(23) D. D. Watkins, Jr., D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **15**, 387 (1976).
(24) D. H. Busch, *Helv. Chim Acta, Alfred Werner Commemoration Volume*, 174 (1967); R. Sperati, Ph.D. Thesis, The Ohio State University, 1971.
(25) (a) A. Hudson and H. J. Whitfield, *Inorg. Chem.*, **6**, 1120 (1967); (b) T. H. Moss and A. B. Robinson, *ibid.*, **7**, 1692 (1968); (c) I. Dezsi, A. Balazs, B. Molnar, V. D. Gorobchenko, and I. I. Lukashevich, *J. Inorg. Nucl. Chem.*, **31**, 1661 (1969).

Hydroxo-Bridged Platinum(II) Complexes. 1. Di-μ-hydroxo-bis[diammineplatinum(II)] Nitrate, $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$. Crystalline Structure and Vibrational Spectra

R. Faggiani,[1a] **B. Lippert,**[1b] **C. J. L. Lock,*** [1a] **and B. Rosenberg*** [1b]

Contribution from the Department of Biophysics, Michigan State University, East Lansing, Michigan 48823, and from the Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada. *Received June 4, 1976*

Abstract: The crystal structure of the complex di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ has been determined by x-ray diffraction. The triclinic crystal, space group $P\bar{1}$, has cell dimensions $a = 6.763$ (12) Å, $b = 7.890$ (18) Å, $c = 7.256$ (13) Å, $\alpha = 92.3$ (1)°, $\beta = 133.1$ (1)°, and $\gamma = 91.0$ (2)° and has one formula unit in the unit cell. Data were collected using Mo Kα radiation and a Syntex $P\bar{1}$ diffractometer. The crystal structure was determined by standard methods and refined to $R_2 = 0.0575$. The cation is a centrosymmetric hydroxo-bridged dimer with each platinum atom having roughly square planar coordination. Infrared and Raman spectra are discussed.

Coordination complexes of platinum have received much attention in recent years because they represent a new class of potent antitumor agents.[2] *cis*-Dichlorodiammineplatinum(II), the first active platinum complex discovered, is meanwhile in phase II clinical trials in man and results show that it is a drug of high activity in a series of malignant diseases.[3] Of the "second generation" platinum drugs with antitumor activity the so called "platinum-pyrimidine blues" are particularly interesting.[4] They are water soluble, deep blue or purple compounds formed when the diaquo species of *cis*-dichlorodiammineplatinum(II), $[cis\text{-}Pt(NH_3)_2(H_2O)_2]^{2+}$, is reacted with 2,4-dihydroxopyrimidines or substituted derivatives. Although the nature and structure of these completely amorphous compounds are still unclear there are indications from their EPR spectra as well as from the platinum concentration dependency of their formation that they might contain species which exhibit strong metal–metal interactions.[5] It was in this respect interesting that from a solution of the platinum starting material, *cis*-diaquodiammineplatinum(II) dinitrate, an air-stable dimeric hydroxo-bridged platinum compound, di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, could be isolated and characterized. Moreover, this compound is formed in a pH range where, with the 2,4-dihydroxopyrimidine, the blues are formed. It is one of the very rare examples of isolated hydroxo complexes of platinum(II). To our knowledge only one other platinum(II)–hydroxo complex, a dimer with two phosphinato bridges and tertiary phosphines and hydroxo groups as terminal ligands is sufficiently well characterized.[6] Other isolated platinum(II) complexes claimed to contain hydroxo groups are generally doubted today.[6,7] It is known, however, that platinum(II) hydroxo complexes exist in aqueous solution and that their formation from the corresponding aquo complexes is responsible for the acidity of many dissolved platinum(II) complexes.[7] Di-μ-hydroxo-bis[diammineplatinum(II)] nitrate has been prepared previously but its dimeric structure was not recognized and the obtained product had been formulated as a monomer, *cis*-monohydroxomononitratoplatinum(II), $cis\text{-}Pt(NH_3)_2(OH)(NO_3)$.[8]

Experimental Section

Preparation of Compounds. Di-μ-hydroxo-bis[diammineplatinum(II)] nitrate was prepared in the following way: 3 g of *cis*-dichlorodiammineplatinum(II) (Engelhard Industries) was stirred with 3.35 g of $AgNO_3$ (99% of theory) in 50 ml of water in a stoppered flask at room temperature for 20 h. The flask was wrapped in Al-foil because of the photosensitivity of the formed diaquo species.[9] The precipitated silver chloride was filtered and washed with 5 ml of water. The pale yellow solution (pH $\simeq$ 2) was then titrated with 1 N NaOH to pH 6.44, slightly warmed to prevent early precipitation, quickly filtered, and kept in a stoppered flask for 1 day at 0 °C in the refrigerator. The precipitate was then filtered, washed with 20 ml of water, then with ether, and dried under rotary pump vacuum for several hours; 1.56 g of the white microcrystalline compound was thus obtained. It was recrystallized once from water.

Concentration of the filtrate (rotary evaporator, 30 °C water bath) to 30 ml volume and cooling to 0 °C for 24 h gave a second crop of crystals, yield 0.2 g.

Further concentration of the filtrate to 15 ml volume produced a yellow solution and after a day at 0 °C, 0.1 g of the colorless platinum dimer was obtained and also 0.25 g of a crystalline species which was deep yellow and transparent. Single-crystal x-ray analysis showed that it is a cyclic hydroxo-bridged platinum trimer. We shall report on this in detail later.[10]

The yield of the second and third crop of di-μ-hydroxo-bis[diammineplatinum(II)] nitrate could be increased if the pH of the filtrate of the previous fraction was readjusted to about 6.4 by means of NaOH. The yield of the compound was decreased if the solution of the *cis*-diaquodiammineplatinum(II) dinitrate was titrated to a pH to below 6.44, for example, only to 4.5–6.

Crystals of the compound of suitable size for x-ray analysis were obtained if the preparation was slightly modified such that the titrated and filtered solution of pH 6.44 was kept in an open beaker in a water bath at 37 °C which was covered with Al-foil. After 18 h very pale yellow transparent crystals up to 3 mm long were filtered, washed with 10 ml of water, and dried as mentioned above. The yield of the first fraction was 0.56 g. The pH of the filtrate was readjusted from 5.0 to 6.44 and after two more days 0.76 g of the compound was collected. A further crop was obtained after two more days (pH readjusted to 6.44). The crystals were no longer pale yellow, however, but light

Table I. Final Atomic Positions and Thermal Parameters[a] ($\times 10^3$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	241.30 (8)	392.56 (5)	−113.18 (8)	20.9 (3)	21.0 (3)	21.3 (3)	−3.1 (2)	15.2 (2)	1.8 (2)
O(1)	350 (2)	628 (1)	−135 (2)	28 (4)	22 (4)	30 (4)	−4 (3)	20 (4)	4 (3)
N(1)	162 (3)	154 (2)	−81 (2)	29 (6)	32 (6)	29 (5)	−6 (4)	17 (5)	4 (4)
N(2)	−161 (2)	427 (2)	−367 (2)	25 (5)	34 (6)	31 (6)	−1 (4)	17 (5)	9 (5)
N(3)	393 (2)	124 (1)	596 (2)	37 (6)	28 (5)	30 (5)	3 (4)	25 (5)	0 (4)
O(2)	623 (2)	189 (1)	772 (2)	30 (5)	45 (6)	44 (6)	−5 (4)	25 (5)	5 (5)
O(3)	231 (3)	192 (2)	385 (2)	76 (9)	38 (6)	44 (6)	9 (6)	42 (7)	11 (5)
O(4)	308 (2)	−6 (1)	616 (2)	42 (6)	35 (5)	51 (6)	−13 (5)	29 (5)	2 (5)

[a] Estimated standard deviations from the least-squares programs are given in parentheses. The temperature factor parameters U_{ij} were obtained from $\beta_{ij} = 2\pi^2 \mathbf{b}_i \mathbf{b}_j U_{ij}$ where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ in the structure factor expression and $\mathbf{b}_i$ are the reciprocal lattice vectors.

amber. The volume of the starting solution was allowed to diminish gradually to 20 ml after 5 days.

Anal. (Galbraith Laboratories) First fraction (cooling 0 °C): H, 2.44; N, 13.82; O, 20.59; Pt, 63.29. First fraction (waterbath 37 °C): H, 2.29; N, 13.75; O, 21.50; Pt, 62.11. Theory requires: H, 2.27; N, 13.61; O, 20.8; Pt, 63.3.

The molecular weight (Galbraith Laboratories) gave 298 and 280 amu for the first fractions prepared at 0 and 37 °C, respectively, and was determined osmometrically in water.[11] The solubility at room temperature is 2.1 g/100 ml (±10%). The pH of a saturated solution is 6.6. The compound is air-stable and starts decomposing above 188-190 °C.

The deuterated species of the title compound was prepared by recrystallizing the compound once from hot 99.8% D_2O.

pH Considerations. *cis*-diaquodiammineplatinum(II) nitrate, [*cis*-$Pt(NH_3)_2(H_2O)_2$]$(NO_3)_2$ is a dibasic acid with $pK_1 = 5.56$ and $pK_2 = 7.32$ according to Jensen[12] but $pK_1 = 5.63$ and $pK_2 = 9.25$ according to Perumareddi and Adamson.[9] Titration of the diaquo species with base to a pH exactly between pK_1 and pK_2 ($pH = 0.5\,(pK_1 + pK_2)$) should lead to a solution which contains predominantly [*cis*-$Pt(NH_3)_2(H_2O)(OH)$]$^+$ or a subsequent product like the obtained dimer. We chose pH 6.44, which we calculated from Jensen's pK values, because we thus obtained pure di-μ-hydroxo-bis[diammineplatinum(II)] nitrate in high yield. From a solution titrated to pH 7.44 (calculated from Perumareddi's and Adamson's pK values), however, we obtained the dimer in much lower yield together with another not yet identified compound as the major product.

Apparatus. pH measurements were performed by means of a Corning pH meter Model 7 with a combination electrode. The instrument was calibrated with two buffers of different pH.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer in the range 4000-400 cm^{-1} as Nujol mulls. The spectra were calibrated against polystyrene.

Raman spectra were obtained from powder samples at room temperature in the range 1700-50 cm^{-1} on a Spex spectrometer Model 1401 with a Coherent Radiation Argon Laser Model 52. The spectra were calibrated against CCl_4.

Collection of X-ray Diffraction Data. A pale yellow crystal, chosen after examination under a polarizing microscope for homogeneity, was ground to an approximate cylinder of dimensions 0.30 mm long × 0.15 mm diameter.

Precession photographs of zero and first layers suggested the crystal was triclinic. The crystal was transferred to a Syntex P1 diffractometer and mounted along the long direction (roughly [1$\bar{6}$1]). Accurate parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 medium angle ($20° < 2\theta < 35°$) reflections: $a = 6.763$ (12), $b = 7.890$ (18), $c = 7.256$ (13) Å; $\alpha = 92.3$ (1), $\beta = 133.1$ (1), $\gamma = 91.0$ (2)° (λ 0.710 69 Å for Mo Kα at 21 °C). A Delaunay reduction showed no hidden symmetry. With $Z = 1$ (for a dimer) ρ_{calcd} was 3.64 g cm^{-3} and the ρ_{obsd} was 3.9(2) g cm^{-3}. The density was measured by displacement in light paraffin. The large error was caused by the small amount of material available for the measurement.

Intensity data were recorded on a Syntex P$\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation for the hemisphere defined by h, $\pm k$, $\pm l$, up to $2\theta = 55°$. Data were collected by using a coupled θ (crystal)-2θ (counter) scan 1° on either side of the peak, scan rates ranging from 4 to 24° and being selected by the program supplied with the instrument. The stability of the system was monitored by measuring a standard reflection after every 49 reflections. The counting esd of the standard peak was 1.25% and an analysis of the standard counts showed an overall variation of 1.43% with no systematic variation with time. The intensity of a reflection, I, and its esd, σ_I, were calculated as outlined previously.[13] Independent reflections (1305) were recorded, of which 1229 were considered observed ($I < \sigma_I$). The linear absorption coefficient was 260 cm^{-1}. Absorption corrections[14] were made using the above crystal dimensions. Variation in transmission coefficient was 6.25 to 19.9. Unscaled structure factor amplitudes, F, and the standard deviations, σ_F, were calculated from the expression $F = (I/LP)^{1/2}$, $\sigma_F = \frac{1}{2}[1/(LP)^{1/2}](\sigma_I{}^2/I)^{1/2}$. LP, the Lorentz-polarization factor is $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Solution of the Structure. The space group $P\bar{1}$ was assumed at the beginning and was confirmed by the successful solution of the structure. The coordinates of the platinum atom were found from a three-dimensional Patterson synthesis and three-dimensional electron density and difference maps revealed the two nitrogen atoms and oxygen atom bonded to platinum. Least-squares refinement of these atom positions followed by further three-dimensional electron density synthesis and difference calculations revealed the atoms of the nitrate ion. At this stage, the temperature factors for all atoms, which were isotropic in the initial stages of structure solution, were made anisotropic. Further refinement using a Cruickshank weighting scheme with weights equal to $(10.13 - 0.5275|F_o| + 0.008\,993F_o{}^2)^{-1}$ and full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was terminated at $R_1 = 0.0506$, $R_2 = 0.0575$.[15] In the last cycle of refinement no parameter shifted by more than 0.02 of its esd. Corrections were made for secondary extinction.

The final difference map showed little variation, the variation over most of the map lying between +0.6 and −0.5 e/Å^3. The only significant features were two peaks, +2.7 and +2.6 e/Å^3, at 0.15, 0.37, 0.74 and 0.35, 0.42, 0.03, close to the Pt atom and two valleys, −2.7 e/Å^3, each at 0.35, 0.42, 0.87 and 0.15, 0.35, 0.92 also close to the platinum atom. We have examined all the other peaks greater than 0.35 e/Å^3 to see whether we could detect the hydrogen atoms. Some do lie close to expected hydrogen atom positions, but many do not, and we cannot conclude anything about hydrogen atom positions.

Throughout the refinement the scattering curves used were taken from the International Tables[16] and anomalous dispersion corrections from International Tables[17] were applied to the curves for platinum. The atom parameters for the non-hydrogen atoms are listed in Table I.[18]

Results and Discussion

Infrared and Raman Spectra. The vibrational spectra of di-μ-hydroxo-bis[diammineplatinum(II)] nitrate allow a separation of bands attributable to the vibrational modes of the anion and the cation. We shall consider the anion first.

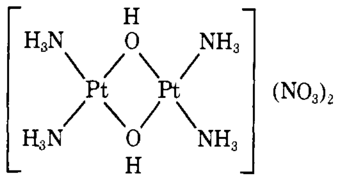
The absorption bands of the anion in both the infrared and Raman spectra, combined with the results of the elemental analysis that ruled out any additional ligands, led us to the conclusion that the compound must be a dimer (**1**) rather than a monomer (**2**) and stimulated an x-ray analysis.

Ionic nitrate (point group D_{3h}) gives rise to four fundamental frequencies of absorption,[19] all observable in the spectra

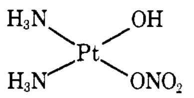
Table II. Infrared and Raman Bands of Di-μ-hydroxo-bis[diammineplatinum(II)] nitrate (A) and Its Deuterated Analogue (B) between 4000 and 400 cm^{-1}

IR (Nujol)[a]		Raman (solid)[b]		
A	B	A	B	Assignment
3360 sh, 3320 s, 3290 . . . 3090 vs	2505 w, 2460 sh, 2428 s, 2398 s, 2320 s, 2270 s			ν(OH (OD), ν(NH_3 (ND_3))
2730 w	2720 w			$2\nu_3(NO_3)$
2680 w	2680 w			
2440 w, 2390 w				$\nu_1(NO_3) + \nu_3(NO_3)$
2340 w				$\delta_s(NH_3)$ + δ(PtO-H)
2220 w				
2065 w	2040 w			$2\nu_1(NO_3)$
1890 w, b				$\rho_r(NH_3)$ + δ(PtO-H)
1770 w, 1755 m	1765 w, 1750 w			$\nu_1(NO_3) + \nu_4(NO_3)$
1725 w, b				$2\rho_r(NH_3)$
1620 s, 1600 sh	1270 sh,			δ_d(NH_3 (ND_3))
1580 s	1175 s, 1150 s			
1370 vs	1370 vs	1370 (0)		$\nu_3(NO_3)$
1320 vs, 1310 vs	1035 s, 1020 s			δ_s(NH_3 (ND_3))
1170 sh				
		1045 (10)	1045 (10)	$\nu_1(NO_3)$
1040 s	772 vs			δ(PtO-H, (PtO-D))
918 s, 870 s, 840 m, 770 sh	680 m, 655 m, 630 m			ρ_r(NH_3(ND_3))
820 s	820 s			$\nu_2(NO_3)$
720 w, 705 vw	710 w	717 (2), 702 (0)		$\nu_4(NO_3)$
585 m	563 s			
		558 (8)	524 (8)	
		552 (6)	514 (6)	
550 m	526 s			stretching vibrations of the N_2Pt O_2 Pt N_2 skeleton
532 s	518 sh			
		504 (4)	506 (2)[c]	
495 s	498 s, 484 s			
		488 (0)	496 (2)	

[a] IR-intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad. [b] Raman intensities relative to strongest Raman band at 1045 cm^{-1} with arbitrary intensity 10. [c] Shoulder of 514-cm^{-1} band.



1



2

of our compound at frequencies close to the reported ones (Table II). In contrast, coordinated nitrate, has lowered symmetry (C_{2v} or C_s for monodentate nitrate), and exhibits six fundamental vibrations which are active both in the infrared and Raman spectra and absorb at distinctly different frequencies from those of ionic nitrate.[19,20] No evidence for these can be found in the vibrational spectra of our compound. The strong band observed in the infrared spectrum at 1040 cm^{-1} seems to contradict the required inactivity of the N-O stretching vibration, although it is reported[21] that this mode sometimes becomes weakly IR-active if the nitrate ion is somewhat deformed in the crystal field. Since, however, this band is shifted upon deuteration, it is not possible to assign this to a nitrate band but is attributed to a Pt-OH bending vibration (see below).

The vibrations of the binuclear cation can be divided, as a first approximation, into those in which the protons of the NH_3 and OH ligands move relative to N and O, respectively, and those in which the ligands move as units against the heavy platinum ions in the $N_2PtO_2PtN_2$ skeleton. The former include stretching (ν_{as}, ν_s), deformation (δ_d, δ_s), and rocking (ρ_r) modes of the NH_3 ligands and stretching and deformation modes of the OH bridges. The latter are the Pt-N and Pt-O stretching and deformation modes.

In the 3 μ region of the IR spectrum there is a broad band with several badly resolved maxima between 3320 and 3090 cm^{-1} and a shoulder at higher wavenumber (3360 cm^{-1}). In the spectrum of the deuterated compound these bands are better resolved and appear between 2505 and 2270 cm^{-1}. The observed frequency shifts νXH/νXD are smaller than the theoretical $2^{1/2}$ for harmonic oscillators and indicate hydrogen bonding as does the relatively low absorption frequency of the OH stretching vibration ($\leq$3360 cm^{-1}). Because the stretching modes of NH_3 and OH are superimposed, it is not possible to make a reasonable assignment and, likewise, a complete assignment for the bands of the deuterated analogue can only be speculative. From intensity considerations it is reasonable, however, to attribute the strong band at 2428 cm^{-1} to the asymmetric stretching vibrations of the ND_3 groups and the somewhat less intense band at 2270 cm^{-1} to the symmetric stretching vibrations of the same groups.

The bands of the degenerate deformation modes of the NH_3 groups occur between 1620 and 1580 cm^{-1}, those of the symmetric deformation modes at 1320 and 1310 cm^{-1}.

The positions of the latter reflect the effect of the positive charge of the platinum dimer which shifts the symmetrical and also the rocking deformation vibrations to higher frequencies relative to similar neutral ammine complexes.[22] A comparison with the corresponding absorptions in a series of positively charged and neutral ammine complexes shows that our doubly charged platinum dimer is similar in this respect to singly

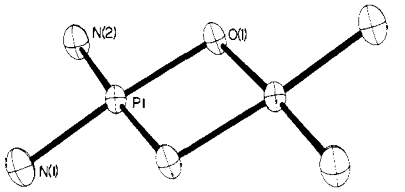


Figure 1. Molecular structure of the {di-μ-hydroxo-bis[diammineplatinum(II)]} cation. The labeling of the atoms is as in Table I.

charged monomeric platinum complexes such as [Pt$(NH_3)_3X$]Y.[23]

The nitrate vibration ν_2 at 820 cm^{-1} is flanked on both sides by a series of bands ranging from 918 to 770 cm^{-1} with its most intense centerband at 870 cm^{-1}. Since, with the exception of the nitrate bands, all these bands are removed upon deuteration and appear at 680, 655, and 630 cm^{-1} in the Nujol-spectrum of the deuterated species they are assigned to individual NH rocking motions of the ammine groups.

Infrared studies on some binuclear hydroxo-bridged complexes of Co(II),[24a] Cr(III),[25] and Cu(II)[26] as well as metal complexes with terminal OH groups[27] always reveal the existence of a band in the region of 900 to 1120 cm^{-1} which is close to the upper limit of metal-OH bending vibrations found in some metal hydroxides.[24b] In the infrared spectrum of our platinum dimer an intense band appears at 1040 cm^{-1} which cannot be assigned to any of the NH-vibrations but shifts in the spectrum of the deuterated species to 772 cm^{-1} (δOH/δOD = 1.348). We therefore assign this bond to the Pt-OH bending vibration.

For the {di-μ-hydroxo-bis[diammineplatinum(II)]} cation, which the x-ray structure shows has nearly the ideal D_{2h} symmetry (OH and NH_3 treated as monoatomic groups), group theory predicts 18 normal vibrations of the $N_2PtO_2PtN_2$ skeleton. Eight of these ($2B_{1u}$, $3B_{2u}$, $3B_{3u}$) are infrared active, nine (4 A_g, $3B_{1g}$, $1B_{2g}$, $1B_{3g}$) are Raman active, and one (A_u) is inactive. Since we did not extend our infrared studies into the range where most of the skeletal deformations absorb, only stretching vibrations (2 B_{2u}, $2B_{3u}$) were expected to be found in the IR range of 600 to 400 cm^{-1}. In the same range in the Raman spectrum four vibrations ($2A_g$, $2B_{1g}$) were also expected.

Table III. Interatomic Distances (Å) and Angles (deg)[a]

	Bonded Distances		
Pt-O(1)	2.03 (1)	Pt-O(1)*	2.03 (1)
Pt-N(1)	2.01 (1)	Pt-N(2)	2.02 (1)
N(3)-O(2)	1.23 (1)	N(3)-O(3)	1.23 (2)
N(3)-O(4)	1.27 (2)		
	Nonbonded Distances		
Pt-Pt*	3.085 (1)	O(2)-N(2)′	2.96 (2)
O(2)-O(1)	2.84 (2)	O(3)-N(1)	3.08 (2)
O(3)-N(2)*	3.05 (2)	O(4)-N(1)′	3.19 (2)
	Angles		
O(1)-Pt-O(1)*	81.3 (4)	N(1)-Pt-O(1)*	94.5 (5)
O(1)-Pt-N(1)	175.6 (6)	N(1)-Pt-N(2)	89.3 (6)
O(1)-Pt-N(2)	94.9 (5)	N(2)-Pt-O(1)*	176.1 (6)
O(2)-N(3)-O(3)	121 (2)	O(3)-N(3)-O(4)	117 (1)
O(2)-N(3)-O(4)	122 (1)		

[a] Pt* and O(1)* are related to Pt and O(1) given in Table I by inversion through ½,½,0, and N(2)* is related to N(2) by inversion through 0,½,0. N(2)′ is related to N(2) by the translation 1,0,1 and N(1)′ is related to N(1) by the translation 0,0,1.

In Table II we have compiled all observed bands of the vibrational spectra which we attribute to skeletal stretching vibrations and have made a classification scheme for the eight bands which must be regarded as tentative. A comparison of IR and Raman bands of the platinum dimer in the range 600-400 cm^{-1} reveals that there are no coincident Raman and infrared bands (as expected for a molecule with a center of symmetry). Any attempt to assign individual metal-oxygen or metal-nitrogen stretching vibrations, as has been done, for example, in similar complexes of Cr(III), Fe(III), and Cu(II) where the metal-oxygen stretching vibrations absorb around

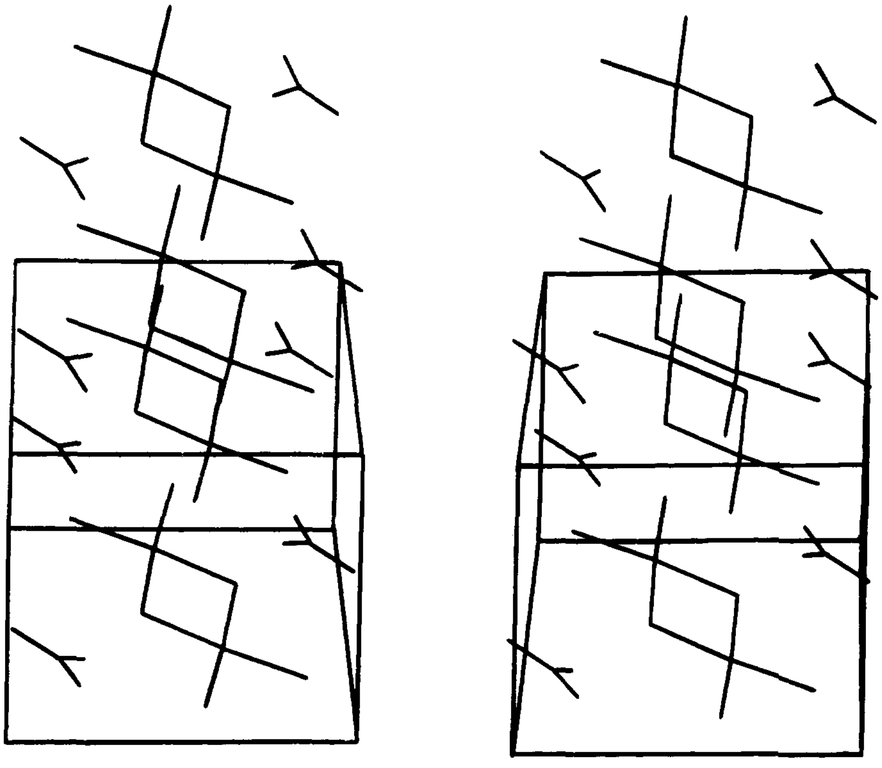


Figure 2. Stereogram (stereoscopic pair of perspective projections) of di-μ-hydroxo-bis[diammineplatinum(II)] nitrate. The contents of four unit cells are shown. **a** and **b*** are parallel to the side and top of the page, respectively, and the view is down **c***.

500 cm^{-1} and the metal–nitrogen stretching vibrations around 300 cm^{-1},[28] is impossible, since the individual motions are not only likely to be of similar energy, but are also of the same symmetry, thus making coupling very likely and leading to mixed character. The approximately equal Pt–N and Pt–O distances, obtained from x-ray data, agree with this.

Crystallography. The molecular cation is illustrated in Figure 1 and selected interatomic distances and angles are given in Table III. The molecular ion is clearly a dimer bridged by hydroxyl groups.[29] The dimer unit is essentially planar although the platinum atoms lie 0.02 Å out of the best plane. The Pt–N bond lengths (2.01 (1), and 2.02 (2) Å) are as expected[30] as are the Pt–O distances (2.03 (1) Å).[31] The decrease in the O(1)–Pt–O(1)* angle (81.3 (4)°) from the ideal 90°, caused by the steric requirements of the bridged system is relieved by increases in N(2)–Pt–O(1) and N(1)–Pt–O(1)* (94.9 (5), 94.5 (5)°). The geometry of the nitrate ion is normal within the errors.[32]

The packing of the ions within the unit cell is illustrated in Figure 2. The coarse features of the structure are dominated by the arrangement of the dimeric cations in layers parallel to the ac plane and centered at $y = \frac{1}{2}$. These layers are separated by the nitrate ions which lie in a similar plane centered at $y = 0$. Quite apart from the ionic attraction, hydrogen bonding is clearly important in determining the structure. As can be seen in Table III, practically every oxygen atom on the nitrate groups is within 3.2 Å of either a hydroxide or ammonia group on the cation, and in a position to form hydrogen bonds. There are no direct platinum–platinum interactions between dimeric cations. In the **c** direction (shortest Pt–Pt distance is 7.08 Å between the ions at x, y, z and $x, y, 1 + z$), the ammonia groups from the cation at $1 + x, y, 1 + z$ interleave the ions at x, y, z and $x, y, 1 + z$, giving an NH_3–OH contact in the first case and an NH_3–NH_3 contact in the second case. Shorter Pt–Pt distances are observed between pairs of dimers at x, y, z and $1 + x, y, 1 + z$ (4.57 Å) but these distances are still far too long for any Pt–Pt interactions. In the direction of this short interaction, [101], the dimeric cations are stacked roughly like tiles on a roof. The nitrate ions are also arranged such that their planes nearly contain the [101] direction and the dihedral angle between the dimeric cation and the nitrate ions is only 30°. The centrosymmetrically related nitrate pairs along the [101] direction form a pair of chains, the bases of the triangles in each chain lying roughly along [101], and the remaining apices pointing very roughly towards the centrosymmetrically related chain. The chain of nitrate groups is arranged such that it lies between the N(2) ammonia groups on adjacent [101] stacks of dimers by the **c** translation.

Acknowledgments. We wish to thank the National Cancer Institute, Engelhard Industries, Matthey-Bishop, Inc., and International Nickel as well as the National Research Council of Canada and the McMaster University Science and Engineering Research Board for financial support of this work.

Supplementary Material Available: A table of the moduli of the observed and calculated structure factor amplitudes (4 pages). For ordering instructions, consult any current masthead page.

References and Notes

(1) (a) McMaster University. (b) Michigan State University.

(2) See, for example, (a) B. Rosenberg, *Cancer Chemother. Rep.*, **59**, 589 (1975); (b) T. A. Connors and J. J. Roberts, Ed., "Platinum Coordination Complexes in Cancer Chemotherapy", Springer, Berlin, Heidelberg, New York, 1974.

(3) See, for example, (a) J. A. Gottlieb and B. Drewinko, *Cancer Chemother. Rep.*, **59**, 621 (1975); (b) J. M. Hill, E. Loeb, A. MacLellan, N. O. Hill, A. Khan, and J. J. King, *ibid.*, **59**, 647 (1975).

(4) J. P. Davidson, P. J. Faber, R. G. Fischer, Jr., S. Mansy, H. J. Peresie, B. Rosenberg, and L. VanCamp, *Cancer Chemother. Rep.*, **59**, 287 (1975).

(5) B. Lippert and B. Rosenberg, to be submitted for publication.

(6) J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968).

(7) F. R. Hartley, "The Chemistry of Platinum and Palladium", Wiley, New York, Toronto, 1973, pp 168, 169, and references therein.

(8) (a) H. J. S. King, *J. Chem. Soc.*, 1338 (1938); (b) R. G. Fischer, Jr., and H. J. Peresie, personal communication.

(9) J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, **72**, 414 (1968).

(10) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, submitted to *Inorg. Chem.*

(11) The molecular weight was determined by an osmometer which measured the temperature difference caused by condensation of solvent vapors into a drop of solvent and a drop of solution held in a constant temperature (38.5 or 65 °C) chamber saturated with solvent vapors. The results obtained indicate that ionization of the compound is not complete, otherwise one should find $616/3 \simeq 205$ amu.

(12) K. A. Jensen, *Z. Anorg. Chem.*, **242**, 87 (1939).

(13) R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, and G. Turner, *Inorg. Chem.*, in press.

(14) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRON from the X-RAY71 package were used for preliminary treatment of data. The full-matrix least-squares program, CUOLS, Fourier programs, SYMFOU, and least squares planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams prepared using the program ORTEP by C. K. Johnson, U.S. Atomic Energy Commission Report, ORNL 3794, Revised June 1965.

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

(16) D. T. Cromer and J. A. Waber, "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, 1974, Table 2.2A, p 72 ff.

(17) D. T. Cromer, ref 16, Table 2.3.1., pp 149–150.

(18) See paragraph at end of paper regarding supplementary material.

(19) (a) C. C. Addison and D. Sutton, *Prog. Inorg. Chem.*, **8**, 195 (1967); (b) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(20) C. C. Addison, N. Logan, and S. C. Wallwork, *Q. Rev., Chem. Soc.*, **25**, 289 (1971).

(21) S. I. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, **75**, 4870 (1953).

(22) G. F. Svatos, D. M. Sweeny, S. I. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).

(23) Compounds with X = Cl, Y = Cl, NO_3 were prepared according to published methods and identified by elemental analysis.

(24) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970, (a) p. 169 (b) p. 82.

(25) G. Hoch, H.-E. Sasse, and M. L. Ziegler, *Z. Naturforsch. B*, **30**, 704 (1975).

(26) J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, **6**, 1382 (1967).

(27) See, e.g., (a) D. Scargill, *J. Chem. Soc.*, 4444 (1961); (b) R. L. Williams and R. J. Page, *Ibid.*, 4143 (1957).

(28) J. R. Ferraro, R. Driver, W. R. Walker, and W. Wozniak, *Inorg. Chem.*, **6**, 1586 (1967).

(29) The postulated structure was confirmed by doing alternate refinements changing O(1) with N(1) and N(2) in turn. Structure factors and R values for the changed sets were: O(1) and N(1) interchanged N(1) (bridged position); U_{11}, 0.017; U_{22}, 0.011; U_{33}, 0.018; U_{12}, −0.004; U_{13}, 0.012; U_{23}, 0.002; O(1) (N(1) position), U_{11}, 0.039; U_{22}, 0.044; U_{33}, 0.040; U_{12}, −0.006; U_{13}, 0.024; U_{23}, 0.005; $R_1 = 0.0512$; $R_2 = 0.0585$. N(2) (bridged position), U_{11}, 0.017; U_{22}, 0.011; U_{33}, 0.018; U_{12}, −0.004; U_{13}, 0.012; U_{23}, 0.003. O(1) (N(2) position) U_{11}, 0.035, U_{22}, 0.047; U_{33}, 0.042; U_{12}, −0.001; U_{13}, 0.024; U_{23}, 0.011; $R_1 = 0.0511$, $R_2 = 0.0583$. The bridged position nitrogen temperature factors are unacceptably low. There were minor changes in other parameters.

(30) C. J. L. Lock, R. A. Speranzini, and J. Powell, *Can. J. Chem.*, **54**, 53 (1976).

(31) A. C. Villa, A. G. Manfredotti, A. Giacomelli, C. Guastini, and A. Indelli, *Inorg. Chem.*, **14**, 1654 (1975), and references therein.

(32) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18** (1965).