

Table 4. Hydrogen-bond distances and angles with estimated standard deviations in parentheses

$D-H\cdots A$	Position of acceptor atom	Distance (Å)		Angle (°)
		$D\cdots A$	$H\cdots A$	$D-H\cdots A$
O(3)-H(1) $\cdots$ N(6)	$x, y, z$	2.897 (8)	2.09 (5)	147 (6)
O(3)-H(2) $\cdots$ N(5)	$x, y, z - 1$	2.96 (1)	2.07 (8)	158 (6)
N(5)-H(4) $\cdots$ O(2)	$1 - x, y, 1 - z$	3.221 (8)	2.27 (5)	164 (5)
N(6)-H(5) $\cdots$ O(1)	$1 - x, 1 - y, 1 - z$	3.16 (1)	2.28 (7)	168 (5)
N(6)-H(6) $\cdots$ O(2)	$x, y, z$	3.045 (7)	2.06 (6)	164 (7)

In  $\text{Cu}(\text{NCO})_2(3\text{-ampy})_2(\text{H}_2\text{O})$  the NCO groups were found as functionally non-equivalent ligands. The monodentate groups which are bound to the  $\text{Cu}^{\text{II}}$  atoms through the N atom maintain linearity, and the bidentate groups, being bound to the  $\text{Cu}^{\text{II}}$  atoms by means of a bridge through the N and O atoms, show a slight deviation from linearity.

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## The Structures of Chloro(diethylenetriamine)platinum(II) Chloride and (Diethylenetriamine)nitratoplatinum(II) Nitrate and Some Comments on the Existence of $\text{Pt}^{\text{II}}-\text{OH}_2$ and $\text{Pt}^{\text{II}}-\text{OH}$ Bonds in the Solid State

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### Abstract

$[\text{Pt}\{\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2\}\text{Cl}]\text{Cl}$ ,  $\text{C}_4\text{H}_{13}\text{ClN}_3\text{Pt}^+\text{Cl}^-$ , (I) is orthorhombic,  $Pca2_1$ , with  $Z = 4$ ,  $a = 13.954$  (3),  $b = 4.828$  (1),  $c = 13.272$  (4) Å.  $[\text{Pt}\{\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2\}\text{ONO}_2]\text{NO}_3$ ,  $\text{C}_4\text{H}_{13}\text{N}_4\text{O}_3\text{Pt}^+\text{NO}_3^-$ , (II) is orthorhombic,  $Pbca$ , with  $Z = 8$ ,  $a = 12.777$  (4),  $b = 9.749$  (3),  $c = 17.145$  (4) Å. (I) is isostructural with  $[\text{Pt}\{\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2\}\text{Br}]\text{Br}$  and its structure was solved using the Pt position from the bromide and difference methods. The structure of (II) was solved by heavy-atom methods. Both were refined by full-matrix least squares to  $R = 0.031$ ,  $R_w = 0.039$  (I);  $R = 0.065$ ,  $R_w = 0.050$  (II), based on 1561 and 2314 reflections respectively. The basic cation units are similar for (I)

and (II). Bond lengths [ $\text{Pt}-\text{N}$ , range 1.984 (8)–2.063 (10),  $\text{Pt}-\text{Cl}$  2.312 (3),  $\text{Pt}-\text{O}$  2.030 (8) Å] are normal. Hydrogen bonds to the chloride ion are important in determining the packing of (I) and hydrogen bonds to the uncoordinated nitrate ion and to the coordinated O atom of the bound nitrate ion determine the packing of (II). An explanation is given as to why (II) was obtained rather than the  $[\text{Pt}\{\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2\}\text{OH}_2]^{2+}$  cation on crystallization and conditions necessary for the isolation of the latter cation as a salt are suggested.

### Introduction

For some time we have been attempting to isolate  $\text{Pt}^{\text{II}}$  amine complexes containing coordinated aqua

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or hydroxo groups. Attempts to crystallize  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2\text{OH}]^+$  or  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$  from aqueous solutions, postulated to contain these ions, have been unsuccessful and at intermediate pH ( $\sim 7$ ) we have obtained compounds containing the *cis*-hydroxo-bridged dimeric and trimeric cations  $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2]^{2+}$  and  $[(\text{NH}_3)_2\text{Pt}(\text{OH})_3]^{3+}$  (Faggiani, Lippert, Lock & Rosenberg, 1977*a,b*, 1978; Lippert, Lock, Rosenberg & Zvagulis, 1978). Crystallization at low pH (nitric acid), in an attempt to protonate the hydroxo bridge, thus breaking it, yielded *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{ONO}_2)_2]$  instead of the expected aqua complex (Lippert, Lock, Rosenberg & Zvagulis, 1977). In order to suppress the formation of *cis*-bridging hydroxo groups we have been attempting to block three of the coordination positions using diethylenetriamine (dien) as a ligand, with the hope of obtaining  $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$  or  $[\text{Pt}(\text{dien})(\text{OH})]^+$ . As we shall show, we have been unsuccessful so far, isolating the  $[\text{Pt}(\text{dien})(\text{ONO}_2)]^+$  cation instead. Because of previous problems in isolating  $[\text{Pt}(\text{dien})X]^+$  complexes (Britten & Lock, 1979, 1980) we have characterized all our complexes crystallographically, including the starting product  $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ . It is isostructural with  $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$  (Melanson, Hubert & Rochon, 1975) and we report it here briefly. In addition, using Brown's bond-valence model (Brown, 1981; Brown & Shannon, 1973), we are able to rationalize the results obtained above and predict the conditions necessary for isolating  $\text{Pt}^{\text{II}}\text{-OH}$  and  $\text{Pt}^{\text{II}}\text{-OH}_2$  complexes.

## Experiments

$[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$  (I) was prepared by the method of Watt & Cude (1968). The product (yield 23%) was recrystallized from water at 295 K. Found: C, 12.7; H, 3.7; N, 12.8%. Calculated for  $\text{C}_4\text{H}_{13}\text{Cl}_2\text{N}_3\text{Pt}$ : C, 13.0; H, 3.6; N, 11.4%.  $[\text{Pt}(\text{dien})(\text{ONO}_2)]\text{NO}_3$  (II) was prepared from  $[\text{Pt}(\text{dien})\text{I}]\text{I}$  (Watt & Cude, 1968).  $[\text{Pt}(\text{dien})\text{I}]\text{I}$  (1.97 g) was slurried with water (10 ml) and reacted with  $\text{AgNO}_3$  (1.21 g) in water (10 ml). The mixture was stirred for 16 h in the dark. The precipitate of  $\text{AgI}$  was removed by filtration and the filtrate allowed to evaporate to dryness giving colourless multiple crystals. The product (yield <50%) was recrystallized from water in the dark at 295 K. Found: C, 11.0; H, 3.3; N, 15.8%. Calculated for  $\text{C}_4\text{H}_{13}\text{N}_3\text{O}_6\text{Pt}$ : C, 10.9; H, 3.4; N, 15.9%.

Raman spectra were excited by a Spectraphysics 164 argon ion laser by 300 mW of 5145 Å radiation and recorded on a Spex Double Monochromator Model 14018 at 295K. The solution of  $[\text{Pt}(\text{dien})(\text{ONO}_2)]\text{NO}_3$  was prepared in the minimum amount of water. The spectra are shown in Fig. 4.

### Collection of the X-ray data

Crystals of the two compounds were selected after examination under a polarizing microscope for homogeneity. Precession photographs showed that the pale-yellow crystals of  $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$  (I) were iso-morphous with  $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$  (Melanson, Hubert &

Table 1. Additional crystal data and refinement details

	(I)	(II)
$M_r$	369.16	422.27
Systematic absences	$0kl, l = 2n + 1$ ; $h0l, h = 2n + 1$	$hk0, h = 2n + 1$ ; $h0l, l = 2n + 1$ ; $0kl, k = 2n + 1$
Space group	$Pca2_1$	$Pbca$
Volume ( $\text{\AA}^3$ )	894.2 (4)	2135.6 (1)
$Z$	4	8
$D_c$ ( $\text{g cm}^{-3}$ )	2.74	2.63
$D_o$ ( $\text{g cm}^{-3}$ )	2.74 (2)	2.63 (2)
$\mu$ ( $\text{cm}^{-1}$ )	157.5	138.6
Absorption coefficient limits, $A^*$	6.681–5.957	6.266–5.527
Max. $2\theta$ , reflections collected	$50^\circ, h, k, \pm l$	$55^\circ, h, k, \pm l$
Temperature	295 K	295 K
Number of independent reflections	1593	2481
Number with $I > 0$	1561	2314
Final $R_1, R_2^\dagger$	0.031, 0.039	0.065, 0.050
$x$ (secondary extinction)	0.00086	0.00019
Final difference map		
Max., location	$2.30 \text{ e \AA}^{-3}; 0.12, 0.20, 0.25$	$2.00 \text{ e \AA}^{-3}; 0.05, 0.46, 0.13$
Min., location	$-2.29 \text{ e \AA}^{-3}; 0.18, 0.21, 0.32$	$-1.87 \text{ e \AA}^{-3}; 0.42, 0.04, 0.14$
Weighting scheme	$w = (\sigma^2 + 0.0007F_o^2)^{-1}$	$w = (\sigma^2 + 0.0007F_o^2)^{-1}$
Error in an observation of unit weight	1.058	1.062

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

Rochon, 1975) and that the colourless crystals of [Pt(dien)ONO<sub>2</sub>]NO<sub>3</sub> (II) were also orthorhombic. Unit-cell parameters for each crystal were obtained from a least-squares fit of  $\chi$ ,  $\phi$ ,  $2\theta$  for 15 well centred reflections in the range  $19^\circ < 2\theta < 36^\circ$  recorded on a  $P2_1$  diffractometer using graphite-monochromated Mo  $K\alpha_1$  radiation ( $\lambda = 0.70926 \text{ \AA}$ ). Additional crystal data and data-collection information are summarized in Table 1. The densities were determined by flotation in benzene–bromoforn (I) and diiodomethane–carbon tetrachloride (II) mixtures. Intensities were measured on the Syntex  $P2_1$  diffractometer using a coupled  $\theta$ (crystal)– $2\theta$ (counter) scan. The methods of selection of scan rates and initial data treatment have been described (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert *et al.*, 1977). Corrections were made for Lorentz–polarization effects and absorption.

### Solution of the structures

The coordinates of the Pt atoms for [Pt(dien)Br]Br (Melanson *et al.*, 1975) were used as starting coordinates and after refinement the remaining non-hydrogen atoms were located from a difference map. It was not possible to use all the parameters from [Pt(dien)Br]Br directly, for the chosen cell; the positional coordinates are related to those of the bromide by  $x, y, z = x', y', \frac{1}{2} - z'$ . Refinement proceeded smoothly. For [Pt(dien)ONO<sub>2</sub>]NO<sub>3</sub> the coordinates of the Pt atom were found from a three-dimensional Patterson synthesis, and a series of least-squares refinements, followed by three-dimensional electron density difference synthesis, revealed all the non-hydrogen atoms. At this stage temperature factors of the Pt, Cl, N and O atoms for both structures were made sequentially anisotropic. Tests were made to show that the use of increased parameters was justified (Hamilton, 1965). Further refinement using full-matrix least squares and minimizing  $\sum w(|F_o| - |F_c|)^2$  was terminated when the maximum shift/error was  $< 0.22$  for (II) and  $< 0.01$  for (I).

Attempts were made to locate H atoms, but for (I) they were unsuccessful. For (II) ten of the thirteen H atoms were found from the difference map. Attempts to find the remaining H atoms from a difference map using a weighting scheme\* giving increased weight to the low-angle reflections were unsuccessful. In further refinements each H atom was given a varying temperature factor 1.5 times that of the atom to which it was attached. Further refinement, including the H atoms, was terminated when the largest shift/error for non-hydrogen atoms was 0.22 and for H atoms was 0.98. Correction for secondary extinction was applied using

\* The weighting scheme is described under *FMAP* in *SHELX*. The value of *S* chosen was 0.3.

Table 2. Atomic positional parameters ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2$ ) ( $\times 10^3$ ) for [Pt(dien)Cl]Cl

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> <sub>eq</sub> *
Pt	1813.3 (2)	2008.7 (6)	2500	24.0 (2)*
Cl(1)	2932 (2)	4711 (7)	1673 (2)	41 (1)*
N(1)	2618 (6)	1462 (20)	3789 (7)	33 (5)*
C(1)	1961 (7)	306 (28)	4581 (8)	37 (3)
C(2)	1249 (8)	−1679 (21)	4082 (8)	31 (2)
N(2)	801 (5)	−62 (20)	3258 (7)	28 (4)*
C(3)	180 (6)	−1560 (18)	2527 (15)	35 (2)
C(4)	−36 (8)	502 (24)	1680 (9)	35 (2)
N(3)	869 (7)	1611 (20)	1312 (7)	34 (5)*
Cl(2)	819 (2)	6610 (6)	−474 (2)	35 (1)*

$$* U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

Table 3. Atomic positional parameters ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2$ ) ( $\times 10^3$ ) for [Pt(dien)ONO<sub>2</sub>]NO<sub>3</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> <sub>eq</sub> *
Pt	1262.6 (3)	4421.4 (3)	1233.7 (2)	32.0 (2)*
N(1)	1538 (8)	4521 (9)	65 (6)	48 (5)*
C(1)	2636 (10)	4906 (13)	−63 (7)	48 (3)
C(2)	3005 (9)	5800 (12)	607 (6)	40 (2)
N(2)	2737 (7)	5035 (9)	1333 (4)	34 (2)
C(3)	2836 (9)	5834 (11)	2090 (6)	35 (2)
C(4)	2256 (10)	4994 (13)	2681 (6)	46 (3)
N(3)	1192 (8)	4669 (10)	2417 (5)	47 (5)*
O(1)	−282 (6)	4004 (8)	1091 (5)	51 (4)*
O(2)	−68 (7)	1927 (8)	1566 (5)	61 (5)*
O(3)	−1607 (6)	2636 (9)	1178 (5)	64 (6)*
N(4)	−652 (7)	2807 (10)	1296 (5)	44 (2)
O(4)	4405 (7)	3135 (10)	1690 (5)	65 (5)*
O(5)	5887 (7)	2508 (10)	1247 (5)	75 (7)*
O(6)	4586 (8)	2604 (11)	485 (5)	79 (7)*
N(5)	4976 (8)	2776 (10)	1142 (5)	47 (2)

$$* U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

*SHELX*.\* Throughout the refinement scattering curves were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974) and the real components of the anomalous-dispersion corrections (Cromer, 1974) were applied to the curves for Pt and Cl. The atom parameters for non-hydrogen atoms are listed in Tables 2 and 3.†

\* All calculations were carried out on a Cyber 170/730 computer. The programs *DATCO 5*, *ABSORB* and *DATRDN* from the XRAY 76 package (Stewart, 1976) were used for preliminary data treatment. The structure was solved using *SHELX* (Sheldrick, 1976). Plane and dihedral-angle calculations were made using *NRC-22* (Pippy & Ahmed, 1978) and diagrams were prepared using *ORTEP-II* (Johnson, 1976).

† Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36797 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Results and discussion

The molecular cations are illustrated in Fig. 1 and selected interatomic distances and angles are given in Table 4. We have compared our results with previous structural determinations of the  $[\text{Pt}(\text{dien})X]^{n+}$  unit (Melanson, Hubert & Rochon, 1975; Melanson, Rochon & Hubert, 1979; Melanson & Rochon, 1978, 1979) and the averages quoted here refer to values based on those determinations.

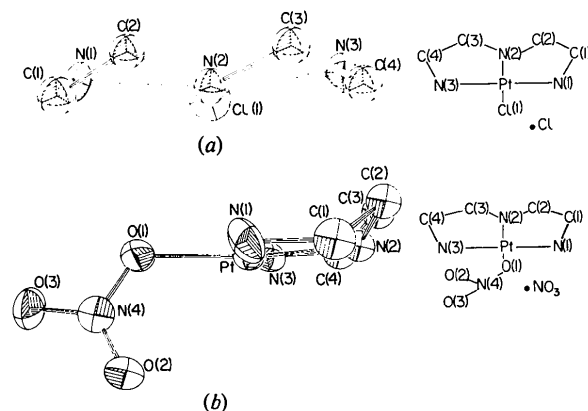


Fig. 1. (a) The  $[\text{Pt}(\text{dien})\text{Cl}]^+$  cation viewed down the N(2)-Pt axis. Pt is hidden by N(2). (b) The  $[\text{Pt}(\text{dien})\text{ONO}_2]^+$  cation showing the monodentate nitrate ion.

The cation of (I) is almost identical to  $[\text{Pt}(\text{dien})\text{Br}]^+$ . In the cation of (II) the nitrate ion is monodentate being coordinated through O(1), and the dihedral angle between the nitrate ion and the ligand plane is  $71(1)^\circ$ . The Pt-O(2) distance of  $3.020(8) \text{ \AA}$  is probably too long to be considered a bonding interaction.

Pt-N(1) and Pt-N(3) [range  $2.036(9)$ – $2.063(10) \text{ \AA}$ ] in both (I) and (II) are longer than Pt-N(2) [ $2.002(8)$ ,  $1.984(8) \text{ \AA}$ ]. This was not detectable from previous results because of larger errors. N-C and C-C distances agree well with the average of previous results. It is not possible to state, because of the errors, that a given C-C bond is longer than a given C-N bond in (I) and (II) but the N(1,3)-C(2,4), C(1,4)-C(2,3), C(2,3)-N(2) averages of  $1.48(1)$ ,  $1.52(1)$ ,  $1.49(1) \text{ \AA}$  for (I) and (II) agree well with the averages for previous results ( $1.48$ ,  $1.52$ ,  $1.48 \text{ \AA}$ ) and are consistent with a difference in the C and N covalent radii of about  $0.04 \text{ \AA}$  (Pauling, 1960). There are differences in some angles; the larger X-Pt-N(2) angle [ $175.6(3)^\circ$ ] for X = Cl [*vs.*  $173.7(3)^\circ$ , X = O] being compensated by the smaller N(1)-Pt-N(3) angle [ $165.7(4)$  *vs.*  $168.0(4)^\circ$ ]. These small differences are probably caused by packing constraints. That O,Cl(1)-Pt-N(1,3) angles [range  $93.4(4)$ – $97.0(3)^\circ$ ] are larger than N(1,3)-Pt-N(2) angles [range  $83.5(4)$ – $85.5(4)^\circ$ ] has been noted previously (Melanson & Rochon, 1978, 1979; Melanson *et al.*, 1975, 1979).

Table 4. Selected interatomic distances ( $\text{\AA}$ ) and angles (deg)

	(I)	(II)		(I)	(II)		(I)	(II)
Pt-Cl(1)	2.312 (3)	—	Pt-O(1)	—	2.030 (8)	Pt-N(1)	2.063 (9)	2.036 (9)
Pt-N(2)	2.002 (8)	1.984 (8)	Pt-N(3)	2.063 (10)	2.044 (9)	N(1)-C(1)	1.50 (1)	1.47 (2)
C(1)-C(2)	1.53 (2)	1.52 (2)	C(2)-N(2)	1.48 (1)	1.49 (1)	N(2)-C(3)	1.49 (2)	1.52 (1)
C(3)-C(4)	1.53 (2)	1.50 (2)	C(4)-N(3)	1.46 (2)	1.47 (2)	O(1)-N(4)	—	1.31 (1)
N(4)-O(3)	—	1.25 (1)	N(4)-O(2)	—	1.23 (1)	N(5)-O(4)	—	1.24 (1)
N(5)-O(5)	—	1.21 (1)	N(5)-O(6)	—	1.24 (1)			
Possible hydrogen bonds								
(I)	Cl(2)⋯N(1) <sup>i</sup>	3.347 (9)	Cl(2)⋯N(2) <sup>ii</sup>	3.273 (9)	Cl(2)⋯N(3)	3.385 (9)		
	Cl(2)⋯N(3) <sup>iii</sup>	3.384 (9)						
(II)	N(1)⋯O(5) <sup>iv</sup>	3.11 (1)	N(1)-H(N11)	1.0 (1)	H(N11)⋯O(5) <sup>v</sup>	2.2 (1)		
	N(2)⋯O(4)	2.89 (1)	N(2)-H(N2)	0.7 (1)	H(N2)⋯O(4)	2.2 (1)		
	N(3)⋯O(4) <sup>v</sup>	3.13 (1)	N(3)-H(N31)	0.9 (1)	H(N31)⋯O(4) <sup>v</sup>	2.2 (1)		
	N(3)⋯O(5) <sup>v</sup>	3.14 (1)	H(N31)⋯O(5) <sup>v</sup>	2.4 (1)	N(1)⋯O(1) <sup>vi</sup>	2.93 (1)		
	N(3)⋯O(2) <sup>vii</sup>	3.15 (1)						
	(I)	(II)		(I)	(II)		(I)	(II)
Cl(1)-Pt-N(1)	95.6 (3)	—	Cl(1)-Pt-N(2)	175.6 (3)	—	Cl(1)-Pt-N(3)	97.0 (3)	—
O(1)-Pt-N(1)	—	93.4 (4)	O(1)-Pt-N(2)	—	173.7 (3)	O(1)-Pt-N(3)	—	95.8 (4)
N(1)-Pt-N(2)	84.5 (4)	84.6 (4)	N(1)-Pt-N(3)	165.7 (4)	168.0 (4)	N(2)-Pt-N(3)	83.5 (4)	85.5 (4)
Pt-N(1)-C(1)	107.2 (6)	109.0 (7)	N(1)-C(1)-C(2)	109.0 (9)	109 (1)	C(1)-C(2)-N(2)	105.3 (9)	105.9 (9)
C(2)-N(2)-Pt	109.6 (6)	107.3 (6)	Pt-N(2)-C(3)	109.0 (8)	107.9 (6)	C(2)-N(2)-C(3)	118.1 (9)	116.0 (8)
N(2)-C(3)-C(4)	106.1 (8)	104.9 (8)	C(3)-C(4)-N(3)	108.3 (9)	111.5 (9)	C(4)-N(3)-Pt	109.4 (7)	106.9 (7)
O(1)-N(4)-O(3)	—	115.5 (9)	O(1)-N(4)-O(2)	—	120.4 (9)	O(2)-N(4)-O(3)	—	124.1 (9)
O(4)-N(5)-O(5)	—	121 (1)	O(4)-N(5)-O(6)	—	119 (1)	O(5)-N(5)-O(6)	—	120 (1)

Atoms are related to those in Tables 2 and 3 by (i)  $\frac{1}{2} - x, y, z - \frac{1}{2}$ ; (ii)  $-x, -y, z - \frac{1}{2}$ ; (iii)  $x, y - 1, z$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} - y, -z$ ; (v)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ; (vi)  $-x, 1 - y, -z$ ; (vii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

Within the dien ligand angles are close to the tetrahedral angle but it appears that the N(1,3)–C(1,4)–C(2,3) angles (average 109.5°) are larger than N(2)–C(2,3)–C(1,4) angles (average 105.6°). Errors preclude this conclusion on the basis of an angle-for-angle comparison, but the averages for (I) and (II) agree well with the averages for previous results (110°, 106° respectively). The Pt–Cl bond length is normal.

We have previously examined the conformation of the dien molecule in *fac-M*(dien)*X*<sub>3</sub><sup>n+</sup> complexes (Britten & Lock, 1980), and we have undertaken a similar comparison for [Pt(dien)*X*]<sup>n+</sup> and the results are presented in Table 5. The conventions and definitions are as we used previously. All cations adopt the λδ or δλ configuration predicted by Schmidtke & Garthoff (1968), so that the molecules look like a sting ray with the front edges of the 'wings' up and the *X* group forming the tail. An examination of the distances of atoms from the least-squares planes formed by the Pt-bound ligand atoms (the 'ligand planes') shows different distortions. The nitrate complex is distorted towards a square pyramid [N(1) 0.014 (9), N(2) –0.011 (8), N(3) 0.014 (10), O(1) –0.008 (8), Pt\* –0.1160 (3) Å], whereas the chloride, like the bromide, is distorted towards a tetrahedron [N(1) 0.13 (1), N(2) –0.13 (1), N(3) 0.14 (1), Cl(1) –0.010 (3), Pt\* 0.0080 (3) Å]. The direction and magnitude of these distortions appear to be determined by packing considerations, rather than intramolecular factors, since one [Pt(dien)Br]<sup>+</sup> cation in the tetra-

bromide complex (Melanson *et al.*, 1979) is essentially planar, tending to a square pyramid, and the other is distorted towards a square pyramid, and the guanine and inosine complexes (Melanson & Rochon, 1978, 1979) are planar.

For the *fac-M*(dien)*X*<sub>3</sub> complexes, hydrogen bonding caused changes in ligand conformation, significant variation in the distance the *M* atom was out of the N⟨C⟩N plane (range 0.01–0.58 Å) and the NCCN torsional angles (36.6–50.3°) (Britten & Lock, 1980). The variation is generally much less for the [Pt(dien)*X*]<sup>n+</sup> complexes, except for one of the rather distorted cations in the PtBr<sub>4</sub><sup>2-</sup> complex [0.161 (0)–0.322 (0) Å; 45(6)–59(6)°]. Even with cation *B*. [PtBr<sub>4</sub>]<sup>2-</sup> included (Melanson *et al.*, 1979) the distance range is still less, although the torsional-angle range is comparable. The steric restraints on the dien ligand in the [Pt(dien)*X*]<sup>n+</sup> cations are greater and apparently hydrogen bonding can cause less variation.

The packing of (I) is shown in Fig. 2. Like the bromide it is a layer structure with the cations centred at *y* = 0 and the anions at *y* = ½. As shown in Fig. 2, cations along the *c* direction are oriented so that Cl(1) on each molecule is pointing into the same anion layer, but up the *a* direction, the cations are related by the *a* glide plane at *y* = 0, so that alternate molecules have Cl(1) pointing into anion layers on opposite sides. The cations are hydrogen bonded to the anion layer through Cl(2)⋯N(1)<sup>i</sup>, Cl(2)⋯N(2)<sup>ii</sup>, Cl(2)⋯N(3) and Cl(2)⋯N(3)<sup>iii</sup>.

The packing of (II) is shown in Fig. 3. Surprisingly, because of the rather different shape of the cation, the packing is again a layer structure, very similar to that

\* The Pt atom was given no weight in calculating the plane.

Table 5. Comparison of the conformations of [Pt(dien)*X*]<sup>n+</sup> cations

Compound	Distance of C atoms from MNN plane (Å)				Distance of atoms from NN⟨C⟩ plane (Å)				Torsional angles NCCN (°)		Confor- mation	Refer- ence
	N(1)N(2) <i>M</i>		N(2)N(3) <i>M</i>		N(1)N(2) ⟨C(1)C(2)⟩		N(2)N(3) ⟨C(3)C(4)⟩		N(1)C(1) C(2)N(2)	N(2)C(3) C(4)N(3)		
[Pt(dien)Cl]Cl	C(1) –0.22 (1)	C(3) –0.50 (1)	C(2) 0.50 (1)	C(4) 0.21 (1)	Pt 0.161 (0)	Pt 0.177 (0)	C(1) –0.36 (1)	C(3) –0.35 (1)	–54 (1)	53 (1)	λδ	<i>a</i>
[Pt(dien)NO <sub>3</sub> ]NO <sub>3</sub>	C(1) 0.06 (1)	C(3) 0.54 (1)	C(2) –0.62 (1)	C(4) –0.15 (1)	Pt –0.322 (0)	Pt 0.225 (0)	C(1) –0.34 (1)	C(3) 0.34 (1)	52 (1)	–53 (1)	δλ	<i>a</i>
[Pt(dien)Br] <sub>2</sub> PtBr <sub>4</sub> <i>A</i>	C(1) 0.00 (8)	C(3) 0.60 (10)	C(2) –0.58 (6)	C(4) –0.05 (10)	Pt –0.355 (2)	Pt 0.288 (2)	C(1) 0.29 (8)	C(3) 0.33 (10)	45 (6)	–46 (6)	δλ	<i>b</i>
[Pt(dien)Br] <sub>2</sub> PtBr <sub>4</sub> <i>B</i>	C(1) 0.02 (9)	C(3) 0.69 (7)	C(2) –0.83 (8)	C(4) 0.14 (9)	Pt –0.493 (3)	Pt 0.459 (3)	C(1) 0.43 (9)	C(3) 0.29 (7)	59 (6)	–42 (6)	δλ	<i>b</i>
[Pt(dien)Br]Br	C(1) 0.21 (2)	C(3) 0.49 (1)	C(2) –0.57 (2)	C(4) –0.14 (2)	Pt –0.203 (1)	Pt 0.213 (1)	C(1) 0.39 (2)	C(3) 0.32 (1)	58 (2)	–50 (2)	δλ	<i>c</i>
[Pt(dien)Ino](NO <sub>3</sub> ) <sub>2</sub>	C(1) –0.07 (1)	C(3) –0.52 (1)	C(2) 0.53 (1)	C(4) 0.10 (2)	Pt –0.39 (2)	Pt –0.32 (2)	C(1) –0.31 (1)	C(3) –0.31 (1)	–49 (1)	49 (1)	λδ	<i>d</i>
[Pt(dien)Guo](NO <sub>3</sub> ) <sub>2</sub>	C(1) –0.12 (2)	C(3) –0.55 (1)	C(2) 0.54 (2)	C(4) 0.09 (2)	Pt 0.264 (0)	Pt –0.250 (0)	C(1) –0.31 (1)	C(3) –0.31 (1)	–51 (1)	50 (1)	λδ	<i>e</i>
					Pt 0.249 (1)	Pt –0.272 (1)	C(2) 0.31 (1)	C(4) 0.31 (1)				
					C(1) –0.34 (2)	C(3) –0.32 (2)	C(2) 0.34 (2)	C(4) 0.32 (2)				

(a) This work; (b) Melanson, Rochon & Hubert (1979); (c) Melanson, Hubert & Rochon (1975); (d) Melanson & Rochon (1978); (e) Melanson & Rochon (1979).

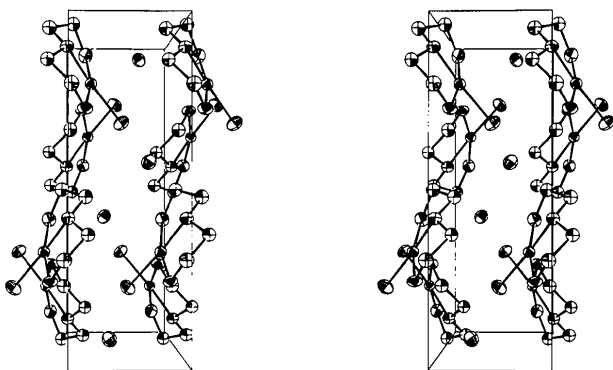


Fig. 2. The packing of  $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$  in the unit cell showing the layer structure. **b** and **a** are parallel to the bottom and side of the page respectively, and the view is down **c**.

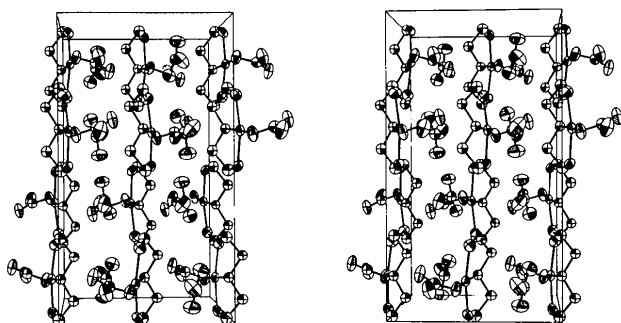


Fig. 3. The packing of  $[\text{Pt}(\text{dien})\text{ONO}_2]\text{NO}_3$  in the unit cell showing the layer structure. **b** and **c** are parallel to the bottom and side of the page respectively, and the view is down **a**.

of the chloride, but now the repeat distance along **b** is doubled, compared to (I). The effects of orientation of the coordinated nitrate group are comparable to (I); cations in a layer form chains up **c** and the nitrate groups on alternate cations lie in opposite anion layers. Each cation is hydrogen bonded by a medium hydrogen bond  $\text{N}(2)\cdots\text{O}(4)$  [ $2.89$  ( $1$ )  $\text{\AA}$ ] and weak  $\text{N}(1)\cdots\text{O}(5)^{\text{iv}}$  and  $\text{N}(3)\cdots\text{O}(4)^{\text{v}},\text{O}(5)^{\text{v}}$  bifurcated hydrogen bonds to nitrate ions in the same anion layer. There is a remaining weak cation-cation link along **c** through  $\text{N}(3)\cdots\text{O}(2)^{\text{viii}}$ . The principal reason for the doubling of the **b** axis and the space-group change is that in (I) all cations with the same **z** have the  $\text{Pt}-\text{Cl}(1)$  pointing in the same direction, whereas for (II) cations with roughly the same **x** have  $\text{Pt}-\text{O}(1)$  oriented in opposite directions in alternate layers along **b**. Of the other structures examined by Melanson and coworkers (Melanson & Rochon, 1978, 1979; Melanson *et al.*, 1975, 1979) only  $[\text{Pt}(\text{dien})\text{Br}]_2(\text{PtBr}_4)$  can be considered a layer structure and it is different from the structures here in that the cations are oriented so that the bound Br atoms all point into the same anion layer.

Although we prepared (II) we were in fact trying to prepare  $[\text{Pt}(\text{dien})\text{OH}_2](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ . Even recryst-

allization from water did not give the desired product although we know that solution in water caused the coordinated nitrate ion to be removed immediately. Thus, the Raman spectrum (see Fig. 4) of the solid shows vibrational bands both for the ionic and coordinated nitrate ions, but the solution spectrum shows that no coordinated nitrate ion is present no matter how soon the spectrum was measured ( $<2$  min) after the solid was dissolved. Only bands from ionic nitrate are observed. We encountered this problem previously with *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_3]$  (Lippert, Lock, Rosenberg & Zvagulis, 1977). Indeed, all our attempts to prepare aqua species of  $\text{Pt}^{\text{II}}$  have been unsuccessful (see *Introduction*). Brown's 'bond valence' concept (Brown, 1981; Brown & Shannon, 1973) allows us to explain why this is occurring and suggests conditions under which it may be possible to obtain aqua- and terminal hydroxo- $\text{Pt}^{\text{II}}$  species.

Brown's model is an extension of Pauling's (1960) bond-order bond-length relationship, the only difference being that Brown assigns a bond valence to all nearest-neighbour interactions, regardless of whether they are covalent 'bonds' or ionic or van der Waals interactions. The only requirement is that the sums of the bond valences shall be equal to the modulus of the formal oxidation state of the atom under consideration; consider Fig. 5(a). The N-O bond valence in the free nitrate ion is  $1.67$  ( $3 \times 1.67 = 5$ ) leaving a residual unsatisfied valence of  $0.33$  ( $1.67 + 0.33 = 2.00$ ) on each O atom, which will normally be satisfied by some ionic, covalent or hydrogen bond. Similar figures are shown for water (Fig. 5c) and hydroxide (Fig. 5e) obtained from Brown's relationships. For the  $[\text{Pt}(\text{dien})]^{2+}$  species, if we assume Pt-N bonds are as strong as Pt-O bonds (a not unreasonable assumption since we have shown in a number of structures that Pt-O bonds are as short or shorter than Pt-N bonds),

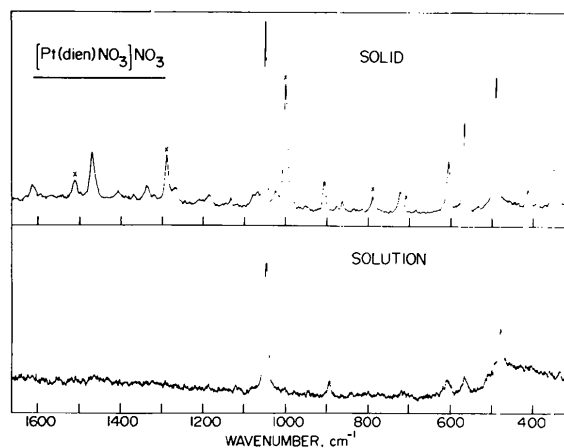


Fig. 4. Raman spectra of  $[\text{Pt}(\text{dien})\text{ONO}_2]\text{NO}_3$ . (a) Solid, (b) aqueous solution. Points marked **x** are characteristic of the coordinated nitrate ion.

Table 6. Comparison of nitrate bond lengths (Å)

Molecule	O(1)—N(4)	N(4)—O(2)	N(4)—O(3)	Reference
<i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ], (NO <sub>3</sub> <sup>-</sup> A)	1.30 (2)	1.22 (2)	1.24 (2)	<i>a</i>
<i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ], (NO <sub>3</sub> <sup>-</sup> B)	1.28 (2)	1.19 (2)	1.22 (2)	<i>a</i>
[Pt(dien)NO <sub>3</sub> ] <sup>2+</sup>	1.31 (1)	1.23 (1)	1.25 (1)	<i>b</i>
[Pt(dien)NO <sub>3</sub> ]NO <sub>3</sub> (free NO <sub>3</sub> <sup>-</sup> )	1.24 (1)	1.21 (1)	1.24 (1)	<i>b</i>
Brown's calculation for Fig. 5(b)	1.29	1.24	1.24	<i>c</i>

Except for the free nitrate ion the atoms are numbered as in Fig. 1(b). References: (a) Lippert *et al.* (1977). (b) This work. (c) I. D. Brown, private communication.

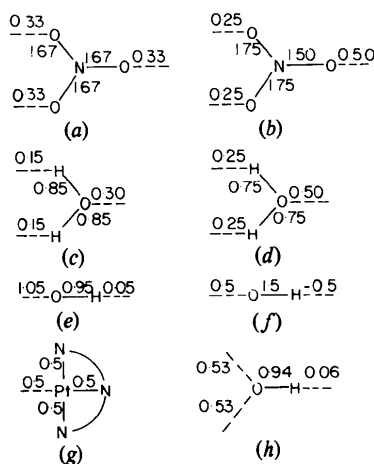


Fig. 5. Bond-valence distributions in various molecules and ions.

we have the situation shown in Fig. 5(g). The [Pt(dien)]<sup>2+</sup> fragment has an unsatisfied bond valence of 0.5. Since a bond can only have one bond valence, [Pt(dien)]<sup>2+</sup> cannot bond directly to either nitrate or water without some redistribution of the bond valence. We have suggested how this might occur in Fig. 5(b,d). The redistribution of bond valence can be tested by comparing observed bond lengths with values calculated from Brown's bond-valence bond-length relationship and the excellent agreement for the nitrate ion is shown in Table 6.

One might expect a strong hydrogen bond to the uncoordinated O atoms of the nitrate ion, but, as Brown (1981) has shown, oxygen is normally four-coordinate, so the residual bond valence of 0.25 at each O atom will be distributed over three hydrogen bonds of only 0.08 bond valence which would represent rather weak hydrogen bonds. In addition, the hydrogen bond to the coordinated O atom O(1) will increase the external bond valence at O(1), weakening O(1)—N(4), strengthening N(4)—O(2) and N(4)—O(3) and further reducing the unsatisfied bond valence at O(2) and O(3).

For water to coordinate to Pt<sup>II</sup> through oxygen there must be an increase in the residual valence at each H atom on the water molecule which must be satisfied by stronger proton-donation hydrogen bonding. Since

hydrogen is normally only two-coordinate (Brown, 1981) the residual bond valence of 0.25 will only be satisfied by one rather strong hydrogen bond.

In aqueous solution this can take place, the water molecules acting as acceptors. In the solid, coordination of the nitrate ion seems to be preferred, insufficient strong hydrogen bonds being formed to stabilize water coordination. Clearly, if one wants to stabilize water coordinated to Pt<sup>II</sup> in the solid state, one must use counter-ions which are good hydrogen-bond acceptors but poor ligands, such as fluoride, or salts which are extensively hydrated and have counter-ions which are poor ligands.

For the hydroxide ion there is no simple rearrangement to allow monofunctional bonding to Pt<sup>II</sup> since it results in a negative unsatisfied bond valence at hydrogen which is impossible (Fig. 5f). The residual bond valence at oxygen of 1.05 can easily be split into 2 × 0.53, each matching the valence at Pt<sup>II</sup> (Fig. 5h) and it is easy to see why hydroxide bridges Pt<sup>II</sup> so readily. An alternative way of satisfying the ~0.5 residual bond valence at oxygen would be to form two strong proton-acceptor hydrogen bonds. This can only occur in aqueous solution or in an extensively hydrated salt. To stabilize such a system the bond valence of the O—H bond should be as large as possible (near 1.0) and thus the residual bond valence at hydrogen will be close to 0.0 and this atom will not be involved in any significant hydrogen bond.

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## Anomalous Scattering by Praseodymium, Samarium and Gadolinium and Structures of their Ethylenediaminetetraacetate (edta) Salts

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### Abstract

Na[Pr(C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>8</sub>)(H<sub>2</sub>O)<sub>3</sub>].5H<sub>2</sub>O ( $M_r = 596.24$ ) is orthorhombic, space group *Fdd2*, with  $a = 19.589$  (3),  $b = 35.763$  (5),  $c = 12.121$  (2) Å,  $U = 8491.5$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.865$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 2.38$  mm<sup>-1</sup>. For the isomorphous Sm salt ( $M_r = 605.68$ ):  $a = 19.503$  (11),  $b = 35.596$  (17),  $c = 12.119$  (5) Å,  $U = 8413.4$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.913$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 2.90$  mm<sup>-1</sup>. For the isomorphous Gd salt ( $M_r = 612.58$ ):  $a = 19.409$  (3),  $b = 35.477$  (4),  $c = 12.119$  (1) Å,  $U = 8344.8$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.950$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 3.29$  mm<sup>-1</sup>. The structures were refined to *R* values of 0.037, 0.030, and 0.024 respectively for 3449, 3368 and 3386 diffraction data measured with Mo *K*α X-rays. Anomalous-scattering

terms  $f''$  derived for this wavelength are 2.87 (11), 3.64 (10), and 3.91 (9) e atom<sup>-1</sup> respectively for Pr, Sm and Gd, in good agreement with theoretical values.

### Introduction

To measure anomalous scattering of X-rays by rare-earth elements in experiments with synchrotron radiation (Templeton, Templeton & Phizackerley, 1980; Templeton, Templeton, Phizackerley & Hodgson, 1982) we needed the crystal structure parameters for sodium (ethylenediaminetetraacetato)praseodymate(III) octahydrate and the isomorphous Sm and Gd salts. In this paper we report determinations of these three structures using Mo *K*α radiation. Values of