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Palladium(II) complexes of 1,4,7-triazacyclononane ([9]aneN_3)

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Abstract

The syntheses of several Pd(II) complexes of 1,4,7-triazacyclononane, [9]aneN_3, and the molecular structure of two complexes by X-ray diffraction are reported. The diprotonated bis complex, $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$, contains the ligands in the *anti* conformation and is structurally similar to the previously reported non-protonated PdL_2^{2+} in $[PdL_2]PF_6$. The acidity constants (pK_a) of $Pd(HL)_2^{4+}$ in 0.1 M ClO_4^- at 25 °C are 2.40 and 4.72, respectively. The structure of the protonated mono complex, $[PdHLBr_2]ClO_4$, is also determined.

Introduction

The metal complexes of 1,4,7-triazacyclononane, [9]aneN_3, are of considerable interest because of the unique characteristics which this small ring ligand imparts to these complexes. The substantial stability and uncharacteristic inertness of the complexes are related to the fixed geometry of the ligating amine groups. Spectroscopic and electrochemical properties of these complexes also show unexpected patterns for amine complexes and several compounds with metal ions in unusual oxidation states have been identified [1]. In most cases [9]aneN_3 functions as a tridentate ligand, however in circumstances where tridentate coordination is not possible the non-bonded amine function has been shown to profoundly influence chemical properties. For example, the planar complexes of Pt(II) and Pd(II) are readily oxidized by air to octahedral Pt(IV) and Pd(III) [2–4]. Further, there is evidence provided by ^{13}C NMR that $[PdL_2]^{2+}$ (L=[9]aneN_3) is fluxional [5].

We are currently investigating the reactivity of metal complexes containing non-coordinated reactive sites. The Pd(II) and Pt(II) complexes of [9]aneN_3 provide examples of these types of compounds and this investigation was initiated to learn more about the chemistry of the Pd(II)–[9]aneN_3 complexes.

We present here the syntheses of several Pd(II) complexes and X-ray crystallographic structural studies of two compounds where the ligands display bidentate coordination and the non-bonded nitrogen atoms are positively charged by the presence of an additional proton. To complement this X-ray study comparisons of structural features are made with the known $[PdL_2](PF_6)_2$ where the non-coordinated nitrogen atoms of the ligand are not positively charged. In addition, the acid dissociation constants of $Pd(HL)_2^{4+}$ have been determined.

Experimental

Materials

Palladium salts were purchased from either Strem Chemicals, Alfa Division/Ventron or Aldrich Chemicals and were used without further purification. [9]aneN_3 was prepared by previously reported procedures [6] or purchased from Aldrich Chemicals. All other chemicals were reagent grade and used without further purification.

Syntheses

General procedure for bis[9]aneN_3 complexes

A stirred 15 ml aqueous solution containing 2.0 mmol [9]aneN_3 and enough acid to keep the pH<4** was purged with dinitrogen and heated to 80 °C. To this solution was added 1.0 mmol of palladium(II) salt†.

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**The pH was kept in the acid range during the initial stages of the reaction to avoid precipitation of a black solid presumably PdO.

†In most cases the palladium salt containing the anion of the reaction product was employed as starting material. In some cases $PdCl_2$ or K_2PdCl_4 was used as starting material, and after the reaction was complete the product was added to a salt solution containing the anion of the desired complex salt. This usually gave the anion salt without a trace of chloride. However, in the case of the mixed chloride–perchlorate system use of these chloride salts, even in the presence of much higher concentrations of perchlorate afford the mixed salt $[PdHL_2](ClO_4)_2Cl \cdot H_2O$.

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Over the course of 2 h the pH of the solution was slowly adjusted to 7 by the addition of 1 M sodium hydroxide. This warm solution was then filtered into 10 ml of 2 M sodium salt solution containing the anion of the desired complex*. Crystals of the bis complexes generally form immediately or after cooling. In the case of the chloride salt the solution must be concentrated to approximately 8 ml to obtain the product. Because of the varying solubilities on these slightly acidic solutions either non-protonated, monoprotonated or diprotonated salts are obtained. Non-protonated complexes are isolated with chloride, perchlorate and bromide; a monoprotonated complex is formed in the presence of nitrate and a diprotonated salt is isolated from solutions containing sulfate ion. Acidification ($HClO_4$) of solutions containing PdL_2^{2+} gives crystals of $[Pd(HL)_2](ClO_4)\cdot H_2O$ suitable for X-ray crystallographic study; whereas, the addition of a stoichiometric quantity of hydrochloric acid to a solution containing $[PdL_2](ClO_4)_2$ gives the mixed salt $[PdHL_2](ClO_4)_2Cl\cdot H_2O$.

Non-protonated complexes

$[PdL_2]Br_2\cdot 2H_2O$. *Anal.* Calc. for $C_{12}H_{34}N_6Br_2O_2Pd$: C, 25.71; H, 6.11; N, 14.99; Br, 28.50. Found: C, 25.69; H, 5.83; N, 14.70; Br, 29.02%. Yield 76%.

$[PdL_2](ClO_4)_2$. *Anal.* Calc. for $C_{12}H_{30}N_6Cl_2O_8Pd$: C, 25.56; H, 5.36; N, 14.90; Cl, 12.58. Found: C, 25.34; H, 5.00; N, 14.94; Cl, 12.62%. Yield 90%.

Monoprotonated complexes

$[PdHL_2](NO_3)_3\cdot H_2O$. *Anal.* Calc. for $C_{12}H_{33}N_9O_{10}Pd$: C, 25.29; H, 5.83; N, 22.92. Found: C, 25.44; H, 5.64; N, 22.36%. Yield 57%.

$[PdHL_2](ClO_4)_2Cl\cdot 2H_2O$. *Anal.* Calc. for $C_{12}H_{35}N_6Cl_3O_{10}Pd$: C, 22.26; H, 5.54; N, 13.21; Cl, 16.72. Found: C, 22.42; H, 5.00; N, 12.95; Cl, 16.63%.

Diprotonated complexes

$[Pd(HL)_2](SO_4)_2\cdot 3.5H_2O$. *Anal.* Calc. for $C_{12}H_{39}N_6S_2O_{11.5}Pd$: C, 23.17; H, 6.32; N, 15.51; S, 10.31. Found: C, 23.02; H, 6.22; N, 13.57; S, 10.42%. Yield 70%.

$[Pd(HL)_2]Cl_4\cdot 3H_2O$. *Anal.* Calc. for $C_{12}H_{38}N_6Cl_4O_3Pd$: C, 25.61; H, 6.81; N, 14.94; Cl, 25.20. Found: C, 25.39; H, 6.23; N, 14.71; Cl 25.40%. Yield 59%.

$[Pd(HL)_2](ClO_4)_4\cdot H_2O$. *Anal.* Calc. for $C_{12}H_{34}N_6Cl_4O_{17}Pd$: C, 18.42; H, 4.38; N, 10.74; Cl, 18.12. Found: C, 18.25; H, 4.35; N, 10.80; Cl, 18.20%. Yield 63% by addition of $HClO_4$ to $[PdL_2](ClO_4)_2$.

Preparation of monocomplexes

$[Pd(HL)Br_2]Br$. To a warm (60 °C) 0.05 M $[PdL_2]Br_2$ solution was added 47% hydrobromic acid until the pH was approximately 3 and remained constant for 0.5 h. The resulting orange solution was cooled and on slow evaporation to one-third the original volume gave red needle-shaped crystals. *Anal.* Calc. for $C_6H_{16}N_3Br_3Pd$: C, 15.12; H, 3.38; N, 8.82; Br, 50. Found: C, 15.15; H, 3.47; N, 8.79; Br, 49%. Yield 80%.

$[Pd(HL)Br_2]ClO_4$. To a warm (60 °C) 0.05 M $[PdL_2]Br_2$ solution containing excess bromide (1 M NaBr) was added 1 M perchloric acid until the solution was at pH 3. On cooling and slow evaporation red–orange needles of the perchlorate salt formed. These crystals were X-ray quality and the X-ray molecular weight was in agreement with the above stoichiometry. Elemental analysis of this material gave correct ratios for C, H. N and Br but percentages tended to be slightly low indicating the presence of a small amount (<1%) of impurity.

pH potentiometry

All measurements were made with a Beckmann Φ71 model pH meter fitted with an Orion 91-02 combined glass-calomel electrode. Since perchlorate ion was present in the supporting medium of solutions used in this study the electrolyte of the reference electrode was filled with sodium chloride in place of potassium chloride to prevent precipitation of potassium perchlorate. The meter-electrode system was calibrated with 4.008 buffer at 25 °C. Correction to the meter was made by measuring the pH of 0.0100 M $HClO_4$ which was 0.1 M in ClO_4^- ($NaClO_4$). The value measured was used to compute a correction factor by assuming that the pH of the 0.0100 M $HClO_4$ was 2.000.

Fifteen solutions were prepared for batch titration by taking 3.00 ml of 0.00706 M $[PdL_2](ClO_4)_2$ and appropriate amounts of 0.2382 M $HClO_4$ and 0.500 M $NaClO_4$ so that on dilution to a total volume of 6.00 ml with water the ratio of moles of acid added to moles of complex ranged from 0.20 to 1.86 and the total concentration of ClO_4^- was 0.100 M. The solutions were kept at 25 °C and purged with dinitrogen during pH measurements. pH measurements were made every 2 to 3 days over the course of several weeks until no further change in pH was detected (±0.004 pH units).

Equilibrium constants were calculated from pH potentiometric data with the program SCOGS2 [7].

Conductance measurements

Conductivity measurements were made with a Leeds and Northrup model 4959 electrolytic conductivity bridge. A Yellow Springs Instrument Co. model 3403 conductivity cell was used and all measurements were made in a thermostatted vessel at 25 °C with a dinitrogen

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*See footnote† p. 61.

TABLE 1. Experimental crystallographic data for $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$ (A) and $[PdHLBr_2]ClO_4$ (B)

	Compound A	Compound B
Formula	$C_{12}H_{34}N_6Cl_4O_{17}Pd$	$C_6H_{16}N_3Br_2ClO_4Pd$
Molecular weight	782.6	495.9
Crystal size (mm)	0.7×0.3×0.15	0.5×0.2×0.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.236(4)	11.677(3)
b (Å)	22.224(9)	7.238(2)
c (Å)	14.348(8)	16.403(5)
β (°)	92.559 (0.04)	102.15(6)
V (Å^3)	2624	1351
Z	4	4
Temperature (°C)	22	22
D_{calc} (g cm^{-3})	1.98	2.44
D_{meas} (g cm^{-3})	2.04	
2θ Range	2.5–64.9	2.8–65.0
No. parameters refined	497	154
No. non-zero reflections ($I = 3\sigma(I)$)	3499	1865
R[a]	0.034	0.088
R_w[b]	0.030	0.090

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma(F)]^{-2}$.

purge made before each reading. The cell constant was obtained by measuring the conductance of 0.0200 M potassium chloride solution. Solution concentration of the complex ions was approximately 0.001 M.

X-ray crystallography

All X-ray measurements were made on a Syntex (Nicolet) $P2_1$ diffractometer with monochromated Mo radiation filtered through a graphite monochromator, $\lambda = 0.71073$ Å, using θ–2θ scans. Cell dimensions were determined by least-squares refinement of 15 reflections. Both structures were determined with the heavy-atom method and refined by full matrix least-squares. Absorption corrections were not made. For $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$ hydrogen atoms were located on difference maps and refined with isotropic temperature factors. Attempts to refine the structure of $[PdHLBr_2]ClO_4$ by placing hydrogen atoms at expected positions failed and only the heavy atoms were included in the calculations. Atomic scattering factors were taken from ref. 8.

Experimental crystallographic data are shown in Table 1.

Discussion

The reaction of Pd(II) salts with $[9]aneN_3$ in aqueous solutions of pH 4–7 yields Pd(II)–$[9]aneN_3$ complexes. In neutral solutions where $[9]aneN_3$ to Pd(II) ratio is 2:1 or greater $[PdL_2]^{2+}$ is readily formed. This complex ion has been isolated in a variety of salts including Br^-, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-} and PF_6^- [4, 5]. If reactions are carried out at lower pH (4 to 5), or acid added to $[PdL_2]^{2+}$ solutions, monoprotonated, $[PdHL_2]^{3+}$, and diprotonated, $[Pd(HL)_2]^{4+}$, complexes are formed. Measurement of the acid dissociation constants of $[Pd(HL)_2]^{4+}$ indicates that formation of $[PdHL_2]^{3+}$ is maximized at pH 3.5. Two monoprotonated salts $[PdHL_2](NO_3)_3 \cdot H_2O$ and $[PdHL_2](ClO_4)_2Cl \cdot H_2O$ have been isolated from these moderately acidic solutions. Complexes containing the diprotonated species are generally isolated from solutions of greater acidity. In acid solutions containing a large excess of Br^- the $[9]aneN_3$ is displaced from Pd(II) forming $[PdHLBr_2]^{2+}$. These complexes possess characteristic red–orange coloration due to the presence of a strong charge transfer band at 320 nm. The bis complexes are generally very pale yellow in color.

Aqueous conductivities for these complexes are in the expected range [9]. The $[PdL_2]^{2+}$ complexes have molar conductivities of approximately 210 mhos and the $[PdHL]^{3+}$ complexes fall in the range of 350 mhos. The diprotonated salts have much greater molar conductivities due to the high cation charge and the strong acidity of the species. Nonayama [10], who first synthesized several Pd(II) complexes containing cyclic triamine ligands obtained conductances in the range of 192 to 249 mhos for several $[PdHL'_2]^{3+}$ species ($L' = [9]aneN_3$ or 1,4,7-triazacyclododecane).

The acid dissociation constants of the diprotonated complex were measured in 0.1 M ClO_4^- media and the values are as follows.

Reaction	pK_a
$Pd(HL)_2^{4+} \rightleftharpoons PdHL_2^{3+} + H^+$	2.40(5)
$PdHL_2^{3+} \rightleftharpoons PdL_2^{2+} + H^+$	4.72(3)

These numbers are not unusual considering that H_3L^{3+} is a strong acid [11] and the presence of the metal center has considerably less effect on the acid dissociation than a proton. In fact, $PdHL_2^{3+}$ which has the same charge as the triprotonated ligand is a moderately weak acid.

The structure of $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$ is shown in Fig. 1 and fractional coordinates, bond lengths and angles are contained in Tables 2–4. The complex adopts the *anti* isomeric conformation which has also been reported for the bis complexes of Pt(II) [3] and Pd(II) [5] with non-protonated [9]aneN_3. The ligands are bidentate and the four bonded nitrogen atoms are arrayed in a planar configuration about the Pd(II) ion. There is considerable deformation from the ideal square with N–Pd–N internal angles of 81.0 and 81.2°. The Pd–N bond distances of 2.062 and 2.076 Å are longer than those found in Pd(II) secondary amine macrocyclic complexes [12], even when the Pd(II) is coordinated by ring nitrogens at only three sites in the plane [13]. The non-bonded nitrogen atoms lie at 3.671 and 3.658 Å from the metal.

A comparison of the molecular structure of $[Pd(HL)_2]^{4+}$ obtained in this study with $[PdL_2]^{2+}$ in $[PdL_2](PF_6)_2$ which contains the *anti* conformation and non-protonated non-coordinated nitrogen [5] shows significant similarity (Fig. 2). The non-bonded Pd(II)---N distance (3.499 Å) differs from the Pd(II)---NH$^+$ of $[Pd(HL)_2](ClO_4)_4$ by only 0.16 Å.

Interestingly, the recently reported monoprotonated complex, $[PdHL_2](PF_6)_2NO_3 \cdot H_2O$, contains the *syn* isomer and this structure exhibits considerably shorter Pd(II)---N non-bonded distances (2.982 and 3.079 Å) than either the non-protonated or diprotonated complexes [4]. Also noteworthy is that one of the Pd(II)–N bond distances is approximately 0.05 Å shorter than the other three which average 2.068 Å. This short bond length involves the same ligand which contains the shorter non-bonded Pd(II)---N distance.

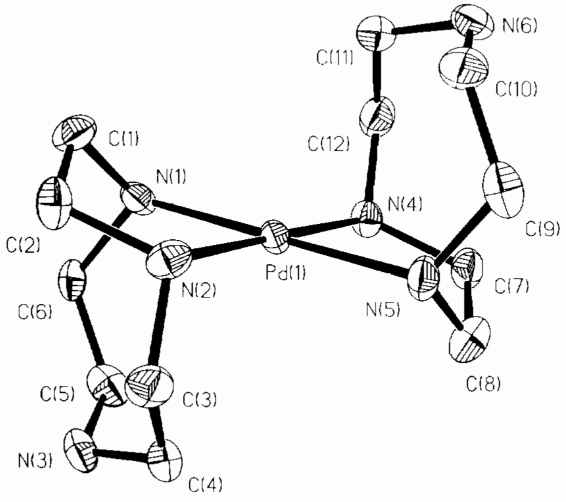

Fig. 1. ORTEP drawing and numbering scheme of $[Pd(HL)_2]^{2+}$ cation in $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$.

TABLE 2. Final values[a] for refined atomic coordinates and temperature parameters for heavy atoms $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$

Atom	*x*	*y*	*z*	B_{eq}[b] (Å^2)
Pd	0.260125(41)	0.128475(12)	0.260898(23)	1.6
Cl1	0.79903(13)	0.37629(6)	0.11818(7)	2.3
Cl2	0.71043(13)	0.11839(6)	0.04867(8)	2.3
Cl3	0.71689(12)	0.37369(6)	0.40357(9)	2.0
Cl4	0.31221(13)	0.36783(7)	−0.02843(7)	2.8
O1	0.85270(50)	0.38369(26)	0.02644(25)	5.4
O2	0.72293(56)	0.31967(25)	0.12388(31)	5.6
O3	0.69151(55)	0.42389(25)	0.13861(31)	6.9
O4	0.93723(40)	0.37812(18)	0.18349(23)	3.4
O5	0.55212(42)	0.14185(21)	0.06467(26)	4.3
O6	0.82610(46)	0.15419(20)	0.09852(31)	4.9
O7	0.73475(51)	0.11972(24)	−0.04956(25)	5.0
O8	0.72287(55)	0.05735(18)	0.08177(27)	4.8
O9	0.67101(46)	0.36566(21)	0.49703(23)	4.0
O10	0.57922(54)	0.38501(32)	0.34700(30)	8.2
O11	0.79039(59)	0.32071(25)	0.37281(35)	6.0
O12	0.82707(60)	0.42222(25)	0.40028(30)	5.9
O13	0.20757(46)	0.39128(26)	0.90212(30)	6.1
O14	0.47493(42)	0.37945(22)	0.95269(27)	4.4
O15	0.27461(60)	0.38389(21)	0.05951(27)	7.1
O16	0.28954(76)	0.30262(23)	0.96892(41)	8.5
OW	0.28260(37)	0.37905(13)	0.25198(24)	3.0
N1	0.10094(41)	0.07377(15)	0.18489(23)	1.7
N2	0.24671(42)	0.05803(15)	0.35478(23)	1.7
N3	0.42911(46)	−0.01795(16)	0.20059(27)	2.4
N4	0.27570(42)	0.19921(15)	0.16720(23)	1.7
N5	0.41969(43)	0.18284(16)	0.33707(24)	2.0
N6	0.09471(48)	0.27618(17)	0.32076(28)	2.7
C1	−0.00726(55)	0.05049(20)	0.25790(32)	2.1
C2	0.10086(57)	0.01953(21)	0.33077(32)	2.2
C3	0.39918(56)	0.02150(24)	0.36669(31)	2.2
C4	0.50045(57)	0.01744(21)	0.28246(34)	2.3
C5	0.34508(60)	0.01727(22)	0.12235(32)	2.4
C6	0.16212(61)	0.02401(21)	0.12570(30)	2.1
C7	0.42277(56)	0.23743(20)	0.19200(32)	2.2
C8	0.52847(55)	0.20633(2)	0.26447(33)	2.4
C9	0.35807(61)	0.23282(22)	0.39665(32)	2.5
C10	0.17646(67)	0.24057(21)	0.39907(32)	2.7
C11	0.02273(56)	0.24034(21)	0.23919(35)	2.3
C12	0.12362(58)	0.23516(22)	0.15500(33)	2.4

[a] e.s.d.s are given in parentheses. [b] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j B_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

The dibromo complex, $[PdHLBr_2]ClO_4$, is shown in Fig. 3 and the fractional coordinates, bond lengths and bond angles are contained in Tables 5–7. Both Pd(II)–N and Pd(II)–Br bond distances are in the expected range. Like other [9]aneN_3 metal complexes [1, 3, 5] the included N–Pd(II)–N bond angle is constrained (82.0°).

TABLE 3. Interatomic distances in $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$[a]

Pd–N1	2.064(4)
Pd–N2	2.071(4)
Pd–N4	2.076(4)
Pd–N5	2.062(4)
N1–C1	1.497(6)
N1–C6	1.496(6)
N2–C2	1.502(6)
N2–C3	1.499(6)
N3–C4	1.511(6)
N3–C5	1.511(6)
N4–C7	1.509(6)
N4–C12	1.489(6)
N5–C8	1.498(6)
N5–C9	1.504(6)
N6–C10	1.508(6)
N6–C11	1.514(6)
C1–C2	1.509(7)
C3–C4	1.501(7)
C5–C6	1.517(7)
C7–C8	1.495(7)
C9–C10	1.508(7)
C11–C12	1.501(7)
Cl1–O1	1.417(4)
Cl1–O2	1.410(7)
Cl1–O3	1.418(6)
Cl1–O4	1.442(4)
Cl2–O5	1.432(5)
Cl2–O6	1.411(6)
Cl2–O7	1.432(4)
Cl2–O8	1.440(7)
Cl3–O9	1.421(4)
Cl3–O10	1.388(5)
Cl2–O11	1.404(7)
Cl3–O12	1.412(6)
Cl4–O13	1.390(5)
Cl4–O14	1.403(5)
Cl4–O15	1.360(5)
Cl4–O16	1.462(7)

[a] e.s.d.s are in parentheses.

TABLE 4. Bond angles in $[Pd(HL)_2)](ClO_4)_4 \cdot H_2O$[a]

N1–Pd–N2	81.2
N1–Pd–N4	99.2
N1–Pd–N5	179.8
N2–Pd–N4	179.5
N2–Pd–N5	98.5
N4–Pd–N5	81.0
Pd–N1–C1	102.6
Pd–N1–C6	120.9
C1–N1–C6	111.6
Pd–N2–C2	110.3
Pd–N2–C3	114.5
C2–N2–C3	112.0
Pd–N4–C7	110.2
Pd–N4–C12	114.0
C7–N4–C12	112.8
Pd–N5–C8	102.9
Pd–N5–C9	120.7
C8–N5–C9	111.4
C4–N3–C5	117.2
C10–N6–C11	116.5
N1–C1–C2	106.9
C1–C2–N2	109.9
N2–C3–C4	115.7
C3–C4–N3	116.5
N3–C5–C6	116.8
C5–C6–N1	116.8
N4–C7–C8	109.9
C7–C8–N5	107.3
N5–C9–C10	117.3
C9–C10–N6	117.0
N6–C11–C12	102.0
C11–C12–N4	116.1

[a] Uncertainties in angles are approximately 0.2° for angles involving Pd and 0.5° for all other angles.

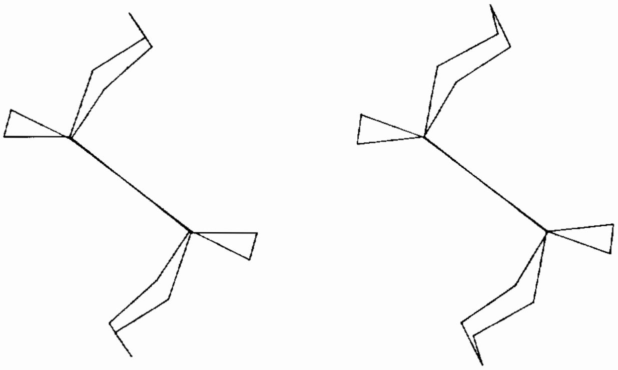

Fig. 2. Structural comparison of $[Pd(HL)_2]^{4+}$ in $[Pd(HL)_2](ClO_4)_4 \cdot H_2O$ (left) and $[PdL_2]^{2+}$ in $[PdL_2](PF_6)_2$ (right) [5]. Ions are viewed in plane formed by PdN_4 with coordinated nitrogen atoms aligned and Pd ion at center of line.

The five-membered chelate rings of [9]aneN_3 appear to pinch the N–M–N bond more than unconstrained ligands which form five-membered rings. The non-bonded Pd(II)---NH^+ distance in this complex is 3.517 Å.

A monoprotonated salt, $[PdHL_2](ClO_4)_2Cl \cdot H_2O$, whose analysis corresponds more closely to a dihydrate, was isolated as nearly colorless crystals and X-ray crystallographic parameters are given in the footnote* below. Unfortunately there appears to be considerable disorder in the crystals and refinement below a value of $R = 0.17$ was unsuccessful. Fourier maps appear to indicate that like $[PdHL_2](PF_6)_2NO_3 \cdot H_2O$ the *syn* isomeric form also occurs in this salt. It remains to be seen if strong H-bonding controls the formation of the *syn* configuration in monoprotonated complexes as has been suggested by Schröder and co-workers [4].

The ligand *cis*-3,5-diaminopiperidine (dapi) has been shown to form both *syn* and *anti* isomers in bis Pd(II) complexes [14]. $[Pd(Hdapi)_2]^{4+}$ and $[PdH(dapi)_2]^{3+}$ have been isolated as perchlorate and nitrate salts,

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*Formula $C_{12}H_{34}N_6Cl_3O_9Pd$, molecular weight 619.2, crystal system triclinic, space group $P1$, $a = 8.02(1)$, $b = 10.50(1)$, $c = 14.20(2)$ Å, $\alpha = 106.3(1)$, $\beta = 92.1(1)$, $\gamma = 89.3(1)°$, $V = 1147$ Å^3.

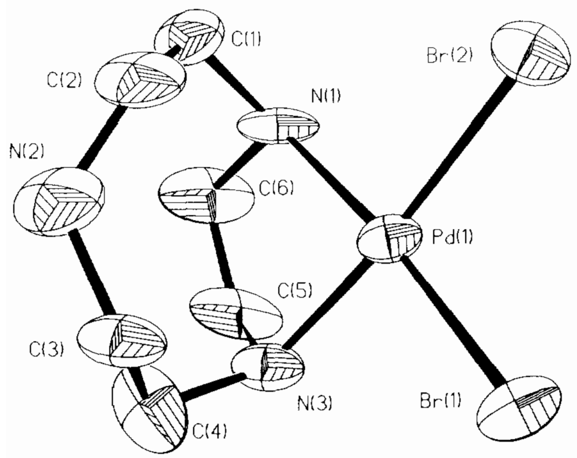

Fig. 3. ORTEP drawing and numbering scheme of $[PdHLBr_2]^{2+}$ cation in $[PdHLBr_2]ClO_4$.

TABLE 5. Final values[a] for all refined atomic coordinates and temperature parameters for $[PdHLBr_2]ClO_4$

Atom	x	y	z	B_{eq}[b] (Å^2)
Pd	0.07776(1)	0.0025(2)	−0.08109(8)	2.7
Br1	−0.1077(3)	0.1237(3)	−0.1596(1)	3.8
Br2	0.0111(2)	−0.3146(3)	−0.0802(1)	4.0
Cl	0.4692(6)	−0.1029(8)	0.6504(3)	3.6
O1	0.4863(16)	−0.2778(24)	0.6138(9)	5.7
O2	0.3443(14)	−0.0759(28)	0.6460(10)	6.0
O3	0.5099(17)	0.0391(24)	0.6056(11)	7.0
O4	0.5291(17)	−0.1050(28)	0.7361(9)	7.6
N1	0.1558(16)	0.2581(21)	−0.0812(9)	3.3
N2	0.2971(21)	0.3038(27)	−0.1982(11)	5.6
N3	0.2410(15)	−0.0674(22)	−0.0152(9)	3.0
C1	0.1793(21)	0.3174(31)	−0.1642(13)	4.3
C2	0.2010(23)	0.1625(35)	−0.2182(13)	5.1
C3	0.2865(20)	−0.1511(27)	−0.1568(12)	3.5
C4	0.3279(20)	−0.1399(39)	−0.0616(12)	5.4
C5	0.2880(22)	0.1094(30)	0.0333(14)	4.9
C6	0.2669(23)	0.2740(34)	−0.0171(15)	5.8

[a]e.s.d.s are given in parentheses. [b]$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

respectively, and both contain the *anti* structure, whereas the perchlorate of $[Pd(dapi)_2]^{2+}$ contains the *syn* structure. An attempt was made to determine the acid dissociation constants of each of the isomeric forms [14]. The authors point out that the pK_a values determined for both complexes are surprisingly similar. This similarity might be explained by a rapid equilibrium in solution between the *syn* and *anti* forms similar to that reported for the Pd(II)–[9]aneN_3 system [5].

It has been shown that Pd(II)–[9]aneN_3 complexes are readily synthesized and may be isolated in a variety of salts where the non-coordinated nitrogen of the ligand may be protonated by controlling the pH of the reaction. In acid solution in the presence of coordinating anions such as Br^- one [9]aneN_3 may be displaced by the anions. The bis[9]aneN_3 complex isolated in this study contained the *anti* isomeric conformation.

TABLE 6. Interatomic distances in $[PdHLBr_2]ClO_4$[a]

Pd–Br1	2.439(3)
Pd–Br2	2.425(3)
Pd–N1	2.06(2)
Pd–N2	2.05(2)
Cl–O1	1.43(2)
Cl–O2	1.46(2)
Cl–O3	1.40(2)
Cl–O4	1.43(2)
N1–C1	1.51(3)
N1–C6	1.49(3)
N2–C2	1.44(3)
N2–C3	1.52(3)
N3–C4	1.49(3)
N3–C5	1.55(3)
C1–C2	1.48(3)
C3–C4	1.54(3)
C5–C6	1.44(3)

[a]e.s.d.s are in parentheses.

TABLE 7. Bond angles in $[PdHLBr_2]ClO_4$[a]

Br1–Pd–Br2	95.4
Br1–Pd–N1	91.2
Br1–Pd–N3	173.0
Br2–Pd–N3	173.0
Br2–Pd–N3	91.5
N1–Pd–N3	82.0
O1–Cl–O2	108.9
O1–Cl–O3	109.6
O1–Cl–O4	108.6
O2–Cl–O3	108.8
O2–Cl–O4	109.0
O3–Cl–O4	111.9
C1–N1–C6	108.5
C2–N2–C3	122.6
C4–N3–C5	110.5
N1–C1–C2	114.3
N2–C2–C1	125.1
N2–C3–C4	111.8
N3–C4–C3	115.6
N1–C6–C5	111.0

[a]Uncertainties in angles are approximately 0.6° for angles involving Pd and 1.3° for all other angles.

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