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Hydroxo-Bridged Platinum(II) Complexes. 2.[1] Crystallographic Characterization and Vibrational Spectra of *cyclo*-Tri-μ-hydroxo-tris[*cis*-diammineplatinum(II)] Nitrate

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The crystal structure of *cyclo*-tri-μ-hydroxo-tris[*cis*-diammineplatinum(II)] nitrate, $[Pt_3(NH_3)_6(OH)_3](NO_3)_3$, has been determined by single-crystal x-ray diffraction. The triclinic crystal, space group $P\bar{1}$, has cell dimensions a = 9.683 (3) Å, b = 12.513 (6) Å, c = 8.832 (3) Å, α = 120.90 (3)°, β = 98.67 (3)°, and γ = 98.32 (3)° and has two formula units 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_1 = 0.0610 and R_2 = 0.0623. The cation is a hydroxo-bridged trimer with each platinum atom having square-planar coordination. The arrangement of ligand atoms around each platinum atom is square-planar with Pt–N distances (range 1.97 (5)–2.06 (2) Å) almost equal to the Pt–O distances (range 1.99 (3)–2.07 (2) Å). Infrared and Raman spectra are discussed.

In a previous paper we reported on a novel dimeric, hydroxo-bridged platinum(II) complex, di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$, and mentioned briefly that a trimeric, hydroxo-bridged platinum(II) complex is also formed during the preparation of the dimer.[1] This new species, *cyclo*-tri-μ-hydroxo-tris[*cis*-diammineplatinum(II)] nitrate, $[Pt_3(NH_3)_6(OH)_3](NO_3)_3$, is another example of the unexpected strength of Pt^{II}–OH–Pt^{II} bridges and their ease of formation. We wish to present here the crystal and molecular structure of the cyclic trimer as well as give a short description of its vibrational spectra which were helpful in predicting the nonmonomeric nature of the compound before its verification by x-ray analysis.

Experimental Section

Preparation. Though the principle of preparation of the title compound was outlined in our previous paper,[1] we wish to describe here a slightly modified procedure for its preparation which gave crystals of better quality. A 0.05-mol sample of *cis*-diaquodiammineplatinum(II) dinitrate in 180 mL of water (prepared according to ref 1) was titrated with 25 mL of a 2 N NaOH solution to pH 6.45 and kept in a stoppered flask at 0 °C for 4 days. Then the precipitated dimer was filtered off, washed, and dried as described earlier;[1] yield 9.25 g. The filtrate was then concentrated (rotary evaporator, 30 °C water bath) to 80-mL volume and cooled for 1 day at 0 °C. The yield of the second crop of the dimer was 0.55 g. The filtrate, which had a pH of 5.1, was now deep yellow. It was allowed to stand in a stoppered flask at 0 °C for 7 days; then the precipitate was filtered and washed with 10 mL of ice-cold water, with some ethanol, and finally with ether. It was dried under rotary pump vacuum at room temperature for several hours. A 1.1-g sample of a crystal mixture which consisted of 80% of the yellow trimer and 20% of the colorless dimer was obtained. The filtrate was further concentrated to 15-mL volume and cooled for another 4 days at 0 °C.

The precipitate was filtered and washed and dried as described. An 0.8-g amount of yellow trimer crystals, which were up to 1 mm long, was obtained (total yield based on Pt was 11%). The yield could be increased up to 16% if the filtrate after removal of the first two dimer crops was concentrated further than described here. The crystals obtained were, however, only of poor quality.

Since the crops of trimer crystals practically always contained crystalline dimer species, the following separation methods were used: (a) mechanical separation under a microscope (relatively easy because of the different colors of the dimer (colorless) and the trimer (yellow)); (b) separation due to different solubilities of trimer and dimer. Since the trimer had an 11-fold greater solubility (23.7 g/100 mL of water at room temperature) than the dimer (2.1 g/100 mL of water at room temperature), the mixture was treated with an amount of water to give a saturated solution at room temperature and filtered from the undissolved dimer, and the yellow filtrate was concentrated with caution and cooled. Warming of the trimer solution was avoided because it favored formation of the dimer. Recrystallization of the compound was done from a saturated (room temperature) solution by cooling to 0 °C for several days.

Elemental analysis (Galbraith Laboratories) for a freshly prepared sample gave 2.30% H, 13.44% N, 22.27% O, and 62.08% Pt. This gives an empirical formula of $[Pt_3(NH_3)_6(OH)_3](NO_3)_3 \cdot H_2O$. Theory requires 2.44% H, 13.38% N, 22.08% O, and 62.10% Pt. The compound readily loses its water of crystallization when kept under reduced pressure at room temperature and changes it color from deep yellow to a lighter yellow. A second elemental analysis of the same compound gives then 2.29% H, 13.51% N, 21.06% O, and 63.17% Pt. Theory for the anhydrous compound requires 2.27% H, 13.64% N, 20.78% O, and 63.31% Pt. X-ray measurements as well as IR and Raman spectra were performed with the anhydrous compound. The molecular weights (Galbraith Laboratories) were determined osmometically in aqueous solution as 315 and 350 respectively for two different samples.[3] The pH of a saturated aqueous solution was 6.2. Decomposition occurred above 175 °C.

The following IR and Raman bands (in cm^{-1}) were observed. Infrared (KBr): 3400 (s),[4a] 3300...3080 (vs), 2920 (sh), 2845 (sh), 2760 (sh), 2610 (vw), 2425 (w), 2395 (w), 2230 (w), 1765 (w), 1650 (sh), 1555 (m), 1380 (vs), 1330 (sh), 1310 (vs), 1130 (w), 1049 (vw), 1020 (m), 975 (sh), 865 (sh), 825 (s), 790 (m), 740 (m), 715 (sh), 600 (m), 570 (sh), 525 (m), 465 (w), 440 (sh), 305 (sh), 285 (m). Raman (solid): 1380 (0),[4b] 1045 (10), 715 (1), 610 (0), 600 (0), 572 (0), 540 (10), 516 (2), 457 (1), 440 (2), 257 (4), 205 (2), 200 (2), 72 (2).

The trimer tended to decompose readily in the laser beams, sometimes explosively. The sample was therefore rotated every 50–100 wavenumbers. The deuterated analogue was prepared by recrystallizing the compound twice from hot D_2O and obtained only in low yield because of the already mentioned dimer formation.

Apparatus. pH measurements were performed with a Corning pH meter, Model 7, and a combination electrode. Calibration was achieved with two buffers of different pH. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer from 4000 to 250 cm^{-1} as KBr pellets and from 4000 to 400 cm^{-1} as Nujol mulls. The spectra were calibrated against polystyrene. Raman spectra were obtained from powder samples at room temperature from 1700 to 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 the X-Ray Diffraction Data. An almost colorless crystal (very pale yellow), chosen after examination under a polarizing microscope for homogeneity, was ground to an approximate cylinder of dimensions 0.30-mm length × 0.10-mm diameter.

Precession photographs of zero and first layers suggested the crystal was triclinic. The crystal was transferred to a Syntex $P\bar{1}$ diffractometer and mounted along the long dimension (roughly [001]). Accurate parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 medium-angle ($20° < 2\theta < 35°$) reflections: a = 9.683 (3), b = 12.513 (6), c = 8.832 (3) Å; α = 120.90 (3), β = 98.67 (3), γ = 98.32 (3)° (λ 0.710 69 Å for Mo Kα at 21 °C). A Delaunay reduction showed no hidden symmetry. With Z = 2 (for a platinum trimer) ρ_{calcd} was 3.56 g cm^{-3} and the ρ_{obsd}, measured by displacement in petroleum ether, was 3.8 (2) g cm^{-3}. The linear absorption coefficient was 252 cm^{-1} and using the above crystal dimensions variation in transmission coefficient was 4.27 to 7.96.

Intensity data were recorded on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized radiation for the hemisphere defined by $h,\pm k,\pm l$[5] up to 2θ = 50°. Data were collected by using a coupled

Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
Pt(1)	0.2761 (1)	0.2397 (1)	0.5155 (1)		N(7)	0.373 (3)	0.329 (2)	0.161 (3)	0.064 (6)
Pt(2)	0.0893 (1)	0.3936 (1)	0.3791 (1)		O(4)	0.386 (3)	0.234 (3)	0.158 (4)	0.106 (8)
Pt(3)	−0.0652 (1)	0.0707 (1)	0.2243 (1)		O(5)	0.283 (3)	0.316 (2)	0.034 (3)	0.088 (7)
N(1)	0.407 (2)	0.367 (2)	0.769 (3)	0.051 (5)	O(6)	0.456 (2)	0.435 (2)	0.280 (3)	0.071 (5)
N(2)	0.411 (2)	0.123 (2)	0.449 (3)	0.045 (5)	N(8)	0.633 (2)	0.212 (2)	−0.065 (3)	0.048 (5)
N(3)	0.042 (2)	0.431 (2)	0.182 (3)	0.049 (5)	O(7)	0.681 (3)	0.133 (3)	−0.046 (3)	0.090 (7)
N(4)	0.258 (2)	0.552 (2)	0.533 (3)	0.039 (4)	O(8)	0.517 (2)	0.175 (2)	−0.182 (3)	0.068 (5)
N(5)	−0.286 (2)	0.026 (2)	0.185 (3)	0.049 (5)	O(9)	0.701 (3)	0.331 (3)	0.029 (4)	0.092 (7)
N(6)	−0.047 (4)	−0.088 (4)	0.214 (5)	0.110 (11)	N(9)	0.191 (2)	0.778 (2)	0.362 (3)	0.042 (4)
O(1)	0.140 (2)	0.360 (1)	0.577 (2)	0.040 (3)	O(10)	0.276 (2)	0.733 (2)	0.417 (3)	0.069 (5)
O(2)	0.150 (2)	0.111 (2)	0.261 (2)	0.047 (4)	O(11)	0.062 (2)	0.708 (2)	0.264 (3)	0.059 (5)
O(3)	−0.075 (2)	0.232 (2)	0.234 (3)	0.070 (5)	O(12)	0.226 (2)	0.892 (2)	0.409 (3)	0.050 (5)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.0247 (4)	0.0336 (5)	0.0333 (5)	0.0045 (3)	0.0016 (3)	0.0205 (4)
Pt(2)	0.0278 (4)	0.0273 (4)	0.0400 (5)	0.0076 (3)	0.0043 (3)	0.0187 (4)
Pt(3)	0.0374 (5)	0.0244 (4)	0.0316 (5)	0.0037 (3)	−0.0063 (4)	0.0114 (4)

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

θ(crystal)–2θ(counter) scan 1° on either side of the peak, scan rates ranging from 4 to 24° min^{-1} 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 reflection, 110,[5] was 1.56% and an analysis of the standard counts showed an overall esd of 2.5% with no systematic variation with time. The intensity of a reflection, I, and its esd, σ_I, were calculated as outlined previously.[6] A total of 3132 independent reflections were recorded, of which 2486 were considered observed ($I > 3\sigma_I$). Corrections were made for absorption assuming the crystal had the dimensions listed above. Unscaled structure factor amplitudes, F, and their standard deviations, σ_F, were calculated from the expressions $F = (I/Lp)^{1/2}$ and $\sigma_F = {}^1/_2(1/Lp)^{1/2}(\sigma_I{}^2/I)^{1/2}$. 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 three platinum atoms were found from a three-dimensional Patterson synthesis and three-dimensional electron density and difference maps revealed the nitrogen and oxygen atoms bonded to platinum. Least-squares refinement[16] of these atom positions followed by further three-dimensional electron density synthesis and difference calculations revealed all of the atoms of the three nitrate ions. At this stage, the temperature factors of the platinum atoms, which were isotropic in the initial stages of structure solution, were made anisotropic. Further refinements using a Cruickshank weighting scheme with weight equal to $(52.589 - 0.7681|F_o| + 0.004056F_o{}^2)^{-1}$ and full least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, were terminated at $R_1 = 0.0610$, $R_2 = 0.0623$.[7] In the last cycle of refinement no parameter shifted by more than 0.04 of its esd. Corrections were made for secondary extinction.

The final difference map showed little variation, most of the map lying between +0.5 and −0.9 e/Å^3, the latter occurring at 0.40, 0.62, 0.77 and lying between N(1) and O(9). Twenty-two peaks were observed with values lying between 0.63 and 1.42 e/Å^3. Examination of the peak position and calculation of internuclear distances showed that few if any of these peaks could be caused by hydrogen atoms. Many were clearly ripple peaks from the platinum atoms. In particular, the largest peaks (1.42 e/Å^3, 0.22, 0.27, 0.66; 1.27 e/Å^3, −0.09, 0.07, 0.33; 1.24 e/Å^3, −0.03, 0.08, 0.13; 1.23 e/Å^3, 0.32, 0.23, 0.40) all lie within 1.1 Å of a platinum atom.

Throughout the refinement, the scattering curves used were taken from ref 8, and anomalous dispersion corrections from ref 9 were applied to the curves for platinum. The atom parameters for the nonhydrogen atoms are listed in Table I.

Results and Discussion

The molecular cation is illustrated in Figure 1 and selected interatomic distances and angles are given in Table II. Figure 1a shows that the complex is a trimer of square-planar $(NH_3)_2Pt(OH)_2$ units, the platinum atoms being held together by bridging OH units. This structure was confirmed by trying alternate refinements placing nitrogen atoms in the bridging positions. The temperature factor for the bridging atoms became unacceptably low (0.022, 0.027, 0.047) and there was an increase in the R factor ($R_1 = 0.0616$, $R_2 = 0.0630$). The units Pt(2)N(3)N(4)O(1)O(3) and Pt(3)N(5)N(6)O(2)O(3) are planar within 1σ; Pt(1)N(1)N(2)O(1)O(2) is planar within 2σ. Examination of the planarity of the Pt(1)Pt(2)Pt(3)-O(1)O(2)O(3) unit shows that O(3) lies almost in the plane of the three platinum atoms (within 0.02 Å). This, coupled with Pt–O–Pt angles of nearly 120° and nearly ideal square-planar geometry at each platinum atom, means that the other two oxygen atoms cannot lie in the platinum atom

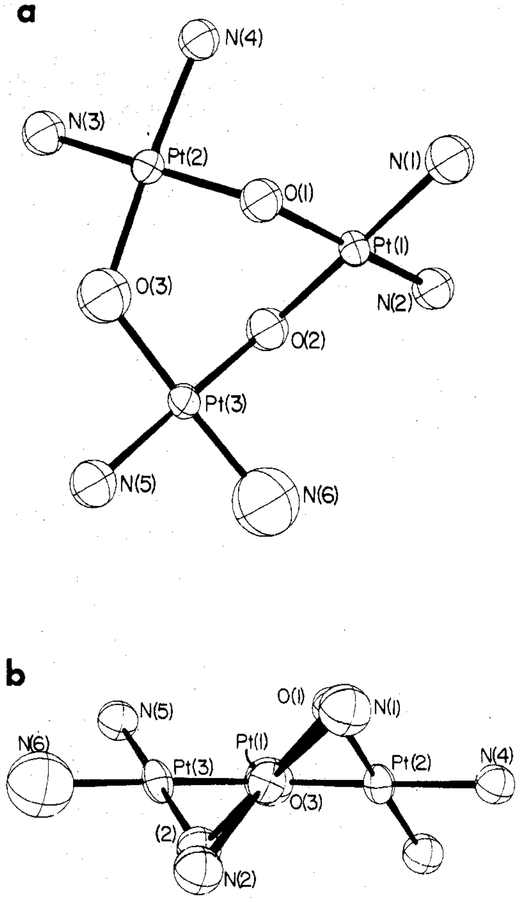

Figure 1. Molecular structure of the *cyclo*-tri-μ-hydroxo-tris[*cis*-diammineplatinum(II)] nitrate cation. The labeling of the atoms is as in Table I: (a) with the three platinum atoms coplanar with the page; (b) viewed along the pseudo-twofold axis.

Table II. Interatomic Distance (Å) and Angles (deg)

Bonded Distances			
Pt(1)–O(1)	2.07 (2)	Pt(1)–O(2)	2.01 (1)
Pt(2)–O(1)	2.00 (2)	Pt(2)–O(3)	2.01 (2)
Pt(3)–O(2)	2.01 (2)	Pt(3)–O(3)	1.99 (3)
Pt(1)–N(1)	2.02 (2)	Pt(1)–N(2)	2.02 (2)
Pt(2)–N(3)	2.03 (3)	Pt(2)–N(4)	2.02 (2)
Pt(3)–N(5)	2.06 (2)	Pt(3)–N(6)	1.97 (5)
N(7)–O(4)	1.20 (5)	N(7)–O(5)	1.24 (4)
N(7)–O(6)	1.23 (3)	N(8)–O(7)	1.23 (5)
N(8)–O(8)	1.24 (3)	N(8)–O(9)	1.27 (3)
N(9)–O(10)	1.24 (4)	N(9)–O(11)	1.28 (2)
N(9)–O(12)	1.24 (3)		
Nonbonded Distances			
Pt(1)–Pt(2)	3.341 (2)	Pt(1)–Pt(3)	3.440 (2)
Pt(2)–Pt(3)	3.521 (2)	Pt(3)–Pt(3)*	3.922 (2)
Pt(2)–Pt(2)*	3.355 (2)		
Angles			
Pt(1)–O(1)–Pt(2)	111 (1)	Pt(1)–O(2)–Pt(3)	118 (1)
Pt(2)–O(3)–Pt(3)	123 (1)	O(1)–Pt(1)–O(2)	93 (1)
O(1)–Pt(2)–O(3)	91 (1)	O(2)–Pt(3)–O(3)	92 (1)
N(1)–Pt(1)–N(2)	93 (1)	N(1)–Pt(1)–O(1)	88 (1)
N(1)–Pt(1)–O(2)	178 (1)	N(2)–Pt(1)–O(1)	178 (1)
N(2)–Pt(1)–O(3)	86 (1)	N(3)–Pt(2)–N(4)	93 (1)
N(3)–Pt(2)–O(1)	179 (1)	N(3)–Pt(2)–O(3)	90 (1)
N(4)–Pt(2)–O(1)	86 (1)	N(4)–Pt(2)–O(3)	177 (1)
N(5)–Pt(3)–O(6)	93 (1)	N(5)–Pt(3)–O(2)	179 (1)
N(5)–Pt(3)–O(3)	89 (1)	N(6)–Pt(3)–O(2)	86 (1)
N(6)–Pt(3)–O(3)	178 (1)	O(4)–N(7)–O(5)	118 (2)
O(4)–N(7)–N(6)	121 (3)	O(5)–N(7)–O(6)	121 (3)
O(7)–N(8)–O(8)	119 (2)	O(7)–N(8)–O(9)	121 (2)
O(8)–N(8)–O(9)	120 (3)	O(10)–N(9)–O(11)	120 (2)
O(11)–N(9)–O(12)	121 (2)	O(11)–N(9)–O(12)	120 (2)

plane; O(1) lies 1.16 Å on one side and O(2) 1.02 Å on the other side of this plane. The trimer thus has a pseudo-twofold axis through Pt(1) and O(3) as is shown clearly in Figure 1b, and the square plane about each platinum atom lies at a substantial angle to the three-platinum plane. For Pt(2) and Pt(3) the dihedral angles (35 and 30°) represent twists about the Pt(2)–O(3) and Pt(3)–O(3) bonds. For Pt(1) the dihedral angle (48°) results from a twist about the Pt(1)–O(3) direction. The Pt–N bond lengths (1.97 (5)–2.03 (3) Å) are normal and not significantly different[10] as are the Pt–O bond lengths (1.99 (3)–2.07 (2) Å)[10] and are comparable to results found by us for the dimeric $(Pt(NH_3)_2OH)_2^{2+}$ ion (Pt–N = 2.01 (1), 2.02 (1) Å; Pt–O = 2.03 (1) Å).[1] The nitrate ions are planar within the errors and bond lengths and angles are normal.[12]

As in the case of di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, the vibrational spectra of the title compound gave the first indications of its nonmonomeric nature as well as the presence of ionic nitrate. The absorption frequencies for the NO_3^- ion in the trimer were close to those observed for the nitrate in the dimer[1] at 1049 cm^{-1} (ν_1, Raman active, weakly IR active), 825 cm^{-1} (ν_2, IR active), 1380 cm^{-1} (ν_3, IR and Raman active), and 715 cm^{-1} (ν_4, IR and Raman active). ν_1, the N–O stretching vibration at 1049 cm^{-1}, though formally IR forbidden, appears weakly in the infrared spectra (KBr and Nujol) of both the trimer and its deuterated analogue. This phenomenon may be caused by a slight deformation of the nitrate ion in the field of the crystal[13] but was not confirmed by the crystal structure because it very likely is smaller than the standard deviations.

The vibrations of the ammine ligands in the cation can be identified by comparing the IR spectra of the trimer and the deuterated analogue (Table III). As expected, their positions do not differ strongly from the corresponding dimer vibrations. There is, however, another intense IR band at about 1075 cm^{-1} in the spectrum of the deuterated trimer species which also appeared in the spectrum of the deuterated dimer but was of an intensity too low to be explained. The appearance and position in the spectrum suggest that it is an ND vibration; its intensity in the trimer spectrum makes an interpretation as a combination band highly unlikely. Moreover, it cannot be the absorption of the degenerate deformation mode of an ND_3 group since the lowest $\delta_d(NH_3)$ at 1555 cm^{-1} would be shifted upon deuteration by a factor exceeding $2^{1/2}$ for a "free" NH_3 group (1555/1075 = 1.446). We therefore assign this band at 1075 cm^{-1} to the highest symmetrical deformation vibration of one (several) ND_3 group(s) though it is not possible to observe the corresponding mode(s) in the spectrum of the nondeuterated compound because of the strong nitrate absorption around 1380 cm^{-1}. The other bands at 1020 and 1010 cm^{-1} (deuterated form) and 1330 and 1310 cm^{-1} (nondeuterated form), respectively, represent the δ_s vibrations of the less hydrogen-bonded ammine groups. The splittings of the latter bands are similar to those observed in *cis*-$Pt(NH_3)_2X_2$ with X = Cl, Br, I and are also attributed to intramolecular interactions between ammine protons and filled d_{xy} orbitals of platinum(II).[14] The existence of an additional $\delta_s(ND_3)$ band at 1075 cm^{-1} implies that there are nonequivalent ND_3 (and consequently NH_3) groups in the cation which differ in their degree of intermolecular hydrogen bonding.

The results of the x-ray analysis indicate that there are indeed differences in the surroundings of the ammine ligands. Table IV shows that, excluding the cis nitrogen and oxygen atoms bonded to the platinum atom, N(1) and N(6) have only three nonbonded oxygen atoms closer than 3.5 Å, whereas N(2)–N(5) all have five or six such atoms.

The crystal structure also revealed that there were differences between the hydroxo bridges as well, as is shown in Table V. The distances between the protons of O(1) and O(3) and the nearest nitrate oxygen atoms were short enough to assume strong hydrogen bonding, whereas this is not so with the proton of O(2). The OH stretching region of the infrared spectrum had a sharp band at 3400 cm^{-1} which is clearly the non-hydrogen-bonded group whereas the OH stretching vibrations of the two hydrogen-bonded groups absorb below 3300 cm^{-1} as is the case of both hydroxo groups in the dimer.

The interpretation of the IR band at 1020 cm^{-1} (shifted upon deuteration to 760 cm^{-1}) as a Pt–OH bending vibration, which is reasonable since no ammine vibrations are expected in this range, even though metal–OH bending modes are known to appear in this range,[15] led to the conclusion that the compound under investigation was at least a dimer. An additional peak at 975 cm^{-1} in the Nujol spectrum which appeared only as a weak shoulder in the corresponding KBr

Table III. IR Frequencies (KBr) of the Ammine Vibrations of the Trimer (I) and Its Deuterated Analogue (II) (cm^{-1})

Assignment	I	II	Shift NH/ND
Antisym, sym str (ν_{as}, ν_s)	3300. . .3080 vs[a,b]	2420. . .2320 vs	1.365. . .1.33
Degen def (δ_d)	1660. . .1555 m	1225 s, 1145 s	1.355, 1.36
Sym def (δ_s)	1330 sh, 1310 vs	1075 s, 1020 sh, 1010 s	1.305, 1.295[c]
Rock (ρ_r)	865 sh, 790 m, 740 m	670 w, 590 sh[d]	1.290, 1.340

[a] Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] Dots between wavenumbers mean multiple, badly resolved maxima and/or shoulders. [c] The deuterium shift for the 1075-cm^{-1} band cannot be calculated because the strong nitrate band at 1380 cm^{-1} presumably superimposes another $\delta_d(NH_3)$ mode (cf. text). [d] Further bands cannot be identified unambiguously because of interference with Pt–N and Pt–O stretching absorption.

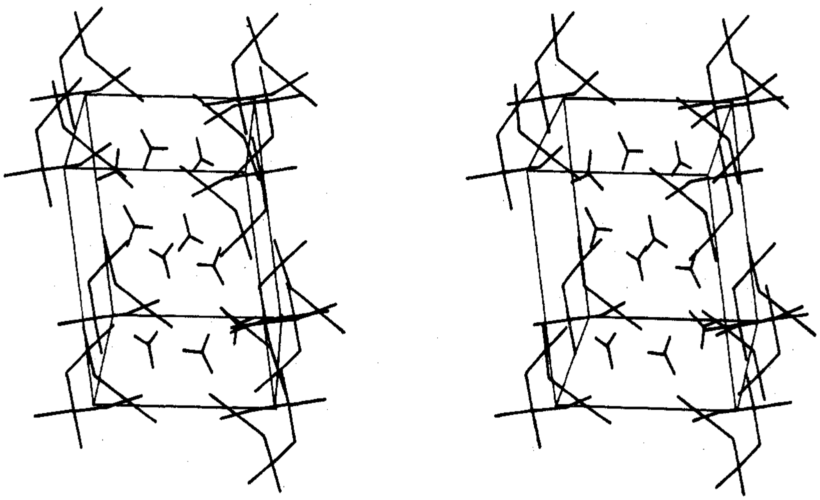

Figure 2. Stereogram (stereoscopic pair of perspective projections) of *cyclo*-tri-μ-hydroxo-tris[*cis*-diammineplatinum(II)] nitrate. The contents of one unit cell plus the partial contents of another seven cells are shown to illustrate the packing. *a* and *a* × *b* × *a* are parallel to the top and side of the page respectively, and the view is down *c**.

Table IV. Nonbonded Atoms within 3.5 Å of Each Ammine Group Nitrogen and the Pt-N-Atom Angles

N(1)			N(2)			N(3)			N(4)			N(5)			N(6)		
Atom^{a}	Dist, Å	Angle, deg	Atom^{a}	Dist, Å	Angle, deg	Atom^{a}	Dist, Å	Angle, deg	Atom^{a}	Dist, Å	Angle, deg	Atom^{a}	Dist, Å	Angle, deg	Atom^{a}	Dist, Å	Angle, deg
O(6)^{a}	2.91	100	O(8)^{b}	2.95	97	O(5)	3.02	89	O(10)	2.92	115	O(7)^{e}	2.96	90	O(5)^{h}	2.90	116
O(8)^{b}	2.96	96	O(12)^{c}	2.99	100	O(11)	3.14	124	O(6)^{a}	2.94	126	O(4)^{h}	2.96	103	O(12)^{c}	3.05	123
O(5)^{b}	3.07	108	O(10)^{a}	3.00	113	O(9)^{e}	3.16	105	O(6)	3.08	94	O(8)^{h}	3.10	137	O(11)^{c}	3.10	165
			O(7)^{d}	3.20	118	O(11)^{f}	3.28	143	O(9)^{a}	3.29	111	O(12)^{g}	3.11	87			
			O(8)^{c}	3.49	152	O(10)	3.43	97	O(3)^{g}	3.38	98	O(10)^{g}	3.23	94			
			O(4)	3.49	72												

^{a} Atoms have the parameters given in Table I except for the following transformations: a, $1-x, 1-y, 1-z$; *b*, $x, y, 1+z$; *c*, $x, y-1, z$; d, $1-x, -y, -z$; e, $x-1, y, z$; f, $-x, 1-y, -z$; g, $-x, 1-y, 1-z$; h, $-x, -y, -z$.

Table V. Intermolecular Distances to Atoms within 3.5 Å of the Bridging Hydroxide Groups and the Pt-N-Atom Angles

Atoms	Dist, Å	Atoms	Angle, deg
O(1)-O(11)	2.86 (1)	Pt(1)-O(1)-O(11)	109
		Pt(2)-O(1)-O(11)	125
O(2)-O(4)	3.07 (1)	Pt(1)-O(2)-O(4)	83
		Pt(3)-O(2)-O(4)	140
O(2)-O(7)	3.46 (1)	Pt(1)-O(2)-O(7)	108
		Pt(3)-O(2)-O(7)	121
O(3)-O(7)	2.73 (1)	Pt(2)-O(3)-O(7)	137
		Pt(3)-O(3)-O(7)	98
O(3)-O(9)	3.46 (1)	Pt(2)-O(3)-O(9)	99
		Pt(3)-O(3)-O(9)	138

spectrum was tentatively assigned to the bending mode of another Pt^{II}-OH group. In the light of the structural results, this assignment is reasonable because for the non- (or less) hydrogen-bonded OH groups (O(2)) a lower bending absorption (but higher stretching absorption!) would be expected than for the corresponding stronger hydrogen-bonded OH groups (O(1) and O(3)). The position of the 1020-cm^{-1} band, which is shifted 15 wavenumbers to lower energy than the corresponding band in the dimer, is apparently related to the larger Pt-O-Pt angle in the trimer rather than to a reduced strength in hydrogen bonding. This interpretation is supported by the fact that the distances between the oxygen atoms of the hydrogen-bonded hydroxo groups and the acceptor oxygens of the nitrate ions are essentially the same in both the dimer and the trimer.

We have not attempted to assign the skeletal vibrations, because, as in the case of the dimer nitrate, undoubtedly they are of mixed Pt-N and Pt-O character.

The packing of the ions within the unit cell is shown in Figure 2. The crude features of the structure are the arrangement of the trimer cations in a layer centered about the *bc* ($x = 0$) plane. These layers are separated by the nitrate ions. The trimer cation and the three nitrate ions are arranged so that the planes of each are very roughly parallel. The angles between the nitrate groups and the three-platinum-atom plane are as follows: N(7) nitrate, 18.7°; N(8) nitrate, 9.8°; N(9) nitrate, 4.5°. Another feature of the structure is the obvious importance of hydrogen bonding. This is suggested both by the nonbonded distances under 3.0 Å shown in Tables IV and V and also by Figure 2. It is remarkable how each nitrate group is oriented so that each oxygen atom is in a position to form a hydrogen bond to an ammonia or hydroxyl group.

There is some possibility of a platinum-platinum interaction between trimer ions. The two nearest Pt(2) atoms related by the inversion center at 0, $^{1}/_{2}$, $^{1}/_{2}$ are 3.355 (2) Å apart, which is only slightly longer than the Pt-Pt distance of 3.25 Å observed for Magnus' green salt. The only other intermolecular Pt-Pt distance under 4.0 Å is the Pt(3)-Pt(3) distance of 3.922 (2) Å (related through the inversion center at 0, 0, 0) which appears to be too long for any metal-metal interaction. In addition, from the diagram it appears that oxygen atoms from the trimer units and nitrate ions are arranged so that the platinum atoms become pseudo-five- and -six-coordinate. The shortest of these distances (Pt(1)-O(4)) is 3.45 (2) Å, however, and we do not consider this represents a bonding interaction but is the consequence of the normal packing requirements of the crystal.

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Registry No. $[Pt_3(NH_3)_6(OH)_3](NO_3)_3$, 61951-02-8; *cis*-diaquodiammineplatinum(II) dinitrate, 52241-26-6.

Supplementary Material Available: A table of the moduli of the observed and calculated structure amplitudes (13 pages). Ordering information is given on any current masthead page.

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

(3) The osmometer 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 chamber (38.5 or 65 °C) saturated with solvent vapors.

(4) (a) IR intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. (b) Raman intensities are relative to the strongest band at 540 cm^{-1} with arbitrary intensity 10.

(5) The indices refer to a cell with $a = 9.683$ (3), $b = 8.832$ (3), $c = 11.007$ (4) Å; $\alpha = 102.64$ (3), $\beta = 106.59$ (2), $\gamma = 81.30$ (2)°. This cell can be obtained from the cell used throughout the paper by the transformation matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 1 \end{bmatrix}$$

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Spectroscopic and Spectromagnetic Study of Trichloro(triphenylarsine)bis(*p*-tolyl isocyanide)osmium(III). Characterization of the Three Isomeric Forms

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The three isomeric forms of the compound $[OsCl_3(AsPh_3)(p\text{-}CH_3C_6H_4NC)_2]$ have been isolated and their probable structures deduced by comparative use of vibrational, electronic, and magnetic measurements. The ground-state configuration of osmium(III) ion in a low-symmetry field is proposed and the perturbing influence of the isocyanide ligand on the metal center is discussed. The differences in the electronic distribution of the isomeric species are also considered.

Compounds of general formula $[OsX_3L_3]$ (X = Cl, Br, I; L = PR_3, AsR_3, SbR_3; R = alkyl, aryl), with D_{2h}, C_{3v}, and C_{2v} symmetry, have been described.[1,2] Symmetries lower than C_{2v} are in general associated with the reduction of the osmium(III) ion, by reaction with carbon monoxide, nitrogen monoxide, alkyl or aryl isocyanide, etc.[3-5] We now report that the reaction of $[OsCl_3(AsPh_3)_3]$ with *p*-tolyl isocyanide gives the new compound $[OsCl_3(AsPh_3)(p\text{-}CH_3C_6H_4NC)_2]$, in three isomeric forms. The electronic d^5 configuration allows the investigation of the symmetry of the ligand field in these species, the bond strength between the osmium atom and ligand molecules, and the strength of the C–N bond, by electronic and magnetic measurements.

Experimental Section

Preparation. A suspension of $[OsCl_3(AsPh_3)_3]$[6] (700 mg, 0.576 mmol) and *p*-tolyl isocyanide (270 mg, 2.3 mmol) in benzene (50 mL) was refluxed until a red-orange solution was obtained (~5 h). Upon evaporation to ~30 mL and addition of methanol (~50 mL) a microcrystalline red-orange solid precipitated, which was a mixture of two structural isomers, I and II, with formula $[OsCl_3(AsPh_3)(p\text{-}CH_3C_6H_4NC)_2]$. After filtration, the solution was evaporated to ~20 mL and a yellow-orange precipitate was obtained, which consisted of isomer III of $[OsCl_3(AsPh_3)(p\text{-}CH_3C_6H_4NC)_2]$ and small quantities of $[OsCl_2(AsPh_3)_2(p\text{-}CH_3C_6H_4NC)_2]$. Analytical data are given in Table I.

The separation of isomers I and II was based on their differing solubilities in benzene. The solid mixture was treated with benzene (~4 mL) at room temperature; isomer II dissolved leaving as residue isomer I. Upon filtration isomer II precipitated from the benzene solution with the addition of methanol (~20 mL). The pure products were obtained by repeating the separation process.

Isomer III was separated from $[OsCl_2(AsPh_3)_2(p\text{-}CH_3C_6H_4NC)_2]$ by dissolving the solid mixture in benzene, at room temperature (~4 mL); on addition of methanol (~20 mL) isomer III precipitated; it was purified by repeating the separation process. Solubility in a solvent less polar than methanol (benzene) follows the order I << II < III. Yields: I, 15%; II, 60%; III, ca. 25%.

Upon treatment of a benzene solution of the osmium(III) isomers with triphenylarsine and reflux for ~2 h, $[OsCl_2(AsPh_3)_2(p\text{-}CH_3C_6H_4NC)_2]$ was obtained, which precipitated as a green solid upon the addition of methanol.

Isomer I is unstable with respect to III, even in the solid state at room temperature; isomer III gave II after short refluxing in benzene.

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer; Raman spectra, on a Coderg PHO krypton laser instrument; and diffuse reflectance electronic spectra, on a Beckman DK-2A spectrophotometer. ESR spectra were recorded on a Varian 4502-11 spectrometer, and the *g* values were calculated by standardization with diphenylpicrylhydrazyl. The magnetic susceptibility measurements were performed by the Gouy method. The molecular weight measurements were carried out with a Hewlett-Packard 302B vapor pressure osmometer.

Results

Vibrational Spectra. The following regions were analyzed: (a) 2300–2000 cm^{-1}, diagnostic for the N–C stretching vibrations;[7] (b) 600–400 cm^{-1}, diagnostic for the Os–C vibrations;[8] (c) 400–200 cm^{-1}, related to the Os–Cl stretching vibrations.[4]

The absorption frequencies of the three isomers are reported in Table II; their possible structures are indicated in Figure 1.