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cis-Dinitratodiammineplatinum(II), *cis*-$Pt(NH_3)_2(NO_3)_2$. Crystalline Structure and Vibrational Spectra

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The crystal structure of *cis*-dinitratodiammineplatinum(II), $(NH_3)_2Pt(NO_3)_2$, has been determined by x-ray diffraction. The orthorhombic crystal, space group *Pbca*, has cell dimensions $a = 9.760$ (4), $b = 10.087$ (7), and $c = 13.495$ (5) Å and has eight formula units in the unit cell. Intensities were measured using Mo Kα radiation and a Syntex $P\bar{1}$ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0538$ and $R_2 = 0.0493$. The molecule has roughly square-planar coordination about the platinum atom, with each nitrate ion coordinated through one oxygen atom (Pt–O, 1.99 (1), 2.03 (1) Å). The Pt–O–N (nitrate) angles are roughly 120° and the planes of the nitrate groups are roughly at right angles to the coordination plane and to each other. Infrared and Raman spectra are discussed.

Our recent work on hydroxo-bridged complexes of platinum has revealed that solutions of salts, made by the action of silver nitrate on aqueous solutions of *cis*-$Pt(NH_3)_2Cl_2$, are extremely complex.[2] Thus, we have shown that, in nitrate solutions at higher pH (4–7), the predominant species are di- and trimeric hydroxo-bridged complexes, rather than the supposed *cis*-diaquodiammineplatinum(II) dinitrate, *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$, and *cis*-hydroxoaquodiammineplatinum(II) nitrate, *cis*-$[Pt(NH_3)_2(H_2O)(OH)]NO_3$.[3] Interest in these solutions exists because *cis*-$Pt(NH_3)_2Cl_2$ has been shown to have a therapeutic effect against a series of human cancers.[4]. Early physiological tests on the supposed *cis*-$Pt(NH_3)_2(NO_3)_2$[5] analogue showed only an increased toxicity of the compound, with no improvement in the therapeutic index, and this was interpreted in terms of differences in the leaving ability of the chloride and nitrate groups,[5] but the tests were probably made on a solution containing a mixture of compounds. More recent work has shown that the dimeric and trimeric platinum compounds proved to be very toxic in our animal test systems and it is clear that before one can come to definite conclusions about the anti-cancer activity of any compound, it is essential to do tests only on carefully prepared, well-characterized materials, rather than the mixtures used previously. To this end we are continuing our work of characterizing the components of the mixtures and in this paper we present the preparation and characterization of *cis*-dinitratodiammineplatinum(II), *cis*-$Pt(NH_3)_2(NO_3)_2$, and x-ray structural and vibrational spectroscopic studies.

Experimental Section

Preparation of Compounds. *cis*-Dichlorodiammineplatinum(II) (3 g) (Engelhard Industries) was stirred with 3.38 g of silver nitrate in 25 mL of water in a stoppered flask at room temperature. The flask was wrapped in aluminum foil because the formed species is known to be somewhat photosensitive.[6] After 20 h the formed silver chloride was filtered and washed with 5 mL of water. The pale yellow solution (pH 2) was then kept in a stoppered flask in the refrigerator (5 °C) for 3 days. Colorless needles formed which were up to 3 mm long and 30 mg of the needles was filtered off. They were washed with 20 mL of water and dried on rotary pump vacuum. The elemental analysis of this compound gives an empirical formula of approximately $H_7N_3O_5Pt$. From its vibrational spectra it is concluded that this compound contains ionic nitrate, ammine groups, and hydroxo group(s), the last very likely bridging two platinum atoms. It is none of the hydroxo-bridged dimeric and trimeric platinum complexes we have reported recently[5] and we are currently examining this compound.

The filtrate was then concentrated (rotary evaporator, 30 °C water bath) to a volume of 10 mL and allowed to evaporate slowly at +5 °C to half of its volume (20 days). By then well-shaped rhombic crystals of *cis*-$Pt(NH_3)_2(NO_3)_2$ had formed which were very pale yellow and up to 0.5 mm long. Yield 2.2 g. The crystals were filtered, washed with 10 mL of water and ether, and dried on rotary pump vacuum.[7]

Elemental analysis (Galbraith Lab.) gave: H, 1.73; N, 15.66; O, 27.33; Pt, 55.09. Calculated for $H_6N_4O_6Pt$: H, 1.70; N, 15.86; O, 27.20; Pt, 55.24. Molecular weight (Galbraith Lab.) gave 108, determined osmometrically in water.[8] IR spectrum (Nujol; cm^{-1}):[9a] 3300 vs, 3280 vs, 3220 vs, 3140 sh, 2720 w, 2660 w, 2460 w, 2245 w, 1790 w, 1690 m, 1630 m, 1565 m, 1510 sh, 1485 vs, 1340 vs, 1295 vs, 1275 sh, 1260 vs, 997 vs, 988 vs, 870 m, 827 w, 818 w, 794 sh, 787 s, 773 w, 708 m, 610 vw, 558 w. Raman (solid; cm^{-1}):[9b] 1589 (1), 1574 (1), 1510 (0), 1488 (2), 1477 (2), 1335 (0), 1272 (4), 1259 (1), 994 (0), 988 (10), 820 (0), 795 (1), 785 (0), 778 (2), 708 (1), 562 (10), 558 (7), 449 (0), 440 (0), 332 (0), 315 (0), 305 (0), 284 (0). The deuterated analogue was prepared by reacting *cis*-$Pt(NH_3)_2Cl_2$ with 2 mol of $AgNO_3$ in D_2O solution (slightly warmed to achieve better exchange) and allowing the filtrate ($c = 0.5$ M) to stand at 0 °C in a stoppered flask for about 8 weeks. Crystals of the deuterated compound were used for the x-ray studies since we did not have good quality crystals from H_2O solution at the time of the x-ray structure determination.

Apparatus. Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer from 4000 to 250 cm^{-1} as KBr pellets and from 4000 to 400 cm^{-1} as Nujol mulls and calibrated against polystyrene; Raman spectra were obtained from polycrystalline and solution samples at room temperature in the range 1700–250 cm^{-1} on a Spex spectrometer 1401 with a Coherent Radiation Argon Laser Model 52 and calibrated against CCl_4. The solid sample was rotated every 100 cm^{-1} since it readily decomposed in the laser beam.

Collection of X-Ray Diffraction Data. A near colorless crystal of the title compound, chosen after examination on a polarizing microscope, was bounded by the faces {001}, 0.097 mm from the center of the crystal, and {111}, 0.120 mm from the center of the crystal.

Precession photographs of zero and first layers suggested the crystal was orthorhombic and the systematic absences $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h = 2n + 1$), revealed the unique space group *Pbca* (No. 61). The crystal was transferred to a Syntex $P\bar{1}$ diffractometer and mounted roughly along **b**. Accurate parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 medium-angle ($20° < 2\theta < 35°$) reflections: $a = 9.760$ (4), $b = 10.087$ (7), $c = 13.495$ (9) Å (λ 0.71069 Å for Mo Kα at 22 °C). With $Z = 8$, ρ_{calcd} was 3.53 g cm^{-3} and ρ_{obsd}, determined by displacement in light paraffin, was 3.7 (2) g cm^{-3}. The linear absorption coefficient was 220.7 cm^{-1} and using the above crystal dimensions variation in transmission coefficient was 16.11 to 41.47.

Intensities were measured using a Syntex $P\bar{1}$ diffractometer and graphite monochromatized Mo Kα radiation for the quadrant $h,k,\pm l$ up to $2\theta = 55°$. Data were collected using a coupled θ(crystal)–2θ(counter) scan 1° on either side of the peak, scan rates varying from 4 to 24° and being selected by the program supplied with the instrument. For this program a reflection is sampled for 2 s, and the point at which the count falls between the chosen minimum and maximum count limits determines the scan rate for that reflection. The high-intensity limit is set at 1500 counts/2 s and higher rates are collected at 24 deg min^{-1}; the low-intensity limit is set at 150.0 counts/2 s and lower rates are collected at 4 deg min^{-1}. Intermediate values cause collection at intermediate rates. Below 5000 counts/s no coincidence correction is made. Between 5000 and 50000 counts/s a coincidence correction is made. Above 50000 counts/s the coincidence correction is considered invalid and such reflections are rejected. The stability of the instrument was monitored by measuring a standard reflection after every 49 reflections. The counting esd of the standard peak was 1.5% and an analysis of the standard counts

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.141 74 (5)	0.114 58 (5)	0.088 19 (4)	0.0213 (3)	0.0287 (3)	0.0308 (3)	−0.0019 (3)	0.0001 (3)	−0.0026 (3)
N(1)	0.030 (1)	0.199 (1)	−0.019 (1)	0.040 (7)	0.035 (8)	0.032 (7)	−0.002 (6)	−0.001 (6)	0.003 (6)
N(2)	−0.004 (1)	0.141 (1)	0.189 (1)	0.033 (6)	0.051 (10)	0.021 (6)	−0.001 (6)	0.008 (5)	−0.008 (6)
O(1)	0.264 (1)	0.039 (1)	0.192 (1)	0.046 (7)	0.030 (6)	0.040 (7)	−0.008 (6)	−0.011 (6)	0.002 (5)
O(2)	0.152 (2)	−0.148 (1)	0.186 (1)	0.062 (9)	0.042 (7)	0.055 (8)	0.000 (7)	−0.021 (8)	0.008 (6)
O(3)	0.330 (2)	−0.128 (1)	0.280 (1)	0.070 (10)	0.065 (9)	0.043 (7)	0.014 (8)	−0.020 (7)	−0.009 (7)
N(3)	0.247 (2)	−0.084 (2)	0.218 (1)	0.034 (7)	0.054 (9)	0.035 (8)	0.007 (7)	−0.007 (6)	0.001 (7)
O(4)	0.303 (1)	0.112 (1)	−0.008 (1)	0.024 (5)	0.048 (7)	0.048 (7)	0.004 (6)	0.008 (5)	−0.011 (7)
O(5)	0.430 (1)	0.010 (2)	−0.106 (1)	0.030 (7)	0.109 (13)	0.054 (10)	0.019 (8)	0.014 (6)	−0.021 (9)
O(6)	0.256 (1)	−0.091 (1)	−0.054 (1)	0.048 (8)	0.029 (6)	0.064 (8)	−0.003 (6)	0.000 (7)	−0.008 (6)
N(4)	0.329 (2)	0.007 (2)	−0.057 (1)	0.043 (9)	0.046 (8)	0.035 (7)	0.009 (7)	−0.001 (6)	−0.005 (7)

^{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 $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and $\mathbf{b}_i$ are the reciprocal lattice vectors.

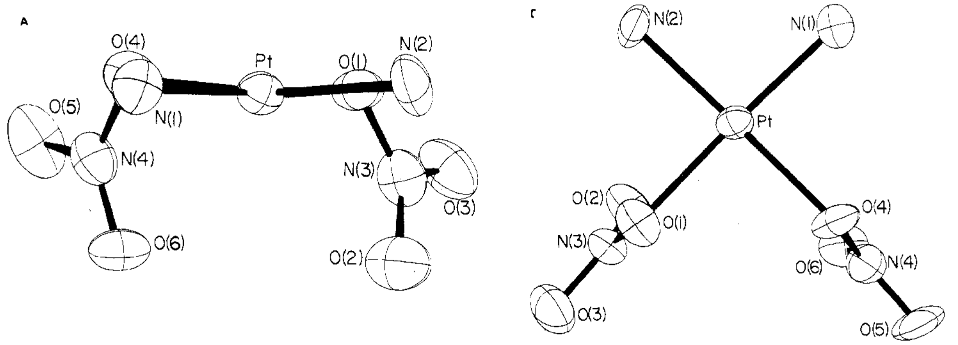

Figure 1. The structure of *cis*-Pt(NH$_3$)$_2$(NO$_3$)$_2$ viewed (A) along the vector Pt–(O(1)–O(4) bisector) and (B) along a vector perpendicular to the N(1)N(2)O(1)O(4) plane.

showed an overall esd of 1.9% with no systematic variation with time. The intensity of a reflection (I) and its esd, $\sigma(I)$, were calculated as outlined previously.[10] Independent reflections, 1399, were recorded of which 975 had $I > 3\sigma(I)$, 344 had $3\sigma(I) > I > \sigma(I)$, and 80 had $\sigma(I) > I$. These last were rejected. Corrections were made for absorption[11] assuming the crystal had the dimensions listed above. Unscaled structure amplitudes, F, and their standard deviations, $\sigma(F)$, were calculated from the expressions

$$F = (I/Lp)^{1/2}$$

$$\sigma(F) = \frac{1}{2}\frac{1}{(Lp)^{1/2}}\left(\frac{(\sigma(I))^2}{I}\right)^{1/2}$$

Lp, the Lorentz-polarization factor was $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$. During the course of the x-ray experiment the crystal gradually turned yellow. This color bleached out on prolonged standing after ceasing x-ray bombardment. We think the color change was a surface effect since no changes could be detected on precession films taken before and after the color change. In particular, there was no evidence of powder lines. In addition, as reported above, there was no significant change in the standard reflection during the period of data measurement. This last point probably precludes the formation of color centers thoughout the crystal. Very strong reflections are most likely to be affected and the intensity of the standard reflection was 75% of the strongest reflection.

Solution of the Structure. The platinum atom was found from a three-dimensional Patterson synthesis and three-dimensional difference maps revealed the oxygen and nitrogen atoms. Full-matrix least-squares refinement of these atom positions using anisotropic temperature factors and minimizing $\sum w(|F_o| - |F_c|)^2$ proceeded smoothly and was terminated at $R_1 = 0.0538$, $R_2 = 0.0493$.[12] A Cruickshank weighting scheme, with weights equal to $(83.411 - 1.1751|F_o| + 0.005F_o^2)^{-1}$, was used and in the final cycle of refinement no parameter shifted by more than 0.08 of its esd. Corrections were made for secondary extinction ($g = 2.588 \times 10^{-8}$) by the method of Larsen.[25] β_{max} was 18.50.

The final difference map showed little variation, the major features being six peaks from 1.6 to 2.0 e/Å^3. Two of these (0.07, 0.08, 0.10, 2.0 e/Å^3 and 0.10, 0.04, 0.08, 1.7 e/Å^3) were near the platinum atom, one (0.03, 0.14, −0.02, 1.7 e/Å^3) was near N(1), and another (0.02, 0.04, 0.15, 1.6 e/Å^3) was near N(2). Only two (0.45, −0.10, −0.07, 1.5 e/Å^3; 0.10, −0.10, −0.07, 1.6 e/Å^3) were near expected hydrogen atom positions. There were no significant valleys below −1.0 e/Å^3, except for a valley (0.14, 0.12, 0.10, 3.5 e/Å^3) very close to the platinum atom position.

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

	Bonded Distances		
Pt–N(1)	2.00 (1)	Pt–N(2)	1.99 (1)
Pt–O(1)	1.99 (1)	Pt–O(4)	2.03 (1)
O(1)–N(3)	1.30 (2)	O(4)–N(4)	1.28 (2)
O(2)–N(3)	1.22 (2)	O(5)–N(4)	1.19 (2)
O(3)–N(3)	1.24 (2)	O(6)–N(4)	1.22 (2)
	Possible Hydrogen Bond Distances		
N(1)–O(2)^5	2.91 (2)	N(2)–O(1)^3	2.96 (2)
N(1)–O(4)^4	2.95 (2)	N(2)–O(2)^6	3.08 (2)
N(1)–O(6)^8	3.01 (2)	N(2)–O(6)^5	3.11 (2)
N(1)–O(3)^7	3.12 (2)	N(2)–O(3)^8	3.13 (2)
N(1)–O(6)^5	3.16 (2)	N(2)–O(3)^3	3.19 (2)
N(1)–O(5)^8	3.37 (2)	N(2)–O(5)^7	3.23 (2)
	Angles		
N(1)–Pt–N(2)	93.0 (6)	O(1)–Pt–O(4)	88.8 (5)
N(1)–Pt–O(1)	175.8 (5)	N(2)–Pt–O(4)	171.8 (6)
N(1)–Pt–O(4)	88.0 (5)	N(2)–Pt–O(1)	89.9 (5)
Pt–O(1)–N(3)	119 (1)	Pt–O(4)–N(4)	120 (1)
O(1)–N(3)–O(2)	120 (1)	O(4)–N(4)–O(5)	116 (2)
O(1)–N(3)–O(3)	117 (1)	O(4)–N(4)–O(6)	123 (2)
O(2)–N(3)–O(3)	123 (2)	O(5)–N(4)–O(6)	121 (2)

Throughout the refinement the scattering curves used were taken from the International Tables,[13] and anomalous dispersion corrections from the International Tables[14] were applied to the curves for platinum. The atom parameters for the non-hydrogen atoms are listed in Table I.

Results and Discussion

The molecule is illustrated in Figure 1 and selected interatomic distances and angles are presented in Table II. The ammonia nitrogen atoms and an oxygen atom from each nitrate group form a rough square-planar arrangement about the platinum atom. There is some distortion of the plane seen clearly in Figure 1A; the platinum atom lies 0.1 Å out of the best plane through the four ligand atoms. In addition the

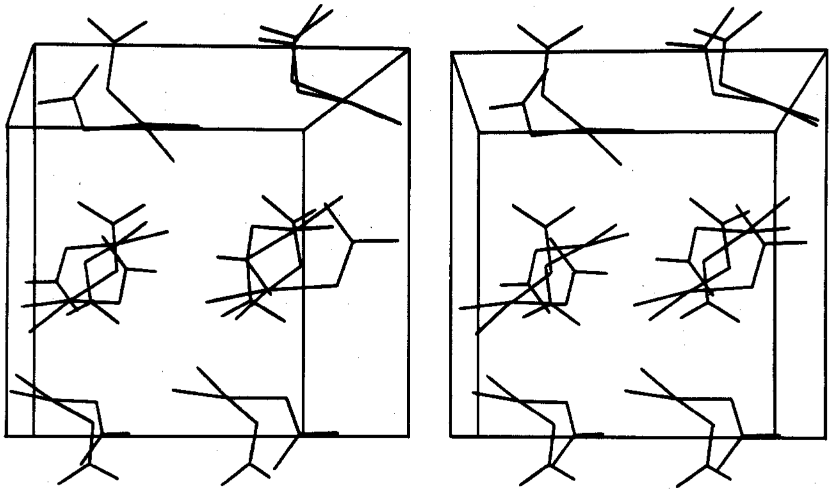

Figure 2. Stereogram (stereoscopic pair of perspective projections) of *cis*-$Pt(NH_3)_2(NO_3)_2$. The contents of one unit cell are shown. **a** and **b** are parallel to the top and side of the page respectively and the view is down **c**.

molecule is twisted such that the dihedral angle between N(1)PtN(2) and O(1)PtO(4) is 8.6°. The nitrate groups are oriented such that the dihedral angles between the nitrate planes and the ligand planes are 73.3° (N(3) nitrate) and 87.2° (N(4) nitrate) and the dihedral angle between the two nitrate planes is 80.6°. In other words, the nitrate groups are nearly perpendicular to the ligand plane and each other, as shown in Figure 1B. The PtO(1)N(3) and PtO(4)N(4) angles are 119 (1) and 120 (1)°, respectively, and the nitrate groups lie on the same side of the ligand plane. Thus, O(2) lies below O(1) and O(6) below O(4) (Figure 1B) and there is no evidence of any bonding interaction of O(2) and O(6) with the platinum atom; thus the nitrate group is monodentate. The Pt–N distances (2.00 (1), 1.99 (1) Å) do not differ significantly from values we have found previously.[2] The Pt–O distances (1.99 (1), 2.03 (1) Å) do not differ significantly, and the distances imply reasonably strong Pt–O bonds. The lengths are comparable to those found by us[2] for stable bridging hydroxo compounds of platinum and to the Pt–N distances. The lengths are shorter than that for the Pt–O distances in $\{(t\text{-Bu})_2(o\text{-tolyl})P\}\cdot\overline{Pt-C_6H_4-P}(t\text{-Bu})_2NO)_3$ (2.14 Å) and $Pt\{(CH_3)_2SO\}_2(NO_3)_2$ (2.07 Å).[15] Coordination appears to cause some distortion of the nitrate group. The N–O(coordinated) bond distances (N(3)–O(1), 1.30 (2) Å; N(4)–O(4), 1.28 (2) Å) appear to be larger than the other N–O distances (range 1.19 (2)–1.24 (2) Å) and the equivalent angles O(4)N(4)O(5) (117 (1)°) and O(1)N(3)O(3) (116 (1)°) appear to be less than the other ONO angles (range 120 (1)–123 (1)°). The errors preclude definite conclusions, but the fact that the distortions are similar for the two nitrate groups and are similar to those observed previously[26] lends credence to the postulate.

Hydrogen bonding between the ammonia and nitrate groups is probable. As shown in Table II, each nitrogen atom is within 3.4 Å of six nitrate oxygen atoms, and some of the distances are sufficiently short that strong hydrogen bonding is implied. Conversely, the oxygen atoms show differences. The coordinated oxygen atoms, O(1) and O(4), are less than 3.4 Å from only one ammonia nitrogen atom whereas the other oxygen atoms are each within 3.4 Å of two or three ammonia nitrogen atoms.

The packing within the unit cell is shown in Figure 2. Clearly hydrogen bonding is very important in determining the packing. The plane of the four atoms coordinated to platinum is very roughly parallel to the **ac** plane with the bisector of N(1)PtN(2) (or O(1)PtO(4)) very roughly parallel to **a**. The ligand plane is twisted relative to the **ac** plane such that the ammonia groups on one molecule are brought close to nitrate oxygen atoms in molecules related by the *a* glide and by the *a* glide followed by the *b* glide. In the **c** direction the prime contact is between the nitrate groups, those on one molecule lying parallel to nitrate groups on molecules above and below. In the **a** direction the prime contacts are between ammonia groups on one molecule and nitrate groups on the next. In the **b** direction packing is again governed by ammonia–nitrate contacts. The nitrate groups are arranged, however, so that one nitrate oxygen atom (O(2)) lies over the fifth, axial position on platinum, opposite to the direction in which the coordinated nitrate groups are pointing. There is no indication of any bonding, however. All contact distances mentioned above are equal to or greater than the van der Waals contact distances.

IR and Raman spectra had suggested that the two nitrate groups, whose presence was indicated by the results of the elemental analysis, were monodentate. The results of the x-ray structure determination verified this and furthermore revealed that the local symmetry of the nitrate ligands was pseudo-C_s. Any reduction of the D_{3h} symmetry of the free nitrate ion removes the degeneracy of the E′ modes of ionic nitrate and also activates the A_2'' mode, thus leading to six fundamental vibrations which are both IR and Raman active.

Though the establishment of monodentate bonding of the nitrate in the solid state does not necessarily mean that the structure is retained in solution, polarization measurements in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solutions indicate that the nitrate in *cis*-dinitratodiammineplatinum(II) that is still coordinated remains monodentate (vide infra). The insignificant frequency shifts between the corresponding nitrate absorptions in the solid state and in solution agree with this. Any change in coordination should have manifested itself in particular in the positions of the two highest frequency absorptions of the nitrate groups and their relative separation.[16]

Bidentate coordination, for example, should have led to a larger separation of the two highest frequency bands than monodentate coordination. The pattern of relative intensities of the three highest frequency Raman bands, which is different for mono- and bidentate coordination, and which is also regarded as highly indicative for the mode of coordination of nitrate,[16] is also in agreement with monodentate coordination. With NO_3 coordinating as a bidentate ligand, the second highest Raman band should be weak whereas in the case of *cis*-$Pt(NH_3)_2(NO_3)_2$ this band is clearly of high intensity. In Table III the six fundamental vibrations of the nitrate ligands

Table III. Observed Absorption Frequencies (in cm^{-1}) of Nitrate in *cis*-$Pt(NH_3)_2(NO_3)_2$ in the Solid State and in DMSO Solution (3 M)

			Approximate description of vibration	
IR(Nujol)[a]	Raman-(polycrystalline)[b]	Raman(DMSO)[c,d]	Bound NO_3 (C_s)	Free NO_3 (D_{3h})
1510 sh	1510 (0)	1495 (1)	NO_2 asym stretching	
1485 vs	1488 (2)			
	1477 (2)			
1275 sh	1272 (4)	1284 (2) p	NO_2 sym stretching	
1260 vs	1259 (1)	1277 (3) p		
		1041 (9) p		NO stretching
997 vs	994 (10)	983 (10) p	NO stretching[e]	
988 vs	988 (10)			
827 w	820 (0)	833 (0)	NO_3 nonplanar rocking	
818 w				
794 sh	795 (1)	772 (1) p	NO_2 bending	
787 s	785 (0)			
773 w	778 (2)			
		722 (0) dp		NO_3 planar rocking
708 m	708 (1)	707 (1) dp	NO_2 planar rocking	

[a] IR intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [b] Raman intensities relative to strongest bands at 994 and 988 cm^{-1} with arbitrary intensities 10. [c] Raman intensities relative to strongest band at 983 cm^{-1} with arbitrary intensity 10. [d] Polarization (p = polarized, dp = depolarized) only listed if determined unambiguously, that is, if band is not obscured by absorptions of the solvent and of sufficient intensity. [e] O coordinated to platinum.

in the solid state and in DMSO solution are listed and assigned. The assignment is based on the criteria mentioned above as well as on the polarization measurements performed on solution spectra. The description of the vibrations used is somewhat simplified but justified by the fact that mixing between internal vibrations of a nitrate group in the case of monodentate coordination, in contrast to bidentate coordination, is not too extensive. Splitting is observed for most of the bands of the solid state spectra and is probably a consequence of coupling between the vibrations of the two nitrate groups in cis positions. Similar splittings have also been reported for compounds such as $Pd(dipy)(NO_3)_2$ and *cis*-$[Pt(NH_3)_2(NO_3)_4]$.[17] In addition to the IR absorptions observed in the Nujol spectrum, the KBr spectrum also exhibits the infrared active absorptions of ionic nitrate. This indicates partial replacement of bound nitrate ligands under the conditions of the pellet preparation. Since these bands are not observed in the Nujol spectrum and also the strongest Raman active absorption of D_{3h} nitrate, $\nu_1(A_1')$ around 1050 cm^{-1}, is absent in the Raman spectrum of the polycrystalline sample, the presence of an impurity containing ionic nitrate can be ruled out.

In the Raman spectrum of a diluted or moderately concentrated aqueous solution (0.3 M) only bands caused by free nitrate appear, thus showing that the complex is completely aquated. This is in agreement with earlier results of conductivity and p*K* measurements.[3b,18] In concentrated aqueous solutions (3 M, 70 °C), however, aquation is not complete and Raman bands of two sets of NO_3 absorptions (point groups D_{3h} and C_s) are observed, but the bands due to ionic nitrate clearly predominate. This is not unexpected and is also reported for concentrated aqueous solutions of various other metal nitrates.[19]

In equally concentrated solutions (3 M) of the platinum complex in dimethyl sulfoxide and dimethylformamide the replacement of coordinated nitrate by solvent molecules is considerably reduced. This manifests itself by the presence of very strong absorptions caused by monodentate as well as ionic nitrate. This, together with the almost complete removal of the splitting of the nitrate bands in the solution spectra, makes us believe that in DMSO and DMF solutions the predominant species is *cis*-$[Pt(NH_3)_2(NO_3)solvent]^+(NO_3)^-$. If it is assumed that the splitting of the nitrate bands is caused by coupling phenomena between the two nitrate groups, then the individual components should be of different polarization and it should show up in the Raman spectra as it does with $Ti(NO_3)_4$ and $Sn(NO_3)_4$.[20] This is, however, not the case for the solution spectra of *cis*-dinitratodiammineplatinum(II). The second and third highest vibrations of coordinated nitrate, for example, which are intense enough and sufficiently separate from solvent absorptions to allow unambiguous polarization measurements, are totally polarized in solution and there are no indications of nonpolarized components in the Raman spectra. As indicated in Table III, the polarization could not be determined for all nitrate bands, but it is quite clear from the degree of polarization of the second and third highest bands that the nitrate does not act as bidentate ligand, because then the second highest frequency band should be depolarized.[16]

The ν_4 mode of free nitrate can be identified readily at 722 cm^{-1}, since it is absent in the solid state Raman spectrum and is, as expected for a E′ type vibration, depolarized. The weak band observed at 820 cm^{-1} (solid) and 833 cm^{-1} (DMSO) is assigned to the out-of-plane rocking vibration. It is, as expected, only of low intensity.[21] The positions of the two remaining NO_2 deformation vibrations are close to those found for the $[Au(NO_3)_4]^-$ anion and are assigned similarly.[22]

If, as a first approximation, the four ligands of Pt(II) in *solid* *cis*-dinitratodiammineplatinum(II) are treated as monatomic ligands, which is reasonable as far as the metal–ligand vibrations are concerned, then group theory predicts nine fundamental frequencies for the N_2PtO_2 skeleton (point group C_{2v}). We shall consider only the four stretching vibrations here since we did not study the IR range below 250 cm^{-1} where the skeletal deformations and, in the solid state, the lattice modes absorb. Two Pt–N as well as two Pt–O stretching vibrations ($A_1 + B_1$) are expected, all of which are both infrared and Raman active. The x-ray results make it very likely that these vibrations are coupled and therefore we do not assign individual Pt–O and Pt–N vibrations. Absorptions are observed at 562 and 558 cm^{-1}, which are strong in the Raman spectrum but only weak and nonresolved in the IR spectrum, as well as at 330 cm^{-1} (strong in IR(KBr), weak in Raman spectrum). Since this band is broad it might actually contain two skeletal stretching vibrations. An alternative explanation would be that one of the bands at lower wavenumbers (305 or 284 cm^{-1}) is caused by the fourth skeletal stretching vibration. The absorptions of the NH vibrations of the individual ammine groups (ν(NH) 3300 vs, 3280 vs, 3320 vs, ..., 3140 sh; δ_d 1630 m, 1565 m; δ_s 1340 vs, 1295 vs; ρ 870 m, 800 w) are very similar to those found for *cis*-$Pt(NH_3)_2X_2$ with X = Cl, Br, I.[23] Exceptions are two bands at 1340 and 870 cm^{-1}. We assign them as symmetric deformation and rocking vibrations, respectively, but their frequencies are somewhat high and do not follow the pattern usually found for neutral ammine complexes but rater that for positively charged platinum ammine complexes.[24] Whether this is a consequence of somewhat polar Pt–O bonds or of differences in hydrogen bonding is not quite clear, but the deuterium shift of the 1340-cm^{-1} band (1.22) favors the latter possibility. Differences in intramolecular hydrogen bonding between the ammine protons and filled, nonbonding d_{xy} orbitals of platinum have been postulated to be the reason for the splitting of the degenerate and the symmetric deformation vibrations in *cis*-$Pt(NH_3)_2X_2$ with X = Cl, Br, I.[23] To assume this kind of proton–electron interaction also in *cis*-$Pt(NH_3)_2(NO_3)_2$ might be reasonable, but from the IR spectrum it is not clear if the 1295-cm^{-1} band is a single band (and the 1340-cm^{-1} band consequently the second one expected for such an interaction) or actually a complex band which is not resolved. Differences in intermolecular hydrogen bonding, that is between ammine protons and nitrate oxygens, might, however, also account for multiple bands. The N(ammine)–O(nitrate) distances are close enough to allow strong hydrogen bonding and there are indeed differences within these distances (Table II) that suggest the additional NH bands are caused by the more strongly bound ammine protons. It is not possible to decide between the two possibilities.

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Registry No. *cis*-$Pt(NH_3)_2(NO_3)_2$, 41575-87-5; *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1.

Supplementary Material Available: A table of moduli of the observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

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