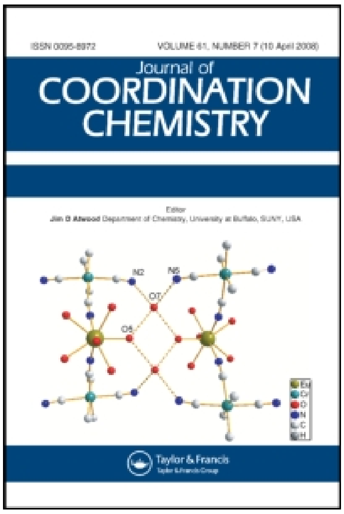

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A NEW TYPE OF ISOMERISM AMONG THE CHELATES OF A NOVEL STEREOSELECTIVE LIGAND: THE CHEMISTRY AND CRYSTAL STRUCTURES OF THREE PALLADIUM(II) COMPLEXES WITH CIS-3,5-DIAMINOPIPERIDINE

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A NEW TYPE OF ISOMERISM AMONG THE CHELATES OF A NOVEL STEREOSELECTIVE LIGAND: THE CHEMISTRY AND CRYSTAL STRUCTURES OF THREE PALLADIUM(II) COMPLEXES WITH CIS-3,5-DIAMINOPIPERIDINE

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Terdentate *cis*-3, 5- diaminopiperidine ("dapi", $C_5H_{13}N_3$) is an excellent rigid ligand for facial coordination in octahedral complexes. The stabilities of some of its $3d^9$ complexes show it to be superior to 1,2,3-triaminopropane and *cis-cis*-1,3,5-triaminocyclohexane. Two molecules of "dapi" are required to complete a square planar coordination, the two additional nitrogen atoms being then also placed rather close to the metal. "Dapi" might thus force some of the heavy d^8-cations, particularly Pd(II), into an octahdral coordination. The 1:2 complex $Pd(dapi)_2^{2+}$ and its protonation products $Pd(dapi)(Hdapi)^{3+}$ and $Pd(Hdapi)_2^{4+}$ were therefore prepared. All three compounds are diamagnetic and show spectra typical of a square planar PdN_4-chromophore. The crystal structures of the following compounds have been determined from X-ray data by Patterson and Fourier methods: $[Pd(Hdapi)_2](ClO_4)_4 \cdot 2H_2O$ (I), $[Pd(dapi)_2](ClO_4)_2$ (II), $[Pd(dapi)(Hdapi)](NO_3)_3 \cdot H_2O$ (III). In all three structures, only the primary amino groups of "dapi" are coordinated with Pd-N distances ranging from 1.98 to 2.08 Å. The piperidine and six-membered chelate rings are all in the chair conformation. In (I) and (III), the non-coordinated piperidine nitrogens are in the expected *anti* position on opposite sides of the coordination square with Pd-N 3.36 and 3.21 Å respectively. Removal of the second proton induces, however, an unexpected isomerisation from the *anti* to the *syn* configuration. In (II), $Pd(dapi)_2^{2+}$ has a basket-like structure, the piperidine nitrogens being on the same side of the coordination plane with Pd-N 3.08 and 3.17 Å. *Syn*-$Pd(dapi)_2^{2+}$ (II) can be rapidly protonated to *syn*-Pd(dapi)-$(Hdapi)^{3+}$ and *syn*-$Pd(Hdapi)_2^{4+}$, whereas *anti*-$Pd(Hdapi)_2^{4+}$ (I) can be rapidly deprotonated to *anti*-$Pd(dapi)(Hdapi)^{3+}$ (III) and *anti*-$Pd(dapi)_2^{2+}$. These equilibra have been investigated. The protolytic equilibra between H^+ and the three *syn*- and three *anti*-species are, however, reached extremely slowly.

INTRODUCTION

Flexible and Rigid Terdentate Ligands

By linking the carbons 2 and 6 of 1,4,7-triazaheptane ("den") with a bridging CH_2 group, the well known flexible terdentate ligand is converted into the rigid molecule 3,5-diaminopiperidine. Its heterocycle will adopt a chair conformation thus minimizing the repulsion between substituents bonded to neighboring ring atoms. In *cis*-3,5-diaminopiperidine ("dapi"), the primary amino groups are oriented either equatorially $(dapi)_{eq}$ or axially $(dapi)_{ax}$. The first of these conformers is evidently more stable, but it cannot function as a chelating ligand. The nitrogens of $(dapi)_{ax}$, however, form an almost equilateral triangle with edge lengths of 2.5 to 3 Å which is close to the distance of neighboring coordination sites of metallic centers.

"Dapi" will therefore coordinate facially to metal cations which form octahedral amine complexes, such as Co(II) and Ni(II). Indeed, ionic equilibra studies show that only two complexes are formed. Their stabilities (Table I) demonstrate that "dapi" acts as a terdentate ligand like "den", K_1 and K_2 being substantially larger than the stability constants of the 1:1 and 1:2 complexes with bidentate ethylenediamine ("en"). They are even larger than for the flexible ligand "den", thus indicating that the change of conformation $(dapi)_{eq} \rightarrow (dapi)_{ax}$ does not require much energy and that not much strain is built up when "dapi" coordinates as a terdentate

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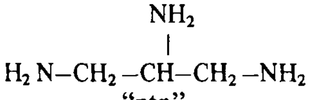
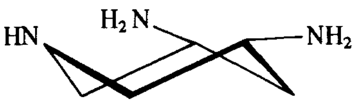
$H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$

"den"

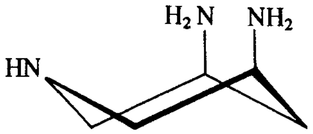


$H_2N{-}CH_2{-}\underset{}{\overset{NH_2}{\overset{|}{CH}}}{-}CH_2{-}NH_2$

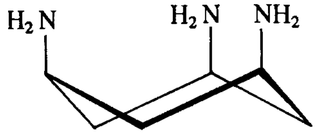
"ptn"



(dapi)$_{eq}$



(dapi)$_{ax}$



(tach)$_{ax}$

ligand. In addition, the d-d spectra of Co(dapi)$_2^{2+}$ and Ni(dapi)$_2^{2+}$ show unequivocally the presence of octahedral MN_6 chromophores.

The d^9-cation Cu^{2+} tends to bind four nitrogen atoms strongly and two very weakly in a distorted octahedral (4+2)-coordination. The flexible "den" can easily fulfil this requirement, in contrast to the rigid ligands "dapi" and "tach" which is clearly indicated by the stabilities of the 1:1 complexes. Cu(dapi)$^{2+}$ is only slightly more stable than Cu(en)$^{2+}$ and much less stable than Cu(den)$^{2+}$. The third and fourth sites of the coordination square are only occupied when Cu(dapi)$_2^{2+}$ is formed which results in K_2 of the "dapi" complexes being larger than K_2 of the "den" complexes. Although the overall stabilities β_2 of the 1:2 complexes with "dapi" and "en" are very similar, the d-d spectra reveal "dapi" to be coordinated as a terdentate ligand, as is "tach" in Cu(tach)$_2^{2+}$ [5] and "den" in Cu(den)$_2^{2+}$.[6]

Similarly, two molecules of "dapi" are needed to form square planar low spin complexes with the d^8-cations Pd(II), Pt(II) and Au(III). The required *cis* N-N distance in the coordination square of approximately 2.9 Å can be obtained more easily between the two primary amino groups than between NH_2 and the piperidine nitrogen. This leads to six-membered chelate rings which are expected to prefer the chair conformation. Assuming the piperidine rings to be also in the chair form, the primary nitrogens are then brought quite close to the metallic center. If these are on opposite sides of the coordination square (*anti* structure) as should be expected, they might also coordinate, resulting in an octahedral configuration as in Ni(dapi)$_2^{2+}$. The stereoselective

TABLE I

Stability constants in aqueous solution I = 0.1 M; 20°C

System	$\lg K_1$	$\lg K_2$	$\lg\beta_2$	ref.
Co^{2+} – dapi	8.6	7.6	16.2	1
Co^{2+} – en^a	5.9	4.7	10.6	2
Co^{2+} – den	8.1	6.0	14.1	3
Co^{2+} – tach	7.5	4.4	12.1	4
Co^{2+} – ptn	6.8	(basicity of 1:1-complex: pK = 6.9) ref. 3		
Ni^{2+} – dapi	11.3	9.9	21.2	1
Ni^{2+} – en^a	7.5	6.3	13.8	2
Ni^{2+} – den	10.7	8.2	18.9	3
Ni^{2+} – tach	10.4	6.4	16.8	4
Ni^{2+} – ptn	9.3	(basicity of 1:1-complex: pK = 6.3) ref. 3		
Cu^{2+} – dapi	11.6	8.8	20.4	1
Cu^{2+} – en^a	10.7	9.3	20.0	2
Cu^{2+} – den	16.0	5.3	21.3	3
Cu^{2+} – tach	10.7	4.8	15.5	4
Cu^{2+} – ptn	11.1	9.0	20.1	3

^{a} 25°C; $\beta_2 = K_1 \cdot K_2$

ligand would then force a cation prefering square planar complexes into an unusual coordination geometry. This could of course be detected in the spectra and in the magnetic properties. The chance of "dapi" forming an octahedral high-spin complex with a heavy d^8-cation certainly is greatest for Pd(II) whose complexes were therefore investigated.

High-spin Pd(II) Compounds

The preparation of octahedral Pd(II) complexes with nitrogen ligands would be of considerable interest. The only paramagnetic Pd(II) compound known to date is solid PdF_2 which forms a distorted rutile structure.[7] The stability of the octahedral complex with respect to the corresponding square planar complex will become smaller with decreasing electronegativity of the ligand element and, indeed, octahedral PdN_6 has never been observed. The statement[8] that 1,2,3-triaminopropane ("ptn") was functioning as a terdentate ligand in its 1:2 complex with palladium has proved to be incorrect. $[Pd(ptn)_2](ClO_4)_2$ is diamagnetic, its spectrum is typical of a square planar PdN_4-chromophore and the presence of un-coordinated amino groups is also demonstrated by the high basicity of the complex ($pK_1 = 7.7$; $pK_2 = 6.7$).[9] This is not surprising since considerable strain is built up within the condensed chelate rings formed by "ptn" functioning as a terdentate ligand. Models show a six-membered chelate ring in the boat form containing several eclipsed hydrogen atoms, two distorted chelate-5-rings and three N-M-N angles considerably smaller than 90°. The stability constants of the complexes $Co(ptn)^{2+}$ and $Ni(ptn)^{2+}$, as well as their appreciable tendency to add a proton (Table I), also show "ptn" to be inferior to "dapi" as a terdentate ligand. One of the amino groups can easily be detached from the metal.

EXPERIMENTAL

Preparation of the Complexes

Solid $PdCl_2$ (0.014 mol) was dissolved in a solution of $[H_3dapi]Cl_3$ (0.029 mol in 125 ml water) by boiling for several hours (reflux). The chloride of the homogeneous solution, deeply yellow because of the presence of $PdCl_4^{2-}$, was then gradually replaced by OH^- by adding an anion exchange resin in its hydroxylated form. The strongly alkaline and almost colorless eluate was neutralized to pH7 with perchloric acid and after having evaporated a part of the solvent, crystals of the composition $[Pd(dapi)_2](ClO_4)_2$ (structure II) were obtained. *Anal.* Calcd for $C_{10}H_{26}N_6O_8Cl_2Pd$: C, 22.42; H, 4.89; N, 15.69; Cl, 13.24; Pd, 19.86. Found: C, 22.35; H, 4.84; N, 15.77; Cl, 13.35; Pd, 19.64%.

Crystals of the doubly protonated complex $[Pd(Hdapi)_2](ClO_4)_4 \cdot 2H_2O$ (structure I) were obtained from solutions acidified to pH2. *Anal.* Calcd for $C_{10}H_{32}N_6O_{18}Cl_4Pd$: C, 15.55; H, 4.18; N, 10.88; Cl, 18.34. Found: C, 15.72; H, 4.19, N, 10.64; Cl, 17.95%. Two molecules of H_2O are removed in vacuum at 100°C. *Anal.* Calcd for $C_{10}H_{28}N_6O_{16}Cl_4Pd$: C, 16.30; H, 3.83; N, 11.41; Cl, 19.25; Pd, 14.47. Found: C, 16.23; H, 3.93; N, 11.39; Cl, 19.07; Pd, 14.22%.

The pK-values (see below) show that the monoprotonated species $Pd(dapi)(Hdapi)^{3+}$ exists only in a narrow pH-range, and that at most 86% of the complex can occur in this form. Its isolation as a crystalline salt depends therefore on stringent solubility requirements. No homogeneous solids could be obtained from perchlorate solutions of intermediate acidity (pH 5 to 6). Crystals were, however, formed from a nitrate solution. The alkaline eluate obtained by the anion exchange was neutralized to pH 6 with HNO_3. After removing a part of the solvent, a precipitate was obtained by adding $NaNO_3$. It was recrystallized from water and had the composition $[Pd(dapi)(Hdapi)](NO_3)_3 \cdot H_2O$ (structure III). *Anal.* Calcd for $C_{10}H_{29}N_9O_{10}Pd$: C, 22.17; H, 5.40; N, 23.27. Found: C, 22.17; H, 5.38; N, 23.44%.

Slow Protonation and Deprotonation Processes

The compositions of the isolated salts show the complex cations I and III to be protonation products of II. $Pd(dapi)_2^{2+}$ behaves as a diprotonic base. In the attempt to determine its basicity constants, it was however discovered that the equilibria are reached very slowly when a strong acid is added to a solution of II or a strong base to a solution of I, indicating that an isomerisation process is superimposed on the protolytic reaction. All three complexes are diamagnetic and have the spectrum of the square planar PdN_4 chromophore with only minor differences in the positions and intensities of the bands. The protonation of the non-coordinated amino groups seems to cause a structural change during which Pd–N bonds are ruptured and newly formed. Because of the considerable inertness of Pd(II)-amine complexes, such an isomerisation is a slow process. This explains why equilibrium is only slowly attained in the protolytic reactions. Eq. (1) relates the equilibrium pH to the degree of protonation $\bar{p}$ obtained by adding H^+ to a diprotonic base or OH^- to its protonation product:

$$\bar{p} + (\bar{p}-1)\cdot K_1^h\cdot[H] + (\bar{p}-2)\cdot K_1^h\cdot K_2^h\cdot[H]^2 = 0 \quad (1)$$

$$K_1^h = [PdH(dapi)_2] / \{[H]\cdot[Pd(dapi)_2]\} = 10^{pK_1}$$

$$K_2^h = [PdH_2(dapi)_2] / \{[H]\cdot[PdH(dapi)_2]\} = 10^{pK_2}$$

$\bar{p}$ is obtained from the concentration C_H of strong acid added to complex II (concentration C) or from the concentration C_{OH} of strong base added to complex I (concentration C):

$$\bar{p} = \{C_H-[H]+[OH]\}/C \text{ and } 2-\{C_{OH}+[H]-[OH]\}/C \text{ respectively.} \quad (2)$$

In addition:

$$\bar{p} \equiv \{[PdH(dapi)_2] + 2\cdot[PdH_2(dapi)_2]\}/C; \quad C = \sum_{p=0}^{2} [PdH_p(dapi)_2] \quad (3)$$

Eq. (1) is valid for any diprotonic base even if the protonation products possess different structures, provided that the equilibrium between the isomers is reached. In order to obtain solutions with different values of $\bar{p}$, various amounts of strong acid or base were added to solutions of salt II and salt I respectively. They were left for up to two weeks to reach equilibrium. However, their $\bar{p}$ and pH values could still not be represented by Eq. (1), indicating that even after this time final equilibrium was not attained. The pH-values reached instantly, determined by plotting the pH-readings versus time and extrapolating to zero, could however be represented by (1). Protonation and deprotonation is therefore instantaneous, and the resulting equilibria can be investigated before isomerisation takes place. The following results were obtained at 20°C and I = 0.1 M ($NaClO_4$):

Basicity of $Pd(dapi)_2^{2+}$ of salt II: $pK_1 = 6.35$, $pK_2 = 4.16$

Basicity of the deprotonated $Pd(Hdapi)_2^{4+}$ of salt I: $pK_1 = 6.43$, $pK_2 = 4.27$

The pK values of the two isomeric bases are surprisingly similar, and their buffer regions are almost the same. The degree of protonation $\bar{p}$ should hardly change during isomerisation, the concentrations [H] and [OH] in Eq. (2) being negligibly small in comparison to C_H and C_{OH}. The corresponding change of the pH should therefore not exceed 0.1 units. However, changes of up to 0.5 pH-units were observed during the ageing of the solutions. This can be explained only by assuming that intermediates are formed in appreciable amounts during isomerisation, possessing pK-values rather different from the species isolated in salts I and II. Attempts to isolate such intermediates were unsuccessful. Salt I is readily converted into salt II by recrystallisation after addition of ammonia. By recrystallising II

TABLE II

Crystal data for $\{Pd(Hdapi)_2\}(ClO_4)_4.2H_2O$ (I), $\{Pd(dapi)_2\}(ClO_4)_2$ (II) and $\{Pd(dapi)(Hdapi)\}(NO_3)_3.H_2O$ (III)

	I	II	III
Formula	$C_{10}H_{32}N_6O_{18}Cl_4Pd$	$C_{10}H_{26}N_6O_8Cl_2Pd$	$C_{10}H_{29}N_9O_{10}Pd$
Crystal symmetry	Orthorhombic, Pbca	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$
Unit cell: a, b, c, β/A,°	14.575(14), 10.815(8), 16.176(15)	16.992(7), 8.305(3), 6.872(3), 98.57(2)	9.663(4), 12.978(6), 9.727(4), 125.18(2)
Formula units/cell	4	2	2
Symmetry of complex	$\bar{1}$	1	$\bar{1}$
Density/g.cm^{-3}	1.99(obs), 2.012(calc)	1.84(obs), 1.854(calc)	1.80(obs), 1.804(calc)
μ(MoKα)/cm^{-1}	12.31	12.83	9.85
Crystal morphology	Pale yellow, pyramidal	Pale yellow, tabular	Yellowish brown, tabular
Crystal dimensions/mm	0.10–0.16	0.62 x 0.44 x 0.10	0.21 x 0.10 x 0.07
Absorption factors	1.09–1.15	1.12–1.72	1.07–1.10
(sinθ/λ)max/Å^{-1}	0.596	0.705	0.539
Reflections measured	2259, 1443 $>3\sigma(I)$	3002, 2622 $>3\sigma(I)$	1314, 902 $>3\sigma(I)$
Parameters refined	205	243	125
Conventional R(|F|)	0.046	0.052	0.105

in the presence of slightly more than 2 moles of $HClO_4$, salt I is obtained in reasonable yield.

Crystal Data and Intensity Data Collection

Crystal data for the three structures and other experimental details are given in Table II. Cell parameters were obtained from precession photographs and refined on the diffractometer. In the case of the monoprotonated complex (III), precession photographs of some crystals revealed satellite reflections indicating long range electron density fluctuations. For crystals from a second batch, these satellites were not observed, indicating a more statistical disorder. They were used for data collection. Owing to the rapid fall-off of intensities at higher angles, however, measurements were made only up to $2\theta = 45°$. Intensity data were collected on an automatic Picker FACS-I diffractometer by the 2θ scan technique using graphique monochromated MoKα radiation. Stationary backgrounds were measured on both sides of the scan. The intensities were corrected for absorption, the dimensions of the crystals having been measured with an optical microscope using the known Miller indices of their faces.

TABLE III
Atomic coordinates of {Pd(Hdapi)$_2$} $(ClO_4)_4.2H_2O$ (structure I). The e.s.d.-s are given in parentheses

Atom	x.10^4	y.10^4	z.10^4
Pd	0	0	0
N(1)	1168(4)	−271(6)	710(4)
N(2)	−706(5)	892(6)	938(4)
N(3)	959(5)	2579(7)	768(4)
C(1)	1391(6)	564(8)	1434(5)
C(2)	539(6)	691(9)	1998(5)
C(3)	−211(6)	1514(9)	1645(5)
C(4)	163(6)	2736(7)	1355(5)
C(5)	1718(6)	1819(8)	1129(5)
Cl(1)	4328(2)	1473(3)	967(2)
Cl(2)	2295(2)	3314(2)	3387(2)
O(1)[a]	3837(41)	570(62)	1319(52)
O(11)[a]	4090(40)	317(53)	1324(48)
O(2)	3824(5)	1812(6)	250(3)
O(3)[a]	3936(16)	2362(35)	1560(24)
O(31)[a]	4468(16)	2446(33)	1525(22)
O(4)[a]	5141(24)	900(28)	722(25)
O(41)[a]	5241(23)	1767(35)	814(25)
O(5)	1872(5)	3524(6)	4181(4)
O(6)	3163(5)	3889(7)	3382(4)
O(7)	1732(5)	3816(6)	2767(4)
O(8)	2390(6)	2027(6)	3258(4)
O(9)[+]	2075(4)	749(5)	4861(4)

[a] population parameter ½
[+] water oxygen

TABLE IV
Atomic coordinates of {Pd(dapi)$_2$} $(ClO_4)_2$ (structure II)

Atom	x.10^4	y.10^4	z.10^4
Pd	2327.3(.4)	0	4160.3(.8)
N(1)	2115(5)	−2063(9)	2483(10)
N(2)	1161(5)	683(10)	3392(10)
N(3)	2055(5)	881(9)	−374(9)
N(4)	2486(4)	2020(9)	5956(10)
N(5)	3455(5)	−823(9)	5057(10)
N(6)	3590(6)	2282(11)	2890(13)
C(1)	1616(6)	−1925(12)	471(12)
C(2)	792(6)	−1271(13)	715(14)
C(3)	804(6)	537(11)	1278(13)
C(4)	1251(6)	1492(13)	−109(14)
C(5)	2001(7)	−875(12)	−915(14)
C(6)	4113(6)	410(12)	5538(14)
C(7)	3922(6)	1624(13)	7130(14)
C(8)	3272(6)	2796(12)	6279(13)
C(9)	3450(7)	3543(12)	4318(16)
C(10)	4274(7)	1268(15)	3613(17)
Cl(1)	847(2)	5187(5)	5027(3)
Cl(2)	3858(2)	6255(3)	80(4)
O(1)	64(6)	5141(17)	4094(13)
O(2)	1363(6)	4659(15)	3797(14)
O(3)	986(9)	6765(12)	5397(16)
O(4)	900(8)	4297(15)	6699(15)
O(5)	3083(5)	5629(10)	−72(14)
O(6)	4413(4)	4988(16)	311(10)
O(7)	3957(6)	7238(12)	1739(13)
O(8)	3911(8)	6972(15)	8386(14)

Structure Determination

The space groups of the three structures were determined from systematic extinctions. The absence of the center of symmetry in structure (II) was indicated by the distribution of the E-values, as well as by the appearance of the Fourier map phased with the palladium atoms. The palladium atoms were found from the Patterson functions, the remaining atoms from successive Fourier maps. The structures were refined by block-diagonal least squares with anisotropic temperature factors and without including the hydrogen atoms to final conventional R-values of 0.046 (I), 0.052 (II) and 0.105 (III), minimizing the quantity $\Sigma w(|F_0| - |F_c|)^2$. The weights used were $w = \sigma^{-2}$, σ being the e.s.d. of an observed structure factor determined by counting statistics and the fluctuations of three periodically measured check reflections. Secondary extinction[10] was refined and found to be negligible. Atomic form factors were taken from Cromer and Waber.[11] Dispersion corrections[12] were included for Pd and Cl. The calculations were carried out with the programs of the X-RAY SYSTEM[13] and ORTEP[14] for the illustrations. Final coordinates are given in Tables III, IV and V.

TABLE V
Atomic coordinates of {Pd(dapi)(Hdapi)} $(NO_3)_3.H_2O$ (structure III). The water molecule was not found

Atom	x.10^4	y.10^4	z.10^4
Pd	0	0	0
N(1)	314(20)	1467(14)	675(18)
N(2)	1751(7)	22(20)	-517(15)
N(3)	3754(20)	238(15)	3373(18)
C(1)	2217(32)	1888(18)	1727(30)
C(2)	2933(30)	1780(19)	713(31)
C(3)	3345(29)	667(18)	568(27)
C(4)	4486(23)	137(23)	2347(23)
C(5)	3310(29)	1302(17)	3556(26)
N(4)	7579(28)	2254(19)	2009(31)
O(1)	6622(23)	1789(16)	664(20)
O(2)	9126(22)	2060(16)	2769(23)
O(3)	7064(23)	2881(19)	2552(25)
N(5)[a]	-674	4669	340
O(4)[a]	851	4489	1025
O(5)[a]	-1376	4290	960
O(6)[a]	-1477	5217	-935

[a] nitrate ion refined as a rigid group with population parameter ½

Observed and calculated structure factors and the anisotropic thermal parameters may be requested from the authors (D.S.).

The following remarks apply to the individual structures:

Salt I Three of the oxygen atoms of one of the two independent perchlorate ions, O(1), O(3) and O(4), showed abnormally elongated thermal ellipsoids at R = 0.048, the longest principal axes being $\sqrt{U} \simeq 0.6$ Å. This and the corresponding Fourier map showing banana shaped electron distributions for the three atoms approximately on the circumference of a circle suggested a rotation or large amplitude vibration of the ion about the Cl(1)–O(2) bond. These atoms were therefore split into pairs of half-weighted atoms which lowered R to 0.046. Although the large anisotropic motions could thereby not be removed completely, Hamilton's[15] significance test shows the lower R to be indeed meaningful. The phenomenon of oxygen disorder in perchlorate ions is well known[16] and leads to Cl–O distances considerably shorter than the accepted value[17] of 1.46 Å.

Salt II Many of the perchlorate oxygens show again abnormally high thermal parameters and short Cl–O distances. Since in this basket-like structure it is important to know whether the uncoordinated nitrogens are connected by a hydrogen bond, the determination of the hydrogen atoms from a difference Fourier map was attempted. This showed numerous small peaks and results were ambiguous. The positions of 22 hydrogen atoms were therefore calculated. Four hydrogen atoms were omitted since there were no corresponding peaks in the Fourier map. Although R was thereby lowered from 0.052 to 0.050, these positions could not be refined by least squares. Results were particularly unsatisfactory for the most interesting hydrogen atoms attached to the secondary nitrogens.

Salt III This structure is necessarily disorded since there are two formula units per cell with space group symmetry $P2_1/c$. The palladium atoms are constrained to occupy centers of symmetry implying statistical equivalence of "dapi" and "Hdapi". Two of the six nitrate ions must be disordered over a fourfold position, the only special positions being centers of symmetry. The half-weight nitrogen atom N(5) was found at a distance of about 1 Å from an inversion center. The corresponding half-weight oxygen atoms O(4), O(5) and O(6) were located approximately using the known geometry of the ion, situated as they were in broad regions of diffuse electron density. The distance between O(4) and the inversion equivalent of O(6) being 0.76 Å, the half-weight ions are also approximately related by a rotation about the line O(4)–O(6). Anisotropic refinement of these atoms resulted in two non-positive definite temperature parameters at R = 0.10. The disordered nitrate was therefore refined as a rigid group with N–O distances of 1.24 Å and individual isotropic temperature factors. The dimensions of the ordered nitrate group are normal.

The two water molecules per unit cell whose presence is clearly indicated by elemental analysis and by the measured density, could not be found at all. They must be severely disordered. In fact, they would otherwise have to occupy centers of symmetry. But all centers are either occupied by palladium or are very close to the disordered nitrate ions.

Another disconcerting feature of this structure is the high value for the thermal parameter U_{22} of many of the atoms. This leads to doubts about the space group $P2_1/c$. The presence of the *c*-glide having been established by many systematic extinctions, desymmetrisation to the space group Pc was unsuccessfully attempted. Treating "dapi" and the nitrate ions as rigid groups, the R-value could be lowered to 0.11 with isotropic temperature factors. Removal of the group constraints or introduction of anisotropic temperature factors lead,

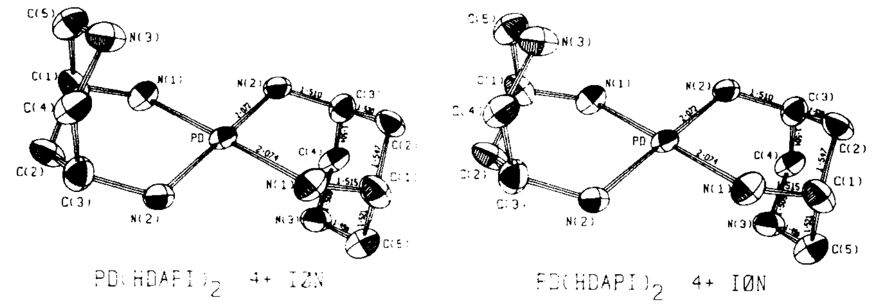


FIGURE 1 Stereoscopic view of the $Pd(Hdapi)_2^{4+}$ ion (I). Standard deviations of the bond lengths are Pd–N 0.006, N–C 0.011, C–C 0.012 Å. The vibrational ellipsoids are drawn at 50% probability levels.

however, to unacceptable distortions or ellipsoids respectively. The difficulties encountered in the refinement of this structure are probably due to the fact that the atomic positions correspond to a symmetrized substructure of an ordered structure with a very large unit cell, as indicated by the satellite reflections observed for some crystals.

DISCUSSION

Figures 1–3 show stereoscopic views and bond lengths of the three complexes. Angles are shown in Table VI. In accordance with their optical and magnetic properties, all structures show a square planar coordination of palladium. As expected, the primary amino groups of "dapi" coordinate, hence all the chelate rings are six-membered. These, as well as the piperidine rings are all in the chair conformation which produces the least strain but brings the uncoordinated ring nitrogens rather close to the metal atom, namely 3.358(8) Å in (I), 3.167 and 3.085 (9) Å in (II), and 3.21 (1) Å in (III). The bonding Pd–N distances are 2.072 and 2.074 (6) Å (I), 2.041, 2.054, 2.067 and 2.077 (7) Å (II), and 1.98 and 2.02 (2) Å (III). The distance between the non-coordinated nitrogen atoms N(3)–N(6) in (II) is 3.383 (15) Å.

The centrosymmetric cations $Pd(Hdapi)_2^{4+}$ (I) and $Pd(dapi)(Hdapi)^{3+}$ (III) have an anti configuration, i.e. the non-coordinated nitrogens are at opposite sides of the coordination square. These are both protonated in (I). The centrosymmetry of (III) can be explained by noting that the short intermolecular N(3) . . . N(3) distance of 2.72 (2) Å as well as the angles C(4)–N(3) . . . . N(3) and C(5)–N(3) . . . N(3) (108 and 101°) suggest a hydrogen bond between neighboring molecules on which the proton can be expected to be disordered. This distributes the single ammonium charge of (III) equally between the non-coordinated nitrogens. The *anti* configuration is to be expected for both structures (I) and (III) since the formal positive charges on N(3) are then at their largest possible distance.

The structure of $Pd(dapi)_2^{2+}$ (II), on the other hand, is very unusual. Since deprotonation of (III) removes the positive charges on the non-coordinated amino groups, they could now move closer to the metallic center and complete an octahedral coordination. The geometry of the chelate and piperidine rings would thereby hardly be changed. Indeed, the Pd–N(3) distances are reduced with respect to (I) by 0.15 Å in (III) and 0.23 Å in (II). Most surprisingly however, the deprotonation induces an isomerisation from the *anti* structure (III) to the basket-like *syn* structure (II). Both non-coordinated nitrogens are now on the

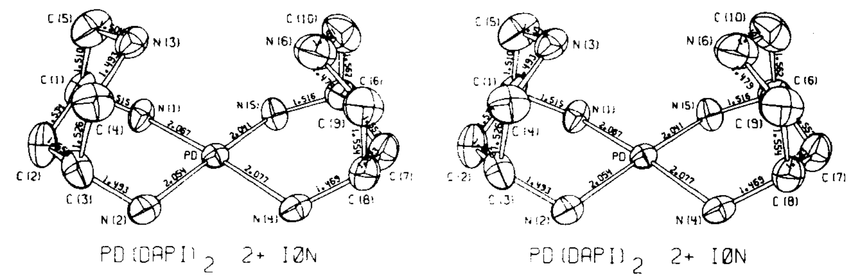


FIGURE 2 Stereoscopic view of the $Pd(dapi)_2^{2+}$ ion (II). Standard deviations of the bond length are Pd–N 0.007, N–C 0.013, C–C 0.015 Å.

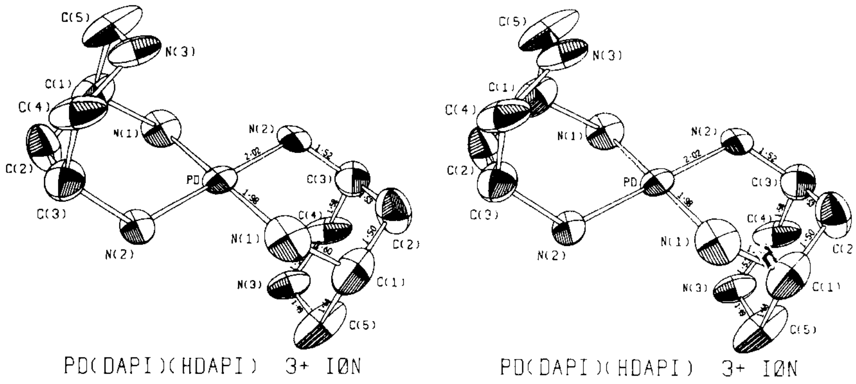


FIGURE 3 Stereoscopic view of the Pd(dapi)(Hdapi)$^{3+}$ ion (III). Standard deviations of the bond lengths are Pd–N 0.02, N–C 0.03, C–C 0.04 Å.

same side of the coordination square. This implies that some of the Pd–N bonds must be broken and newly formed and explains the slow reaction described above. It is very improbable that one of the ligands separates completely from the metal during this process. More likely, the isomerisation is achieved in three steps by replacing in turn N(1) by N(3), N(2) by N(1) and finally N(3) by N(2) (see Figures 1 or 3). Intermediate isomers containing five-membered chelate rings are therefore to be expected. This also explains the changes in pH observed during the isomerisation process.

The fact that the piperidine nitrogens do not just move closer to the metallic center of the *anti*-structure must be caused by repelling forces between the filled 4d$_{z^2}$ orbital of Pd(II) and the lone pair electrons of these nitrogens. This repulsion does not lead to the expected rearrangement of the d-electrons from $t_{2g}{}^6 d_{z^2}{}^2 d_{x^2-y^2}{}^0$ to $t_{2g}{}^6 d_{z^2}{}^1 d_{x^2-y^2}{}^1$, the electron configuration in octahedral, paramagnetic Ni(dapi)$_2^{2+}$, but to a rearrangement of the ligands. It seems to be preferable to place the e$_g$-electrons entirely on one side of the x-y plane and leave room for the bulky lone pair orbitals of the uncoordinated nitrogens on the other side. This could be achieved with hybridisations d^{2}sp^2 or d^{2}p^3, furnishing a set of 5 orbitals directed towards the corners of a square pyramid. The four orbitals within the square bind to the primary amino groups of "dapi" whereas the fifth hybrid orbital can be occupied by two 4d-electrons, the other six being placed in those d-orbitals not needed for hybridisation.

A link between the two piperidine nitrogens by hydrogen bonding might also be considered to assist the formation of the *syn* structure. However, for a bridge N–H . . . O . . . H–N via a water molecule which would be present only in solution, the N–N distance should be about 6 Å. The distance of 3.38 Å between the two non-coordinated nitrogens is almost short enough to allow direct bridging by a proton

TABLE VI
Bond angles (°). The second numbers in the atom identifiers refer to row (b) of structure (II). E.s.d.-s are given in parentheses

	I	IIa	IIb	III
N(1,4)–Pd–N(2,5)	93.9(3)	90.2(3),	93.3(3)	95(1)
Pd–N(1,4)–C(1,8)	121.4(5)	118.3(6),	118.6(6)	120(2)
Pd–N(2,5)–C(3,6)	121.6(5)	117.6(6),	117.9(6)	116(1)
N(1,4)–C(1,8)–C(2,7)	109.7(7)	108.9(7),	111.6(8)	110(2)
N(1,4)–C(1,8)–C(5,9)	110.4(7)	112.5(8),	109.5(7)	109(2)
N(2,5)–C(3,6)–C(2,7)	111.5(7)	108.1(7),	111.5(8)	112(2)
N(2,5)–C(3,6)–C(4,10)	109.2(7)	113.5(7),	109.9(7)	108(2)
C(1,8)–C(2,7)–C(3,6)	114.1(7)	113.0(8),	111.0(8)	113(2)
C(2,7)–C(3,6)–C(4,10)	111.8(7)	109.7(8),	112.4(9)	112(2)
C(3,6)–C(4,10)–N(3,6)	112.1(7)	116.6(8),	108.7(9)	113(2)
C(5,9)–N(3,6)–C(4,10)	112.6(6)	109.7(8),	112.4(8)	116(2)
N(3,6)–C(5,9)–C(1,8)	112.7(7)	114.8(8),	111.4(8)	111(2)
C(5,9)–C(1,8)–C(2,7)	111.3(7)	110.7(8),	111.4(9)	115(2)

which would, however, stabilize the monoprotonated complex Pd(dapi-H-dapi)$^{3+}$. Yet, the isomerisation from *anti* to *syn* apparently takes place only after the second ammonium proton has left the molecule. In addition, the *syn* and *anti* forms of Pd(dapi)$_2^{2+}$ have almost the same basicity (pK_1 = 6.35 and 6.43, pK_2 = 4.16 and 4.27 respectively). A bridging proton would imply pK_1 to be considerably larger and pK_2 smaller for the *syn* than for the *anti* isomer since it would be more strongly bonded.

For a symmetrical diprotonic base, ΔpK = pK_1 - pK_2 depends on the distance between the two basic sites, since the second proton will be repelled by the charge of the first proton. Yet ΔpK is almost the same for the *syn* and *anti* isomers, although the uncoordinated nitrogens are almost at the double distance in the latter complex. This might be explained by assuming a change of conformation of the piperidine rings from chair to boat on protonation of the *syn* form which would increase the distance between the basic sites and might induce the isomerisation.

The mean values of 1.501 and 1.527 Å for N–C and C–C bond lengths in the piperidine ring in structures (I) and (II) are in good agreement with corresponding values[18] reported in the literature. The bond angles are close to tetrahedral. The standard deviations in structure (III) being very high, the large deviations of the distances N(1)–C(1), C(1)–C(5) and C(3)–C(4) from the expected values are not significant.

TABLE VII

Acute angles between least squares planes (°). The planes are defined by the following atoms where the second numbers in the identifiers refer to row (b) of structure (II): (1) Pd, N(1,4), N(2,5); (2) N(1,4), N(2,5), C(3,6), C(1,8); (3) C(1,8), C(2,7), C(3,6); (4) C(1,8), C(3,6), C(4,10), C(5,9); (5) C(4,10), C(5,9), N(3,6)

Planes	I	IIa	IIb	mean	III
(1) ⌢ (2)	20.3	30.5,	27.6,	31.6	32.9
(1) ⌢ (3)	44.9	30.8,	36.7,	33.7	30.1
(1) ⌢ (4)	89.4	77.4,	82.0,	79.7	75.9
(1) ⌢ (5)	40.0	31.6,	26.7,	29.2	30.6

Dihedral angles in the three compounds are given in Table VII. The effect of the protonation is clearly seen in the change of corresponding angles. It is interesting to note that the angles in the monoprotonated complex (III) are quite close to those in the unprotonated complex (II).

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