt distance of 3.22 Å.⁹ Many of these compounds show evidence of metal-metal interactions.¹⁰ Nevertheless, a description of the title compound as a tetramer appears inadequate because there is an absence of ligands bridging the two dimer units and also because the Pt-Pt distance is not short enough to be considered a covalent bond or a strong metal-metal interaction. Examples of such in-

teractions are tetrameric platinum complexes with acetato^{11,12} or carbonyl¹³ bridges and compounds with short Pt-Pt distances such as Pt₃(SnCl₃)₂(C₈H₁₂)₃ (2.58 Å),¹⁴ Pt₂S(PPh₃)₃Co (2.647 Å),¹⁵ and the typical mixed-valence Pt compounds.¹⁶ In addition, as we shall show later, the X-ray results seem to argue against any metal-metal interaction. Thus we have formulated the compound as containing a dimeric cation even though the vibrational spectra show significant differences from those of the corresponding nitrate.³

Experimental Section

Preparation. (1) A total of 308 mg of di- μ -hydroxo-bis[diammineplatinum(II)] nitrate^{3a} was suspended in 10 mL of freshly prepared 0.05 N NaOH and kept in an open flask at room temperature. After about 2.5 h a few deep yellow crystals had formed. Another equivalent of base (0.5 mL of 1 N NaOH) was then added and the open flask put in a refrigerator (0 °C). The pH of the solution at this time was 10.65. After 3 days the yellow solution was poured off and the residue treated five times with 20-mL portions of water to dissolve the unreacted starting material and then washed with ethanol and dried on rotary pump vacuum for 15 min; 80 mg of deep yellow transparent crystals were obtained.

Anal. Calcd for $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$: C, 2.04; H, 3.06; N, 9.54. Pt, 66.40; O, 18.90.¹⁷ Found: C, 1.90; H, 3.32; N, 9.53; Pt, 68.01; O, 16.71. Decomposition of the compound occurred above 140–150 °C. A molecular weight determination was not performed because of the low solubility of the compound in many organic solvents and its hydrolysis in water (vide infra). With dilute HNO₃ the starting compound was re-formed quantitatively. Hydrolysis in water: di- μ -hydroxo-bis[diammineplatinum(II)] carbonate dissolved very slowly in water to give a greenish yellow solution. Upon evaporation of the solvent a new product was obtained whose exact composition is unclear at this moment.¹⁸

Variation of the described procedure of preparation gave the following results: (2) with NaOH excess (3–4 equiv per dimer) formation of the title compound was accelerated, but the crystals were of poor quality. (3) With only 1 equiv of NaOH per dimer the yield of the title compound was reduced to about 30 mg and the supernatant solution changed its color from pale yellow via olive to dark green over a period of 2 days. (4) If carbon dioxide was excluded, no

Table I. Final Atomic Positional and Thermal Parameters (\AA^2)^a

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.29283 (10)	-0.03823 (7)	0.66873 (5)	0.0248 (4)	0.0242 (4)	0.0223 (4)	0.0005 (3)	0.0125 (3)	0.0014 (3)
Pt(2)	0.25955 (10)	0.03483 (6)	0.46728 (5)	0.0223 (4)	0.0200 (3)	0.0204 (3)	0.0002 (3)	0.0103 (3)	0.0004 (3)
O(1)	0.251 (2)	-0.114 (1)	0.542 (1)	0.035 (7)	0.022 (6)	0.025 (6)	-0.012 (6)	0.016 (6)	-0.000 (5)
O(2)	0.319 (2)	0.109 (1)	0.600 (1)	0.036 (7)	0.023 (6)	0.014 (5)	0.009 (6)	0.011 (5)	-0.001 (5)
N(1)	0.289 (3)	-0.188 (1)	0.740 (1)	0.036 (9)	0.024 (8)	0.039 (9)	0.003 (7)	0.022 (8)	0.015 (7)
N(2)	0.337 (3)	0.052 (1)	0.790 (1)	0.040 (9)	0.037 (9)	0.013 (7)	0.006 (8)	0.009 (7)	0.004 (7)
N(3)	0.211 (2)	-0.050 (1)	0.341 (1)	0.027 (8)	0.030 (9)	0.030 (9)	-0.005 (7)	0.005 (7)	-0.008 (7)
N(4)	0.315 (2)	0.186 (1)	0.415 (1)	0.030 (8)	0.034 (8)	0.021 (7)	-0.005 (7)	0.012 (7)	0.004 (7)
O(3)	0.046 (2)	0.257 (1)	0.710 (1)	0.062 (10)	0.025 (7)	0.030 (7)	-0.015 (7)	0.030 (7)	-0.003 (6)
O(4)	0.058 (3)	0.291 (1)	0.569 (1)	0.060 (10)	0.035 (8)	0.028 (7)	0.010 (7)	0.021 (8)	0.001 (6)
O(5)	-0.030 (2)	0.433 (1)	0.642 (1)	0.059 (10)	0.020 (6)	0.033 (7)	0.005 (6)	0.030 (7)	0.002 (5)
C(1)	0.026 (3)	0.326 (2)	0.640 (1)	0.029 (9)	0.026 (9)	0.025 (9)	-0.005 (8)	0.015 (8)	-0.012 (7)
OX(1)	0.193 (2)	0.608 (1)	0.613 (1)	0.049 (9)	0.032 (8)	0.040 (8)	0.000 (7)	0.009 (7)	0.001 (7)
OX(2)	0.346 (3)	0.405 (2)	0.521 (1)	0.071 (13)	0.057 (11)	0.084 (13)	0.084 (13)	0.048 (11)	0.027 (11)

^a Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij} 's appear as a temperature effect of the form $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ and b_i are the reciprocal lattice vectors.

precipitation of the title compound occurred but the solution turned orange-yellow over a period of 3 days. (5) If the supernatant solution mentioned in (1) was allowed to stand in air for a longer period of time (3 days), it changed its color from yellow to olive green and a metallic mirror (presumably Pt(0)) was formed on the surface. If the alkaline yellow supernatant solution, or the aged olive one, was titrated to pH 6.5 or 7 with diluted HNO_3 , a rapid color change to blue-green took place within minutes and a small amount (10 mg) of a blue amorphous compound precipitated from the blue solution.²¹

Apparatus. Infrared spectra were recorded on a Perkin-Elmer 577 grating spectrometer from 4000 to 250 cm^{-1} as KBr pellets and from 4000 to 400 cm^{-1} as Nujol mulls (KBr plates). The spectra were calibrated against polystyrene. Raman spectra were obtained from solid samples on a Coderg PH 1 spectrometer with a He-Ne laser (Spectraphysics) and calibrated by means of the plasma lines of the laser. High-power laser radiation had to be avoided because it decomposed the compound, sometimes explosively.

Collection of the X-ray Diffraction Data. A yellow crystal, chosen after examination under a polarizing microscope for homogeneity, was ground to a sphere of radius 0.06 mm. Precession photographs of the zero and first layers of the reciprocal lattice showed the crystal was monoclinic with the systematic absences $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Thus the space group was $P2_1/c$ (No. 14). The crystal was transferred to a Syntex $P2_1$ diffractometer and mounted along the $[6,3,12]$ direction. Unit cell parameters were obtained from a least-squares fit of χ , ϕ , and 2θ for 15 medium-angle ($20^\circ < 2\theta < 35^\circ$) reflections: $a = 7.127$ (2) \AA , $b = 11.416$ (3) \AA , $c = 15.379$ (4) \AA , $\beta = 119.15$ (2)° (λ 0.71069 \AA for Mo $K\alpha$ at 20°C). With $Z = 4$ (based on a platinum dimer) ρ_{calcd} was 3.52 g cm^{-3} and ρ_{obsd} , measured by displacement in light petroleum oil, was 3.60 (2) g cm^{-3} . The linear absorption coefficient was 265 cm^{-1} and by use of the above crystal dimensions the transmission coefficient varied from 7.28 to 8.80.

Intensity data were recorded on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation for the quadrant defined by $h, k, \pm l$ for $0 < 2\theta < 55^\circ$. Data were collected by using a coupled $\theta(\text{crystal})-2\theta(\text{counter})$ scan 1° on either side of the peak, scan rate ranging from 2.02 to 29.30°/min and being selected by the program supplied with the instrument.²⁴ The stability of the system was monitored by measuring three standard reflections after every 13 reflections. The counting esd's of the standard reflections, 211, 020, 220, were 2.4, 2.0, and 2.5%, respectively, and an analysis of the standard counts showed overall esd's of 3.6, 3.1, and 4.1%, respectively, with no systematic variation with time. The intensity of reflection, I , and its esd, $\sigma(I)$, were calculated as outlined previously.²⁵ A total of 3036 reflections were recorded and after averaging yielded a total of 2247 independent reflections of which 1497 had $I > 3\sigma(I)$ and 750 had $3\sigma(I) > I > \sigma(I)$. Corrections were made for absorption. Unscaled structure factor amplitudes, F , and their standard deviations, $\sigma(F)$, were calculated from the expressions $F = (I/Lp)^{1/2}$, $\sigma(F) = 1/2(Lp)^{-1/2}((\sigma(I))^2/I)^{1/2}$. Lp , the Lorentz-polarization factor, was $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Solution of the Structure. The coordinates of the platinum atoms were found from a three-dimensional Patterson synthesis, and a three-dimensional electron density difference map revealed all the remaining nonhydrogen atoms. After refinement, the temperature

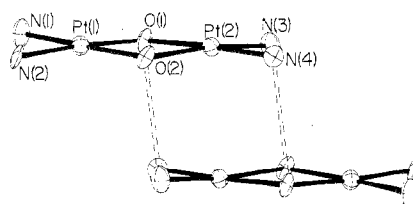


Figure 1. The molecular cation $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2]^{2+}$ and its centrosymmetrically related neighbor drawn such that all platinum atoms are in the plane of the paper. Dotted lines indicate probable hydrogen bonds holding the structure together. The twist of the planes and the distortion such that Pt(2) and Pt(2)^a move out of the square planes away from each other can be seen.

factors of all the atoms, which were previously isotropic, were made sequentially anisotropic. Tests were made at each stage to show that the use of the increased parameters was significant. Further refinement, with weights equal to $[(\sigma(F))^2 + (0.03F_0)^2]^{-1}$ and full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was terminated at $R_1 = 0.0521$, $R_2 = 0.0554$.²⁶ In the last cycle of refinement no parameter shifted by more than 4×10^{-2} of its esd. Corrections were made for secondary extinction using the method of Larson²⁷ (g was 0.9771×10^{-7}). The error in an observation of unit weight is 1.23.

The final difference map showed little variation, except near the platinum atoms. The largest peak was 1.20 $\text{e}/\text{\AA}^3$ at 0.0, 0.97, 0.92 near O(5) and the deepest valley was $-1.55 \text{ e}/\text{\AA}^3$ at 0.29, 0.38, 0.52 near OX(2). Throughout the refinement, the scattering curves were taken from ref 28, and anomalous dispersion corrections from ref 29 were applied to the curves for platinum. The atom parameters for the nonhydrogen atoms are listed in Table I.

Results and Discussion

Crystallography. A pair of molecular cations is illustrated in Figure 1, and selected bond lengths and angles are given in Table II. The basic dimer unit containing two hydroxide-bridged platinum atoms (A) is very similar to the cation found in $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ (B).^{3a} The relevant distances and angles show this (Pt-N (A) 2.02 (2)-2.05 (2), (B) 2.01 (1), 2.02 (2) \AA ; Pt-O (A) 2.02 (1)-2.07 (1), (B) 2.03 (1) \AA ; Pt-Pt (A) 3.104 (1), (B) 3.085 (1) \AA ; N-Pt-N (A) 88.0 (7), 90.0 (7), (B) 89.3 (6)°; trans N-Pt-O (A) 170.5 (4)-175.9 (6), (B) 175.6 (6), 176.1 (6)°; cis N-Pt-O (A) 92.6 (6)-97.5 (6), (B) 94.5 (5), 94.9 (5)°; O-Pt-O (A) 81.9 (5), 80.6 (5), (B) 81.3 (4)°; Pt-O-Pt (A) 98.8 (5), 98.5 (5), (B) 98.9 (5)°).

There are minor differences, however. In dimer B the bonded ligand atoms were very closely coplanar with the platinum atoms. In dimer A the environment around Pt(1) is closely planar (deviations from the best plane (\AA): Pt(1), -0.030; O(1), -0.027; O(2), 0.043; N(1), 0.040; N(2), -0.026), but the environment around Pt(2) is much more distorted (deviations from best plane (\AA): Pt(2), -0.088; O(1), 0.047; O(2), -0.048; N(3), -0.043; N(4), 0.044).³⁰ This distortion

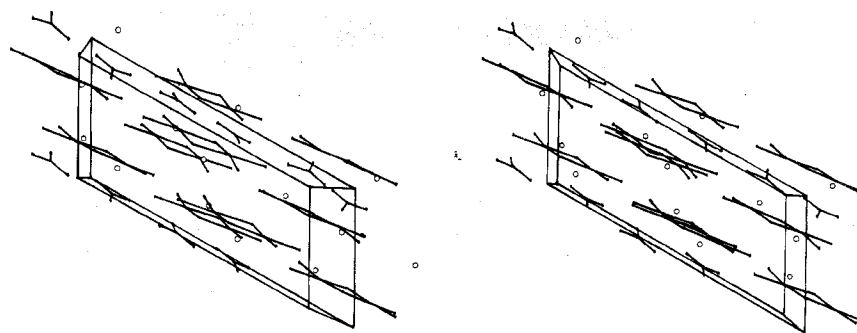


Figure 2. Stereogram (stereoscopic pair of perspective projections) of $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$. The contents of the unit cell plus extra ions and water molecules are shown in order to illustrate the packing. The water molecules are represented by open circles. The a and c^* axes are parallel to the side and top of the page, respectively, and the view is approximately along b .

Table II. Interatomic Distances (Å) and Angles (deg)^a

Distances			
Pt(1)-O(1)	2.02 (1)	Pt(2)-N(4)	2.02 (2)
Pt(1)-N(2)	2.02 (2)	C(1)-O(3)	1.29 (3)
Pt(2)-N(3)	2.04 (2)	Pt(1)-Pt(2) ^b	3.443 (1)
Pt(2)-Pt(2) ^a	3.167 (1)	Pt(1)-N(1)	2.05 (2)
C(1)-O(5)	1.29 (2)	Pt(2)-O(2)	2.06 (1)
Pt(1)-O(2)	2.04 (1)	Pt(1)-Pt(2)	3.104 (1)
Pt(2)-O(1)	2.07 (1)	C(1)-O(4)	1.27 (3)
Possible Hydrogen Bonds			
O(1)-O(4) ^b	2.86 (2)	O(5)-OX(2) ^e	3.05 (2)
O(2)-N(3) ^a	3.09 (2)	O(5)-OX(1)	2.73 (2)
O(3)-N(3) ^b	2.85 (2)	N(2)-OX(2) ^g	3.16 (2)
O(4)-OX(2)	2.82 (3)	O(2)-O(4)	2.68 (2)
O(5)-N(3) ^d	3.00 (2)	O(3)-N(2)	2.97 (2)
N(2)-OX(1) ^g	2.99 (2)	O(4)-OX(1) ^e	2.73 (2)
OX(1)-OX(2)	3.17 (3)	O(5)-N(2) ^c	3.16 (3)
O(1)-N(4) ^a	2.94 (2)	N(1)-OX(1) ^f	2.90 (2)
O(3)-N(1) ^c	2.90 (3)	N(4)-OX(2)	2.94 (3)
O(3)-N(4) ^d	2.85 (2)		
Angles			
O(1)-Pt(1)-O(2)	81.9 (5)	O(2)-Pt(2)-N(4)	93.5 (6)
O(2)-Pt(1)-N(1)	175.9 (6)	O(3)-C(1)-O(4)	122 (2)
O(1)-Pt(2)-O(2)	80.6 (5)	Pt(1)-O(1)-Pt(2)	98.8 (5)
O(2)-Pt(2)-N(3)	175.6 (5)	Pt(2) ^a -Pt(2)-Pt(1) ^b	159.39 (3)
Pt(1)-Pt(2)-Pt(2) ^a	94.05 (2)	O(1)-Pt(1)-N(2)	174.5 (6)
O(4)-C(1)-O(5)	120 (2)	N(1)-Pt(1)-N(2)	88.0 (7)
Pt(2)-Pt(1)-Pt(2) ^b	83.21 (2)	O(1)-Pt(2)-N(4)	170.5 (4)
O(1)-Pt(1)-N(1)	97.5 (6)	N(3)-Pt(2)-N(4)	90.0 (7)
O(2)-Pt(1)-N(2)	92.6 (6)	O(3)-C(1)-O(5)	117 (2)
O(1)-Pt(2)-N(3)	95.6 (6)	Pt(1)-O(2)-Pt(2)	98.5 (5)
Possible Hydrogen Bond Angles			
Pt(1)-O(1)-O(4) ^b	126.0 (8)	Pt(1)-N(1)-O(3) ^c	123.6 (8)
Pt(2)-O(1)-N(4) ^a	92.6 (6)	Pt(2)-N(4)-O(3) ^d	118.7 (7)
Pt(2)-O(2)-O(4)	110.9 (5)	Pt(1)-N(1)-OX(1) ^f	111.3 (8)
Pt(2)-N(3)-O(2) ^a	99.8 (5)	Pt(2)-N(4)-OX(2)	118.4 (9)
Pt(2)-N(3)-O(3) ^b	116.4 (9)	Pt(1)-O(1)-N(4) ^a	104.7 (5)
Pt(2)-N(3)-O(5) ^d	120.3 (8)	Pt(1)-O(2)-O(4)	119.9 (8)
Pt(1)-N(2)-OX(2) ^g	107.4 (8)	Pt(2)-O(2)-N(3) ^a	82.6 (6)
Pt(2)-O(1)-O(4) ^b	72.1 (5)	Pt(1)-N(2)-O(3)	104.9 (6)
Pt(2)-N(4)-O(1) ^a	93.5 (6)	Pt(1)-N(2)-O(5) ^c	105.2 (7)
Pt(1)-O(2)-N(3) ^a	91.7 (5)	Pt(1)-N(2)-OX(1) ^g	102.0 (9)

^a Atoms are related to those given in Table I by the following operations: a, $1-x, -y, 1-z$; b, $-x, -y, 1-z$; c, $-x, 0.5+y, 1.5-z$; d, $x, 0.5-y, 0.5+z$; e, $-x, 1-y, +z$; f, $x, y-1.0, z$; g, $1-x, y-0.5, 1.5-z$.

appears to be related to the interaction between the two dimer units. The two dimer units are arranged so that the Pt(2)-Pt(2)^a distance is relatively short (3.167 (1) Å; cf. 3.25 (1) Å for Magnus' green salt^{8a}), but an attractive platinum-platinum interaction does not seem to be the cause, since if we examine the best plane through the atoms around Pt(2) (see above), Pt(2) is displaced from this plane away from Pt(2)^a. Further, the positive charge on the dimeric units will cause a repulsion between the pairs of dimers. There must be, therefore, other interactions holding the two cations in this

Table III. $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2](\text{CO}_3)\cdot 2\text{H}_2\text{O}$ Spectra (in cm^{-1})^{a1}

	ν_1 (A)	ν_2 (A)	ν_3 (2A)	ν_4 (2A)
IR (KBr)	1060 vw	870 m	1420 vs, 1380 vs	690 m, 680 sh
IR (Nujol)	1060 vw	870 m	n.o. ^a	692 m, 685 sh
Raman (solid, polycrystalline)	1062 (3)		1410 (0), 1373 (0)	

^a n.o. = not observed because of Nujol absorptions.

arrangement. We suggest that the dimers are held together by hydrogen bonding (O(1)-N(4)^a, O(2)-N(3)^a, O(2)^a-N(3), O(1)^a-N(4)) and this hydrogen bonding is responsible for the distortion of the plane about Pt(2). In addition it can be seen clearly in Figure 1 that the plane formed by the ligand atoms is twisted relative to the platinum atom plane. Instead of the dihedral angle being 90° it is 86.6°. The twist also appears to be caused by the exigencies of interdimer hydrogen bonding. The reason that this arrangement is observed for the carbonate complex but not for the nitrate complex may well be related to the stoichiometry. There are twice as many MO_3^- units available as hydrogen bond acceptors in the nitrate salt and thus intercation hydrogen bonding may be unnecessary.

The crystal can be considered as an assembly of cations, anions, and water molecules with hydrogen bonding a major factor in holding the crystal together. The planes of both the cations and anions lie very roughly parallel to the bc plane, as is shown in Figure 2. Pairs of dimeric cations form two parallel rows along the c direction held together by hydrogen bonding. Within the rows along c , each pair of dimers is tilted with respect to the next pair (dihedral angle 13°). This tilt appears to be caused by the requirements of hydrogen bonding. The a translation means that half of a pair of dimers lies almost exactly over the opposite half of the next pair of dimers. Nevertheless the Pt-Pt distance is relatively long (3.443 (1) Å), and this is clearly caused by the intercalation of the carbonate anions; hydrogen bonding is from each dimer to the carbonate ions as opposed to direct dimer-dimer hydrogen bonding which causes the short distance within the pair of dimers. The water molecules determine the packing in the b direction. The water molecules lie almost in the plane of the dimer and hydrogen bond to the dimer, to each other, and to the carbonate anions.

Infrared and Raman Spectroscopy. The space group of the title compound is C_{2h}^5 with four formula units per unit cell. The carbonate ions in the crystal are of C_1 symmetry, lowered from the D_{3h} symmetry of the "free" CO_3^{2-} . Thus the vibrational selection rules are changed and both ν_1 and ν_2 are infrared and Raman active and ν_3 and ν_4 each split into two bands.

The observed spectra are in good agreement with this though not all of the predicted Raman bands can be observed (Table III). Besides the fundamental vibrations there is a series of

Table IV. Correlation for D_{2h} , C_s , and C_1 in the Dimer Cation (A) (Only Stretching Vibrations Are Listed)

D_{2h}	C_s^a	C_1
2 A_g (R)	4 A' (IR, R)	8 A(IR, R)
2 B_{1g} (R)	4 A'' (IR, R)	
2 B_{2u} (IR)		
2 B_{3u} (IR)		

^a In correlating D_{2h} and C_s , the y and z axes are interchanged. In C_s the x and y axes are in the plane of the four Pt atoms.

weak and not very well-resolved bands at higher wavenumbers in the IR spectrum which can be interpreted as combination bands of CO_3^{2-} vibrations. They appear around 1745 ($\nu_1 + \nu_4$), 2280 ($\nu_3 + \nu_4$), and 2485 cm^{-1} ($\nu_1 + \nu_3$).

As briefly mentioned in a previous paper,² the replacement of nitrate in di- μ -hydroxo-bis[diammineplatinum(II)] nitrate by sulfate had essentially no effect on the cation vibrations. In contrast, the title compound cation shows distinct differences in its vibrational spectra when compared with the dimer nitrate and dimer sulfate. Although the differences of NH_3 and OH group vibrations can be explained on the basis of different hydrogen bonding (vide infra), the changes in the skeletal vibrations cannot be interpreted as a mere anion effect. They reflect the observed structural differences between the dimer(s) and the title compound.

For the dimer B, di- μ -hydroxo-bis [diammineplatinum(II)] nitrate,^{3a} the skeletal stretching vibrations were found to absorb at 585 (IR), 558 (R), 552 (R), 550 (IR), 532 (IR) 504 (R), 495 (IR), and 488 (R) cm^{-1} . As demanded by both the D_{2h} symmetry of the free dimer cation and the C_i site symmetry,³² IR and Raman frequencies are clearly noncoincident. In the IR spectrum (Nujol) of the title compound six bands are observed at 553 (s), 545 (s), 532 (s), 520 (sh), 502 (m), and 479 (m) cm^{-1} . From their positions these bands are assigned to skeletal stretching vibrations as well. Whether there are other bands which are of an intensity too low to be observed or which are buried under the more intense bands or some vibrations accidentally degenerate is not clear without further studies. In the Raman spectrum at least five separate bands can be distinguished in this region, namely at 556 (10), 548 (10), 532 (0), 515 (5), and 478 cm^{-1} (1). Another band at 446 cm^{-1} (2) might also be caused by a skeletal mode.

The higher number of skeletal stretching vibrations is clearly caused by the lowered symmetry of the dimer cation in the title compound. If dimer (A) is still regarded as planar, the point symmetry D_{2h} (protons neglected) of the free dimer unit is reduced to C_s because of the position of the other dimer. If, however, the deviations from planarity around Pt(2) within the dimer unit are taken into account, the symmetry of dimer A is reduced to C_1 .

The correlation for the stretching vibrations of the skeleton between point group D_{2h} of the isolated dimer and C_s and C_1 site symmetries, respectively, leads to eight coincident IR and Raman bands in both cases (Table IV).

Though the number of bands obtained can be explained on the basis of either of these two models, the shift of the skeletal vibrations in the title compound compared to the case of dimer B suggests some interaction between the two dimers that cannot be explained by a lowered site symmetry alone.

The absorptions of the individual NH_3 and OH vibrations of the title compound cation differ, as mentioned before, from those of the starting dimer nitrate and its sulfate analogue. One finds that the NH deformation vibrations are shifted to higher wavenumbers in the title compound ($\delta_d(NH_3)$ 1635 (sh), 1630 (s), 1610 (s), 1590 cm^{-1} (s); $\delta_s(NH_3)$ 1355 (vs), 1330 cm^{-1} (s, sh); $\rho_r(NH_3)$ 920 (s), 900 cm^{-1} (m)), suggesting somewhat stronger hydrogen bonding of the NH_3 protons in the title compound. A comparison of the interatomic distances

between the nitrogen atoms of the NH_3 ligands and possible acceptor atoms for hydrogen bonding (O of NO_3^- in the dimer NO_3 , O of CO_3^{2-} and H_2O in the title compound) shows indeed that, with the exception of N(2) in the title molecule, the N atoms are in closer vicinity to oxygen donor atoms (Table II) than the N atoms are in the dimer nitrate (Table III in ref 3a). In contrast to this the OH deformation vibration of the hydroxo bridges is shifted to lower energy (970 cm^{-1} (s)). For the stretching vibrations of NH_3 and OH groups (3330–3040 (vs, b), 3040–2650 cm^{-1} (sh, b)) changes cannot be observed because of the unresolved structure of these bands, but it is noticeable that the half-width of their envelope (KBr spectrum) has more than tripled in the case of the title compound compared to that of the dimer nitrate. Though this is in part caused by the intense absorptions of the stretching vibrations of the lattice water at higher wavenumbers (3560–3340 cm^{-1} (sh, b)), this broadness is also caused by the multiple strong shoulders on the lower wavenumber side, between 3000 and 2650 cm^{-1} . They are typical of strongly hydrogen bonded protons and are attributed to both $NH_3 \cdots OCO_2$ and $NH_3 \cdots OH_2 \cdots OCO_2$ bonds (cf. Table II).

The bending modes of the lattice water absorb around 1660 cm^{-1} , and the broad band centered around 645 cm^{-1} is assigned to vibrational modes of the water molecules.

Acknowledgment. We wish to thank the National Cancer Institute, Engelhard Industries, Mathey-Bishop, Inc., International Nickel Co., National Research Council of Canada, National Cancer Institute of Canada, and the McMaster University Science and Engineering Research Board for financial support of this work. B. L. thanks Dr. Nguyen Quay Dao, Ecole Centrale des Arts et Manufactures, Chatenay-Malabry, France, for helpful discussions on the vibrational spectra.

Registry No. $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](CO_3) \cdot 2H_2O$, 67577-20-2; $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$, 62048-58-2.

Supplementary Material Available: A table of the moduli of the observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Michigan State University. (b) McMaster University.
- (2) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **17**, 1941 (1978).
- (3) (a) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, **99**, 777 (1977); (b) J. A. Stanko, L. S. Hollis, J. A. Schreifels, and J. D. Hoeschele, *Wadley Med. Bull.*, **1**, 138 (1977).
- (4) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **16**, 1192 (1977).
- (5) M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, **38**, 1911 (1976).
- (6) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, to be submitted for publication.
- (7) G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Can. J. Chem.*, **50**, 3694 (1972).
- (8) (a) M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Am. Chem. Soc.*, **79**, 3017 (1957); (b) J. R. Miller, *Proc. Chem. Soc., London*, 318 (1960).
- (9) J. A. Stanko in "Platinum Coordination Compounds in Cancer Chemotherapy", T. A. Connors and J. J. Roberts, Ed., Springer-Verlag, Heidelberg, 1974, p 24.
- (10) See, e.g., L. V. Interrante, Ed., "Extended Interactions between Metal Ions in Transition Metal Complexes", American Chemical Society, Washington, D.C., 1974.
- (11) P. de Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 410 (1976).
- (12) M. A. A. F. de C. T. Carrondo and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 410 (1976).
- (13) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Am. Chem. Soc.*, **91**, 1574 (1969).
- (14) L. J. Guggenberg, *Chem. Commun.*, 512 (1968).
- (15) A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969).
- (16) See, e.g., (a) C. Peters and C. F. Eagen, *Inorg. Chem.*, **15**, 782 (1976); (b) A. H. Reis, Jr., S. W. Peterson, and S. C. Lin, *J. Am. Chem. Soc.*, **98**, 7839 (1976).
- (17) The results fit a formulation as a monohydrate better (theory: C, 2.10; H, 2.80; N, 9.82; Pt, 68.40; O, 16.82) but this is probably only by accident. There was a constant discrepancy for the Pt and O values also in other samples analyzed (C, H, N identical) though all samples consisted of single crystals which were checked for purity under a microscope before being analyzed. In order to check the crystallographic results, alternate

- refinements allowing the occupancy of the water sites to vary were tried. Starting occupancies in various cases were 0.5 and 1.0. In all cases the occupancies refined very close to 1.0 with very similar R_1 and R_2 factors given here. Similar problems have been observed by us previously. (R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **17**, 1941 (1978).)
- (18) According to the IR spectrum, CO_3^{2-} is no longer ionic but coordinated. The positions of the two most prominent CO_3 absorptions (1480 and 1350 cm^{-1}) suggest monodentate coordination¹⁹ rather than bidentate chelation.²⁰
- (19) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 3137 (1958).
- (20) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968).
- (21) This compound contains ionic NO_3^- (IR absorptions at $1380 (\nu_3)$ and $820 (\nu_2) \text{ cm}^{-1}$) and coordinated CO_3^{2-} (highest CO_3 absorptions at 1520 and 1330 cm^{-1}) and exhibits a strong EPR signal ($g \sim 2.37$, $g_{\parallel} \sim 2.04$) very similar to those observed for the so-called platinum-pyrimidine blues²² or the recently described platinum- α -pyridone blue²³ which are mixed-valence-state compounds.
- (22) B. Lippert, *Wadley Med. Bull.*, **1**, 26 (1977).
- (23) J. K. Barton, H. N. Rabinowitz, D. J. Szalda, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 2827 (1977).
- (24) The operation of the program is described in B. Lippert, C. J. L. Lock, B. Rosenberg, and M. Zvagulis, *Inorg. Chem.*, **16**, 1525 (1977).
- (25) R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, and G. Turner, *Inorg. Chem.*, **16**, 314 (1977).
- (26) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o|^2 - |F_c|^2) / \sum w F_o^2]^{1/2}$. All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRDN from the X-ray 71 package were used for preliminary treatment of data. The full-matrix least-squares program CUDLS, Fourier program, SYMFOU, and least-squares-planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared using the program ORTEP by C. K. Johnson, Report ORNL 3794, U.S. Atomic Energy Commission, Oak Ridge, Tenn., revised June 1965.
- (27) A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).
- (28) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974, Table 2.2A, p 72 ff.
- (29) D. T. Cromer, ref 28, Table 2.3.1, pp 149-150.
- (30) In each plane mentioned all atoms were included in the refinement and were given unit weight. The esd in each atom position with respect to the plane is 0.015 \AA .
- (31) IR intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad. Raman intensities are relative to the strongest Raman band at 556 cm^{-1} with arbitrary intensity 10.
- (32) According to space group C_i^1 and $Z = 1$ the D_{2h} symmetry of the free dimer is reduced to C_i site symmetry.

Contribution from the Institute of Materials Research and the Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

Preparation, Vibrational Spectra, and Crystal Structure of Dithionitronium Hexachloroantimonate(V), $(\text{S}_2\text{N})(\text{SbCl}_6)$

ROMOLO FAGGIANI, RONALD J. GILLESPIE,* COLIN J. L. LOCK,* and J. DAVID TYRER

Dithionitronium hexachloroantimonate(V), $(\text{S}_2\text{N})(\text{SbCl}_6)$, has been prepared by the reactions of S_7NH , S_7NBCl_2 , and $1,4\text{-S}_6\text{N}_2\text{H}_2$ with SbCl_5 in liquid SO_2 . The structure of the compound has been determined by single-crystal X-ray diffraction. The orthorhombic crystal, space group $I222$, has cell dimensions $a = 9.299 (3) \text{ \AA}$, $b = 7.976 (3) \text{ \AA}$, and $c = 7.070 (2) \text{ \AA}$ and has two formula units in the unit cell. Intensities were measured using $\text{Mo K}\alpha$ radiation and a Syntex $P2_1$ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0377$, $R_2 = 0.0375$. The crystal is composed of linear S_2N^+ cations ($\text{N-S} = 1.464 (3) \text{ \AA}$) and approximately octahedral SbCl_6^- anions ($\text{Sb-Cl} = 2.351 (3), 2.363 (2) \text{ \AA}$). Infrared and Raman spectra of the solid compound are reported.

Introduction

We have recently studied the reactions of S_4N_4 and $\text{S}_3\text{N}_3\text{Cl}_3$ with certain group 5 pentahalides which have both oxidizing and Lewis acid properties and we have shown that the cyclic cation $\text{S}_4\text{N}_4^{2+}$ is obtained by the reaction of S_4N_4 with SbCl_5 or SbF_5 , and also by the oxidation of $\text{S}_3\text{N}_3\text{Cl}_3$ with SbCl_5 .¹

This work has now been extended to the sulfur imides with particular emphasis on the behavior of heptasulfur imide and 1,4-hexasulfur diimide with Lewis acids. In the only previous study of the Lewis acid chemistry of S_7NH , Heal² isolated the dichloro- and dibromo(heptasulfur imido)boron derivatives of S_7NH by means of a simple condensation reaction of the imide with the appropriate boron trihalide. We have now shown that S_7NH and $1,4\text{-S}_6\text{N}_2\text{H}_2$ do not undergo analogous condensation reactions with SbCl_5 but a complex oxidative process produces the dithionitronium cation S_2N^+ . That this species has not been previously reported is somewhat surprising in view of its relative stability and fact that the analogous NO_2^+ has been known for over 30 years.

Experimental Section

Heptasulfur imide was prepared according to the method of Becke-Goehring.³ The product was crystallized twice from benzene to yield platelike crystals of mp $113 \text{ }^\circ\text{C}$ (lit. mp⁴ $113 \text{ }^\circ\text{C}$). The $1,4\text{-S}_6\text{N}_2\text{H}_2$ was prepared by the late Dr. F. P. Olsen according to the method described by Heal.⁵ The sample was recrystallized twice from benzene and its purity checked by melting point, $130\text{--}131 \text{ }^\circ\text{C}$ (lit. mp⁵ $130, 133 \text{ }^\circ\text{C}$), and its solution infrared spectrum.⁶ Boron trichloride (Matheson of Canada Ltd.) was distilled into a glass storage vessel that had been previously flame-dried under vacuum. The sample

was then degassed several times to remove any HCl present. Antimony pentachloride (J. T. Baker) was used without further purification. Sulfur dioxide (Canadian Liquid Air) was stored as a liquid over phosphoric oxide prior to use.

The Reaction of Heptasulfur Imide with SbCl_5 . Heptasulfur imide (0.001 mol, 0.287 g) and SbCl_5 (0.002 mol, 0.717 g) were each transferred in a drybox to separate bulbs of a double-bulb reaction vessel fitted with a medium glass frit. Sulfur dioxide (5 mL) was then condensed at $-196 \text{ }^\circ\text{C}$ into each bulb and the apparatus was flame-sealed. The mixtures were then allowed to warm to room temperature. The SbCl_5 completely dissolved in the SO_2 at room temperature but as S_7NH is only moderately soluble in liquid SO_2 some remained undissolved. The SbCl_5 solution was then poured through the glass frit into the bulb containing the S_7NH . There was an immediate reaction with the formation of a deep red-brown solution. After 48 h of shaking, a yellow powder formed which was characterized as S_8 , by means of its Raman spectrum. After filtration at room temperature and slow removal of the solvent, an orange crystalline material was obtained which was shown to be S_2NSbCl_6 . The reaction must be allowed to proceed for at least 48 h prior to filtration to ensure that the S_2NSbCl_6 is not contaminated with sulfur. Hydrogen chloride produced during the reaction was identified by means of its infrared spectrum, and SbCl_3 sublimed from the reaction mixture was characterized by comparison of its Raman spectrum with that of a pure sample.

The Reaction of $1,4\text{-S}_6\text{N}_2\text{H}_2$ with SbCl_5 . This reaction was carried out in essentially the same manner as described above using 0.0014 mol (0.317 g) of $1,4\text{-S}_6\text{N}_2\text{H}_2$ and 0.0057 mol (1.705 g) of SbCl_5 . A yellow powder was formed, which was characterized as elemental sulfur by means of its Raman spectrum. After filtration of the mixture at room temperature and slow removal of solvent, an orange crystalline material formed which was shown to be S_2NSbCl_6 . Hydrogen chloride