

Cation and Anion Coordination Chemistry of Palladium(II) with Polyazacycloalkanes. Thermodynamic and Structural Studies[#]

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Abstract. The interaction of PdCl_4^{2-} with the macrocyclic ligands of the series $[3k]\text{aneN}_k$ has been studied both in solution and in the solid state. $[18]\text{aneN}_6$ and $[21]\text{aneN}_7$ form both mono- and binuclear Pd^{2+} complexes, whose stability constants have been determined in $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ at 298.15 K . $[21]\text{aneN}_7$ also forms, in solution, a trinuclear species in which an amino group deprotonates to bridge two Pd^{2+} ions, as observed in the solid state. The crystal structure of the complexes $[\text{Pd}_2([18]\text{aneN}_6)\text{Cl}_2][\text{ClO}_4]_2$ and $[\text{Pd}_3([21]\text{aneN}_7)\text{Cl}_3][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ have been solved by single crystal X-ray analysis. $\text{C}_{12}\text{H}_{30}\text{N}_6\text{Cl}_4\text{O}_8\text{Pd}_2$: monoclinic, space group $C2/m$, $a = 10.876(2)$, $b = 18.117(2)$, $c = 7.043(2) \text{ \AA}$, $\beta = 113.78(2)^\circ$, $V = 1270(12) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.92 \text{ g cm}^{-3}$, $\mu = 16.94 \text{ cm}^{-1}$. $R = 0.063$, $R_w = 0.059$. $\text{C}_{14}\text{H}_{36}\text{N}_7\text{Cl}_5\text{O}_9\text{Pd}_3$: orthorhombic, space group $Pcab$, $a = 13.125(7)$, $b = 13.213(3)$, $c = 33.570(5) \text{ \AA}$, $V = 5822(3) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 2.15 \text{ g cm}^{-3}$, $\mu = 21.20 \text{ cm}^{-1}$. $R = 0.074$, $R_w = 0.061$. In very acidic solutions the polyammonium cations $(\text{H}_k[3k]\text{aneN}_k)^{k+}$ interact with PdCl_4^{2-} forming second sphere coordinated species. These reactions have been followed by a microcalorimetric technique in $2 \text{ mol dm}^{-3} \text{ HCl}$ solutions. The slowness of the reactions of $(\text{H}_{10}[30]\text{aneN}_{10})^{10+}$ with PdCl_4^{2-} has been interpreted in terms of inclusion of the anion into the receptor's cavity as shown by the crystal structure of $[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})][\text{PdCl}_4]_2\text{Cl}_4$: triclinic, space group $P\bar{1}$, $a = 7.760(3)$, $b = 11.448(4)$, $c = 13.399(11) \text{ \AA}$, $\alpha = 96.31(8)^\circ$, $\beta = 104.50(6)^\circ$, $\gamma = 92.30(3)^\circ$, $Z = 1$. $R = 0.046$ and $R_w = 0.039$.

Key words. Macrocyclic chemistry of Pd^{2+} , deprotonation of secondary amino group, supramolecular chemistry, anion coordination chemistry, anion inclusion, crystal structures.

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1. Introduction

Since 1967, when Pedersen's first papers appeared [1, 2] reporting that alkali metal ions bind crown ethers to form highly structured complexes, the field of synthetic macrocyclic compounds has undergone spectacular growth. The growth has largely been due to the synthesis of a great number and variety of synthetic macrocycles

[#] This paper is dedicated to the memory of the late Dr C. J. Pedersen.

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showing remarkably selective behavior [3]. This field has attracted scientists working in many areas, including reaction catalysis, transport processes, industrial applications, model systems and others. A variety of crown ethers have been shown to bind ammonium groups as well as metal–amine complexes giving supramolecular species with second sphere coordination [4]. Among synthetic macrocycles polyazacycloalkanes or azacrowns, in which nitrogen donor atoms have replaced oxygen donor atoms of the analogous crown ethers, have been much studied. Many papers have been published especially dealing with tetraaza macrocycles [5]. More recently much attention has been devoted to azamacrocycles having more than six nitrogen donor atoms (*large polyazacycloalkanes*). The possibility that these compounds bind to more than one metal ion in the macrocyclic framework, as well as the recent development of anion coordination chemistry justify this interest [6–8]. Indeed polyammonium species formed by these macrocycles can both form adducts with anionic complexes and selectively bind nucleotide anions, catalyzing their dephosphorylation [9, 10]. In the former case the chemical properties of the supramolecular species have been studied in an attempt to understand whether the coordination of the complexed anions takes place inside or outside the macrocyclic cavity [7, 11].

In the present paper we report some studies on Pd(II) ion which is able to form both polynuclear cationic complexes and anionic ‘supercomplexes’ with polyazacycloalkanes of different size [12, 13]. The polyazamacrocycles employed in the present study are the $[3k]\text{aneN}_k$ ($k = 6–11$) ligands.

2. Experimental

2.1. CRYSTAL PREPARATION

Yellow crystals of $[\text{Pd}_2([\text{18}] \text{aneN}_6)\text{Cl}_2](\text{ClO}_4)_2$ were obtained by mixing aqueous solutions of $[\text{18}] \text{aneN}_6$ and $[\text{PdCl}_4]^{2-}$. Crystals of $[\text{Pd}_3([\text{21}] \text{aneN}_7)\text{Cl}_3][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ were obtained in the same way. Crystals of $[(\text{PdCl}_4)(\text{H}_{10}[\text{30}] \text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$ suitable for X-ray analysis, were obtained by slow evaporation, at room temperature, of a solution containing $[\text{30}] \text{aneN}_{10} \cdot 10 \text{ HCl}$ (1 mmol) and K_2PdCl_4 (3 mmol) in 50 mL of HCl 2 mmol dm^{-3} .

2.2. CRYSTAL DATA AND STRUCTURES REFINEMENT

All intensity measurements were done on an Enraf-Nonius CAD4 automatic four-circle diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7106 \text{ \AA}$).

For $\text{C}_{12}\text{H}_{30}\text{N}_6\text{Cl}_4\text{O}_8\text{Pd}_2$: $M = 741.01$, monoclinic, space group $C2/m$, $a = 10.876(2)$, $b = 18.117(2)$, $c = 7.043(2) \text{ \AA}$, $\beta = 113.78(2)^\circ$, $V = 1270(12) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.92 \text{ g cm}^{-3}$, $\mu = 16.94 \text{ cm}^{-1}$. 1272 Intensities were collected in the range $5 \leq 2\theta \leq 50^\circ$ and corrected for Lorentz and polarization effects. An absorption correction was applied once the structure was solved [14]. The 1062 reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the structure analysis. The structure was solved by the heavy-atom method, which gave the position of the palladium atom. Successive Fourier syntheses showed all non-hydrogen atoms. The

refinement, performed by means of the full-matrix least-squares method [15], gave $R = 0.063$ and $R_w = 0.059$. Hydrogen atoms were included in calculated positions with an overall temperature factor U of 0.05 \AA^2 . Anisotropic temperature factors were used for all non-hydrogen atoms except for the oxygen atoms of the perchlorate anion, which shows some degree of disorder. Two different models were found for the perchlorate ion; therefore population parameters of 0.5 were used for these oxygen atoms.

For $\text{C}_{14}\text{H}_{36}\text{N}_7\text{Cl}_5\text{O}_9\text{Pd}_3$: $M = 942.93$, orthorhombic, space group $Pcab$ $a = 13.125(7)$, $b = 13.213(3)$, $c = 33.570(5) \text{ \AA}$, $V = 5822(3) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 2.15 \text{ g cm}^{-3}$, $\mu = 21.20 \text{ cm}^{-1}$, 4275 reflections were collected in the range $5 \leq 2\theta \leq 45^\circ$. The intensities were corrected for Lorentz and polarization effects, and an absorption correction was applied once the structure was solved [14]. The 1899 unique reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the structure analysis. The structure was solved by the heavy-atom method, which gave the position of the palladium atoms. Successive Fourier syntheses showed all non-hydrogen atoms. Refinement was performed by means of the full-matrix least-squares method [15] to obtain a final R factor of 0.074 and $R_w = 0.061$. Hydrogen atoms were included in calculated positions with an overall temperature factor U of 0.05 \AA^2 . Isotropic temperature factors were used for all atoms except for the palladium and chlorine.

$[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$: $M = 1327.15$, triclinic, space group $P\bar{1}$, $a = 7.760(3)$, $b = 11.448(4)$, $c = 13.399(11) \text{ \AA}$, $\alpha = 96.31(8)^\circ$, $\beta = 104.50(6)^\circ$, $\gamma = 92.30(3)^\circ$, $Z = 1$. A total of 4061 reflections ($5 \leq 2\theta \leq 50^\circ$) were collected of which 2956 having $I \geq 3\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy atom technique. A ΔF Fourier synthesis showed two different positions for the N(3) atom. The population parameters of these positions were refined. The rather high thermal parameters of the attached carbon atoms are indicative of an extensive disorder around the N(3) atom which affects the values of the bond angles. Final refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.046$ and $R_w = 0.039$.

2.3. EMF MEASUREMENTS

All the potentiometric titrations were carried out at 298.15 K, by using the equipment that has been fully described [16]. The measurements have been performed in 0.5 mol dm^{-3} NaCl in order to avoid the dissociation of the tetrachloro complex PdCl_4^{2-} . Furthermore, competition between the azamacrocycles and the chloride ligands for Pd^{2+} favors the determination of the equilibrium constants of these macrocyclic Pd^{2+} complexes [17]. In order to reach the equilibrium in these complex formation reactions, several minutes were allowed to elapse between each emf reading. The protonation constants of the ligands [18]aneN₆ and [21]aneN₇, redetermined under these experimental conditions, are shown in ref. [18]. The computer program SUPERQUAD [19] has been used to process the data and determine the equilibrium constants.

2.4. MICROCALORIMETRY

The enthalpy changes associated to the interaction of PdCl_4^{2-} with the cations $(\text{H}_k[3k]\text{aneN}_k)^{k+}$ have been determined by means of a BATCH 10700 LKB

microcalorimeter. These reactions were carried out in 2 mol dm⁻³ HCl solutions as the formation of Pd²⁺ complexes were strongly competitive with PdCl₄²⁻ second sphere interaction in less acidic solution. Ratios, $R = [(H_k[3k]aneN_k)^{k+}]/[PdCl_4^{2-}]$, varying from 0.2 to 5 were used. The heat of the reactions were corrected for the heat of dilution of the reagents by blank experiments.

2.5. SPECTROPHOTOMETRIC MEASUREMENTS

Electronic spectra were recorded on a Perkin Elmer Model Lambda 9 instrument.

3. Results and Discussion

3.1. METAL COMPLEXES

Crystal Structure of [Pd₂([18]aneN₆)Cl₂][ClO₄]₂ and [Pd₃([21]aneN₇)Cl₃][ClO₄]₂ · H₂O

The structure of the compound [Pd₂([18]aneN₆)Cl₂][ClO₄]₂ consists of a dinuclear [Pd₂([18]aneN₆)Cl₂]²⁺ cation and disordered uncoordinated perchlorate anions. In the dinuclear complex, which possess a 2/m symmetry, each palladium ion shows a square-planar geometry involving three nitrogen atoms and one chloride ion. Each

Table I. Positional parameters ($\times 10^4$) and their estimated standard deviations in parentheses for (Pd₂[18]aneN₆)Cl₂(ClO₄)₂.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pd ^a	1526(1)	0	846(2)
Cl(1) ^a	1018(4)	0	3717(6)
Cl(2) ^a	5000	1852(3)	5000
N(1) ^a	2252(12)	0	-1329(17)
N(2)	1701(9)	1123(4)	718(16)
C(1)	3017(11)	699(7)	-1104(20)
C(2)	2106(14)	1286(7)	-919(23)
C(3)	675(11)	1632(6)	960(24)
O(1) ^a	4329(31)	1176(22)	4987(60)
O(2) ^a	4634(25)	1863(15)	2679(45)
O(3) ^a	4315(25)	2469(18)	4082(45)
O(4) ^a	3674(32)	1880(20)	4914(49)

^aAtom with occupancy factor 0.5.

Table II. Selected bond distances (Å) and angles (°) for (Pd₂[18]aneN₆)Cl₂(ClO₄)₂.

Bond distances		Bond Angles	
Pd—N(1)	1.99(1)	N(2)—Pd—N(2')	166.5(4)
Pd—N(2)	2.049(9)	N(1)—Pd—N(2)	83.9(3)
Pd—Cl(1)	2.301(5)	Cl(1)—Pd—N(2)	95.6(3)
		Cl(1)—Pd—N(1)	171.4(4)

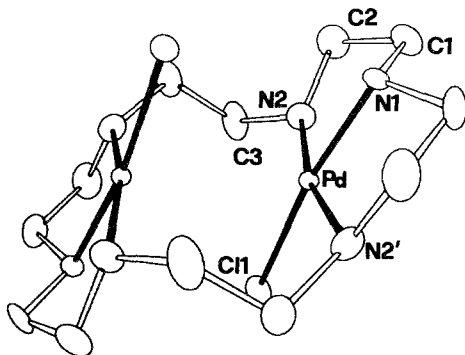


Fig. 1. ORTEP drawing of the $[\text{Pd}_2([\text{18}]\text{aneN}_6)\text{Cl}_2]^{2+}$ cation.

metal ion lies 0.14 Å out of the plane identified by the donor atoms N(1), N(2), N(2'), Cl(1). The two palladium atoms are 3.04 Å apart and point towards each other with respect to the two planes containing the donor atoms (see Figure 1).

In $[\text{Pd}_3([\text{21}]\text{aneN}_7)\text{Cl}_3][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ the ligand and three chlorine atoms bind the three palladium atoms in a square planar fashion. An amino group of the macrocyclic ligand, which has undergone deprotonation on complex formation, bridges two palladium atoms. The coordination planes containing Pd(1) and Pd(2) are nearly parallel, the angle between them being 1.0°. The third square plane containing N(3), N(4), N(5), Cl(3) and Pd(3) forms an angle of 92.0° with the other ones. The Pd(1) and Pd(2) atoms lie significantly out from their mean coordination planes, 0.084 Å and 0.048 Å, respectively, pointing towards each other (see Figure 2). The distance Pd(1)—Pd(2) [3.057(4) Å] is the shortest among the three contact interactions between the three metal atoms, the other being 3.232(4) Å for Pd(1)—Pd(3) and 3.478(4) Å for Pd(2)—Pd(3). The macrocyclic geometry is

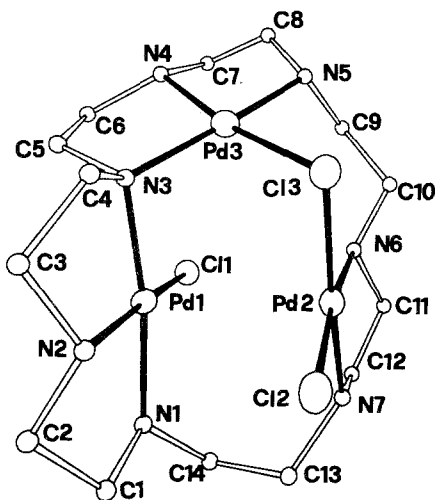


Fig. 2. ORTEP drawing of the $[\text{Pd}_3([\text{21}]\text{aneN}_7)\text{Cl}_3]^{2+}$ cation.

Table III. Positional parameters ($\times 10^4$) with their estimated standard deviations in parentheses for $[\text{Pd}_3(\text{[21]aneN}_7)\text{Cl}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

Atom	x/x	y/a	z/c	Atom	x/a	y/b	z/c
Pd(1)	1594(2)	3162(2)	4152(1)	C(8)	5781(26)	-1685(28)	3204(11)
Pd(2)	4482(2)	2063(2)	3779(1)	N(5)	5089(24)	-940(23)	3325(9)
Pd(3)	664(2)	287(2)	1155(1)	C(9)	4957(29)	-241(29)	2981(11)
Cl(1)	-2120(6)	6694(7)	6516(3)	C(10)	4225(26)	670(25)	3052(10)
Cl(2)	946(6)	7731(7)	5619(3)	N(6)	4717(19)	1554(19)	3212(8)
Cl(3)	880(6)	5473(7)	5975(3)	C(11)	4581(26)	2460(24)	2970(9)
Cl(4)	657(10)	3141(10)	596(4)	C(12)	5015(28)	3375(27)	3142(11)
Cl(5)	1985(14)	4087(15)	2272(6)	N(7)	4738(19)	3417(18)	3541(7)
N(1)	6760(18)	3362(19)	4156(9)	C(13)	5330(22)	4269(24)	3765(10)
C(1)	6537(27)	3751(24)	4545(10)	C(14)	6397(24)	4088(25)	3831(10)
C(2)	6739(23)	2947(21)	4874(9)	O(1)	474(28)	2218(30)	428(11)
N(2)	6245(17)	2105(20)	4726(7)	O(2)	539(31)	3910(27)	342(11)
C(3)	6498(24)	1137(23)	4934(10)	O(3)	145(40)	3273(42)	912(15)
C(4)	6087(26)	285(27)	4676(10)	O(4)	1618(30)	3096(33)	655(12)
N(3)	6456(20)	313(20)	4276(8)	O(5)	2425(34)	4814(36)	2474(16)
C(5)	7454(25)	-196(25)	4281(10)	O(6)	1210(39)	3705(40)	2357(16)
C(6)	7786(30)	-666(32)	3900(12)	O(7)	1809(48)	4188(46)	1889(17)
N(4)	6858(21)	-1129(20)	3706(10)	O(8)	-2792(34)	6457(35)	7758(14)
C(7)	6759(28)	-1394(30)	3284(12)	O(9)	3426(19)	3008(19)	1233(8)

determined by the coordination spheres around the palladium atoms, which are able to arrange the nitrogen donor atoms on the three different coordination planes. The Pd—N distances in the present structures are very similar to those found in other reported structures of Pd^{2+} complexes with saturated tri- and tetraazamacrocycles [20], although some shorter distances have been observed.

3.1.2. Solution Chemistry

The formation of Pd^{2+} complexes by the macrocyclic ligands $[\text{18]aneN}_6$ and $[\text{21]aneN}_7$ has been followed in solution by means of potentiometric and spectrophotometric techniques. For $[\text{18]aneN}_6$ mono- and dinuclear species have been observed while for $[\text{21]aneN}_7$ mono-, di- and trinuclear species are formed. The logarithms of the stability constants determined for these systems are presented in Table VII. The electronic spectra indicate that Pd^{2+} is coordinated in these complexes in a square planar mode. Therefore, in the mononuclear complexes, two nitrogens of $[\text{18]aneN}_6$ and three of $[\text{21]aneN}_7$ remain uncoordinated. The decrease of the stability constants when passing from $[\text{Pd}([\text{18]aneN}_6)]^{2+}$ [$\log K = 29.2$] to $[\text{Pd}([\text{21]aneN}_7)]^{2+}$ [$\log K = 24.5(1)$] can be attributed to the presence of a larger chelate ring in the latter which lowers its stability. Furthermore, two protonated complexes for $[\text{18]aneN}_6$ and three for $[\text{21]aneN}_7$ have been found, in agreement with the number of uncoordinated nitrogens in each complex.

The molar conductivity of pure water solutions containing $[\text{Pd}_2([\text{18]aneN}_6)\text{Cl}_2](\text{ClO}_4)_2$ in the dilution range 10^{-1} – 10^{-4} mol dm^{-3} showed that no appreciable dissociation of the chloride ligands takes place in the cation

Table IV. Selected bond distances (Å) and angles (°) for $[\text{Pd}_3(\text{12}] \text{aneN}_7)\text{Cl}_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

Bond Distances		Bond Angles	
Pd(1)—Cl(1)	2.3556(88)	Pd(2)—N(6)	2.0422(254)
Pd(1)—N(1)	2.0249(250)	Pd(2)—N(7)	1.9887(243)
Pd(1)—N(2)	2.0105(237)	Pd(3)—Cl(3)	2.3407(89)
Pd(1)—N(3)	2.0657(260)	Pd(3)—N(3)	1.9521(263)
Pd(2)—Cl(2)	2.2756(92)	Pd(3)—N(4)	1.9769(277)
Pd(2)—Cl(3)	2.3063(94)	Pd(3)—N(5)	2.0874(299)
		N(2)—Pd(1)—N(3)	87.61(1.1)
		N(1)—Pd(1)—N(3)	167.99(1.10)
		N(1)—Pd(1)—N(2)	81.04(1.08)
		Cl(1)—Pd(1)—N(3)	97.98(0.76)
		Cl(1)—Pd(1)—N(2)	173.42(0.75)
		Cl(1)—Pd(1)—N(1)	93.13(0.79)
		N(6)—Pd(2)—N(7)	84.02(1.01)
		Cl(3)—Pd(2)—N(7)	176.62(0.76)
		Cl(3)—Pd(2)—N(6)	93.70(0.75)
		Cl(2)—Pd(2)—N(7)	92.84(0.74)
		Cl(2)—Pd(2)—N(6)	173.04(0.75)
		Cl(2)—Pd(2)—Cl(3)	89.15(0.33)
		N(4)—Pd(3)—N(5)	81.83(1.20)
		N(3)—Pd(3)—N(5)	168.78(1.17)
		N(3)—Pd(3)—N(4)	88.88(1.13)
		Cl(3)—Pd(3)—N(5)	94.65(0.89)
		Cl(13)—Pd(3)—N(4)	171.18(0.83)
		Cl(3)—Pd(3)—N(3)	95.42(0.80)

Table V. Positional parameters ($\times 10^4$) for $[\text{C}_{20}\text{H}_{60}\text{N}_{10}(\text{PdCl}_4)](\text{PdCl}_4)_2\text{Cl}_4$ with their e.s.d. in parentheses.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Pd(1)	0	5000	0	N(31) ^b	-931(47)	1952(30)	6031(27)
Pd(2)	0	0	0	N(4)	-2153(10)	4999(6)	6655(6)
Pd(3)	5000	0	5000	N(5)	-4277(10)	7250(7)	7244(5)
Cl(1)	2782(3)	5280(2)	1119(2)	C(1)	5816(13)	3041(8)	11417(7)
Cl(2)	1269(3)	4926(2)	-1376(2)	C(2)	4572(11)	2651(7)	9437(6)
Cl(3)	73(3)	-1963(2)	226(2)	C(3)	5098(11)	2002(8)	8544(7)
Cl(4)	2683(3)	-55(2)	-417(2)	C(4)	1963(13)	1547(10)	7415(8)
Cl(5)	3630(4)	-175(2)	3251(2)	C(5)	849(15)	1371(11)	6292(9)
Cl(6)	4376(4)	1935(2)	5167(2)	C(6)	-1139(15)	3038(11)	6404(8)
Cl(7)	3674(3)	4634(2)	6462(2)	C(7)	-1324(13)	4196(8)	6006(7)
Cl(8)	1690(4)	8164(3)	6316(2)	C(8)	-2067(14)	6234(8)	6424(8)
N(1)	6094(9)	2595(6)	10381(5)	C(9)	-2381(12)	7118(8)	7278(7)
N(2)	3834(10)	2113(7)	7534(6)	C(10)	-4475(12)	7835(9)	8264(7)
N(3) ^a	342(14)	2418(10)	5890(9)				

^aOccupancy factor 0.76.^bOccupancy factor 0.24.

$[\text{Pd}_2([\text{18}] \text{aneN}_6)\text{Cl}_2]^{2+}$. This result agrees with the fact that the electronic spectra of solid $[\text{Pd}_2([\text{18}] \text{aneN}_6)\text{Cl}_2][\text{ClO}_4]_2$ and its solution (ϵ 1330 at $\lambda = 342$ nm, in 0.5 mol dm^{-3} NaCl) are essentially the same. The very high stability of the complex $[\text{Pd}_2([\text{18}] \text{aneN}_6)\text{Cl}_2]^{2+}$ ($\log K = 51.8$), which is formed in very acidic solutions, is accompanied by a marked kinetic inertness towards acid dissociation. Some months are required for the complete dissociation of $[\text{Pd}_2([\text{18}] \text{aneN}_6)\text{Cl}_2]^{2+}$ in 2 mol dm^{-3} HCl solution. Also $[\text{21}] \text{aneN}_7$ forms a very stable dinuclear species with estimated stoichiometry $[\text{Pd}_2([\text{21}] \text{aneN}_7)\text{Cl}]^{3+}$ ($\log K > 52$). This complex can react with a further PdCl_4^{2-} ion forming a trinuclear species whose electronic spectrum (ϵ 2400 at $\lambda = 377$ nm, in 0.5 mol dm^{-3} NaCl) is quite similar to the reflectance spectrum of the $[\text{Pd}_3([\text{21}] \text{aneN}_7)\text{Cl}_3][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ solid compound. The titration curves show that the binding of the third Pd^{2+} causes the release of a further equivalent of H^+ ion. These results suggest that the overall structure of $[\text{Pd}_3([\text{21}] \text{aneN}_7)\text{Cl}_3]^{2+}$ observed in the solid state, in which a nitrogen deprotonates to bridge two Pd^{2+} ions, is also likely to be maintained in solution.

3.2. ANION COORDINATION

3.2.1. Crystal Structure of $[(\text{PdCl}_4)(\text{H}_{10}[\text{30}] \text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$

The crystal structure (see Figures 3 and 4) consists of $[(\text{PdCl}_4)(\text{H}_{10}[\text{30}] \text{aneN}_{10})]^{8+}$ cations, where the $(\text{PdCl}_4)^{2-}$ anion (A) is enclosed into the $(\text{H}_{10}[\text{30}] \text{aneN}_{10})^{10+}$ cavity, and of isolated $(\text{PdCl}_4)^{2-}$ (B), (C) and Cl^- counterions. All the tetrachloropalladate(II) anions are centrosymmetric, the metal atom residing on an inversion centre in each case. The structural features of $(\text{PdCl}_4)^{2-}$ are not influenced by the inclusion into the decacharged $(\text{H}_{10}[\text{30}] \text{aneN}_{10})^{10+}$ macrocycle, as shown by the small deviation

Table VI. Bond distances (Å) and angles (°) for $[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$ with their e.s.d. in parentheses.

Bond distances		Bond Angles	
Pd(1)—Cl(1)	2.287(2)	N(3)—C(6)	1.629(17)
Pd(1)—Cl(2)	2.293(3)	N(31)—C(5)	1.536(38)
Pd(2)—Cl(3)	2.301(2)	N(31)—C(6)	1.319(37)
Pd(2)—Cl(4)	2.288(3)	N(4)—C(7)	1.471(13)
Pd(3)—Cl(5)	2.300(2)	N(4)—C(8)	1.483(12)
Pd(3)—Cl(6)	2.285(2)	N(5)—C(9)	1.475(12)
N(1)—C(1)	1.496(12)	N(5)—C(10)	1.501(13)
N(1)—C(2)	1.508(10)	C(2)—C(3)	1.491(13)
N(2)—C(3)	1.481(10)	C(4)—C(5)	1.522(14)
N(2)—C(4)	1.529(13)	C(6)—C(7)	1.482(16)
N(3)—C(5)	1.399(17)	C(8)—C(9)	1.515(14)
		Cl(1)—Pd(1)—Cl(2)	89.63(0.09)
		Cl(3)—Pd(2)—Cl(4)	90.08(0.08)
		Cl(5)—Pd(3)—Cl(6)	90.13(0.09)
		C(1)—N(1)—C(2)	117.44(0.67)
		N(3)—C(5)—C(4)	114.02(1.05)
		C(5)—N(3)—C(6)	123.53(2.70)
		C(5)—N(31)—C(6)	113.06(0.72)
		C(7)—N(4)—C(8)	110.87(0.70)
		C(9)—N(5)—C(10)	114.48(0.79)
		N(4)—C(9)—C(8)	
		N(1)—C(2)—C(3)	106.21(0.68)
		N(2)—C(3)—C(2)	112.46(0.71)
		N(2)—C(4)—C(5)	112.77(0.85)
		C(3)—N(2)—C(4)	113.85(0.70)
		N(31)—C(5)—C(4)	118.20(1.56)
		N(31)—C(6)—C(7)	136.44(1.75)
		N(3)—C(6)—C(7)	104.80(0.85)
		N(4)—C(7)—C(6)	110.40(0.79)
		N(4)—C(8)—C(9)	113.38(0.75)

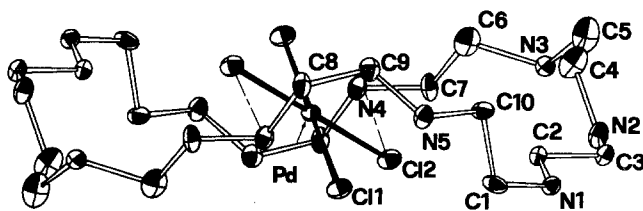
Table VII. Logarithms of the equilibrium constants of Pd²⁺ complexes with [18]aneN₆ and [21]aneN₇ determined in 0.5 mol dm⁻³ NaCl solution at 298.15 K.

Reaction	[18]aneN ₆	log K	[21]aneN ₇
Pd ^a + L	29.2(1) ^b		24.55(6)
Pd + L + H	37.47(7)		34.52(6)
Pd + L + 2H	42.40(7)		42.63(4)
Pd + L + 3H			47.13(4)
2Pd + L + 2Cl	51.8(8)		
2Pd + L + Cl			> 52
PdL + H	8.3		10.0
PdLH + H	4.9		8.1
PdLH ₂ + H			4.5

^aCharges have been omitted for simplicity.

^bValues in parentheses are standard deviations on the last significant figure.

from orthogonality of the Cl(1)—Pd(1)—Cl(2) angle. Furthermore Pd—Cl bond distances differ by less than 0.016 Å for the three anions. The deca protonated macrocycle is centrosymmetric, the centre of symmetry being coincident with that of the (PdCl₄)²⁻ anion. The macrocycle displays an S-shaped conformation which produces an elongated macrocyclic cavity, of approximate dimensions 9 × 11 Å (see Figure 3). The plane of the tetrachloropalladate(II) anion is perpendicular to the direction of main elongation of the cavity, with the chlorine atoms standing out of the macrocyclic frame. Such arrangement allows the chlorine atom Cl(2) of (A) (see Figure 3) to interact via a hydrogen bond with the N(4) protonated nitrogen atom of the receptor [Cl(2)⋯HN(4) 2.308(7) Å]. The (PdCl₄)²⁻ anion (A) further interacts via hydrogen bonds with the nitrogen atoms of a symmetry related supercomplexed species [Cl(1)⋯HN(4) 2.411(9) Å and Cl(2)⋯HN(1) 2.611(7) Å]. Hydrogen bond interactions with the macrocycle are also formed by the chlorine atoms of the (PdCl₄)²⁻ anion (B) [Cl(3)⋯HN(1) 2.699(8) Å and Cl(4)⋯HN(1) 2.024(8) Å], as well as by those of (C) [Cl(5)⋯HN(2) 2.415(8) Å, Cl(6)⋯HN(2) 2.399(8) Å and Cl(6)⋯HN(4) 2.589 Å]. The hydrogen bond framework is completed by several other interactions involving the chloride counterions Cl(7) and Cl(8).

Fig. 3. ORTEP drawing of the [(PdCl₄)(H₁₀[30]aneN₁₀)⁸⁺]⁸⁺ 'super complex'.

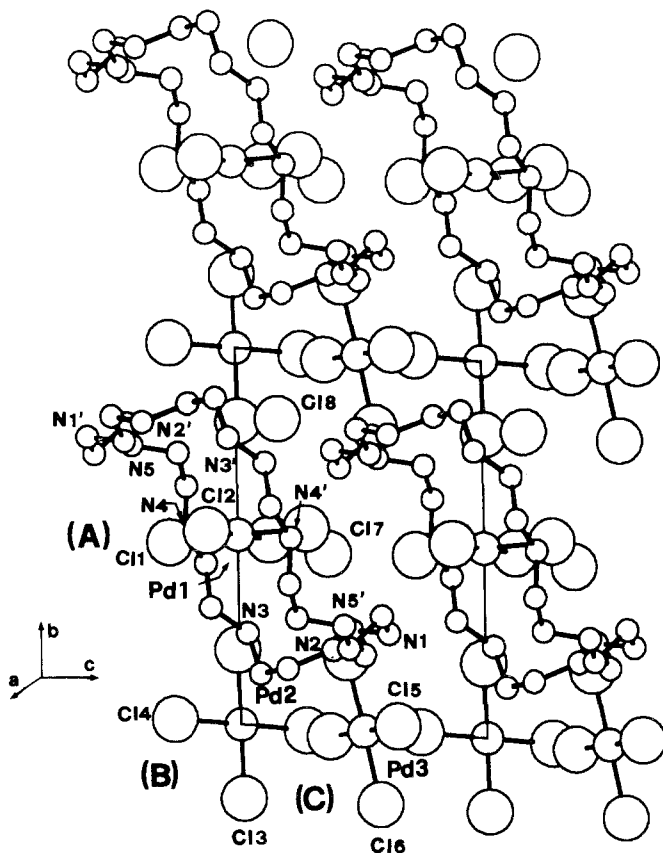


Fig. 4. Crystal packing of $[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$.

3.2.2. Solution Chemistry

The interaction between PdCl_4^{2-} and the polyammonium cations $(\text{H}_k[3k]\text{aneN}_k)^{k+}$ has been studied by direct microcalorimetry in 2 mol dm^{-3} HCl solutions. These experimental conditions have been chosen in order to avoid dissociation of the PdCl_4^{2-} anion and to prevent the formation of palladium(II) complexes of the macrocyclic ligands. All the reactions are exothermic. In the cases of $(\text{H}_6[18]\text{aneN}_6)^{6+}$ and $(\text{H}_7[21]\text{aneN}_7)^{7+}$, the reactions are fast for all the experimental ratios, $R = [(\text{H}_k(3k)\text{aneN}_k)^{k+}]/[\text{PdCl}_4^{2-}]$, between 0.2 and 5. The enthalpy changes for both reactions are the same within experimental error ($\Delta H^\circ = -1.5(1) \text{ kcal mol}^{-1}$). The reaction of $(\text{H}_8[24]\text{aneN}_8)^{8+}$ with PdCl_4^{2-} is also fast, with a $\Delta H^\circ = -1.6(1) \text{ kcal mol}^{-1}$ for $1 \leq R \leq 5$. However for $0.2 \leq R \leq 1$, a slight increment of the reaction enthalpy is observed. For $1 \leq R \leq 5$ the three larger polyammonium cations $(\text{H}_9[27]\text{aneN}_9)^{9+}$, $(\text{H}_{10}[30]\text{aneN}_{10})^{10+}$ and $(\text{H}_{11}[33]\text{aneN}_{11})^{11+}$ react slowly with enthalpy changes of $-2.9(1)$, $-3.9(1)$ and $-3.1(1) \text{ kcal mol}^{-1}$ respectively. In these cases, remarkable increases of the reaction heats were observed for R values lower than 1. The reactions of PdCl_4^{2-} with

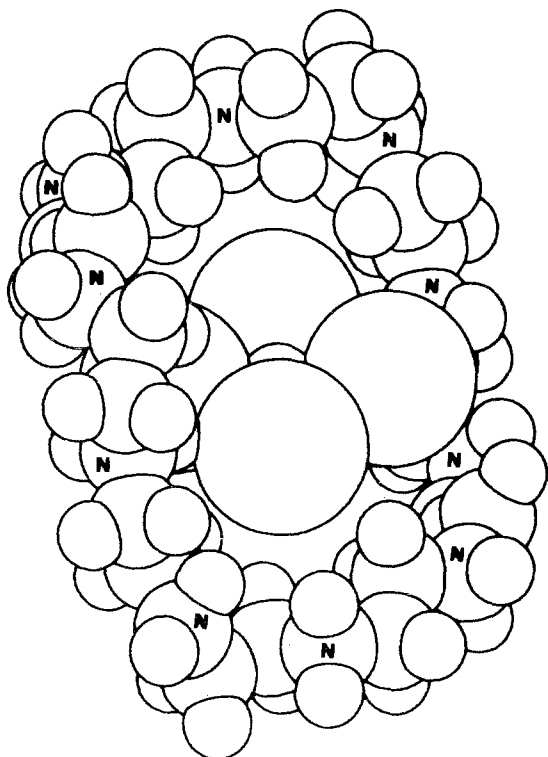


Fig. 5. Space-filling representation of the $[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})]^{8+}$ cation.

$[(\text{PdCl}_4)(\text{H}_k[3k]\text{aneN}_k)]^{(k-2)+}$ ($k = 8-11$) are fast. These results suggest that the two smaller polyammonium receptors $(\text{H}_6[18]\text{aneN}_6)^{6+}$ and $(\text{H}_7[21]\text{aneN}_7)^{7+}$ form just 1:1 species while, $(\text{H}_8[24]\text{aneN}_8)^{8+}$ and even more clearly $(\text{H}_9[27]\text{aneN}_9)^{9+}$, $(\text{H}_{10}[30]\text{aneN}_{10})^{10+}$ and $(\text{H}_{11}[33]\text{aneN}_{11})^{11+}$ interact with more than one PdCl_4^{2-} anion. The slowness of the reactions of the larger macrocycles can be explained in terms of the structure of the solid compound $[(\text{PdCl}_4)(\text{H}_{10}[30]\text{aneN}_{10})](\text{PdCl}_4)_2\text{Cl}_4$ (see Figure 5). In this structure a PdCl_4^{2-} anion is included in the cavity of the decaprotonated cation $(\text{H}_{10}[30]\text{aneN}_{10})^{10+}$ being disposed along the shortest axes of the macrocycle. If this inclusion is also maintained in solution the conformational energy of the receptor, needed to accommodate the guest species inside the cavity so as to form a compact structure, would be greater. Indeed, the reactions of PdCl_4^{2-} with the polyammonium receptors $(\text{H}_6[18]\text{aneN}_6)^{6+}$ and $(\text{H}_7[21]\text{aneN}_7)^{7+}$, whose cavities are too small to include PdCl_4^{2-} , are fast. If the observed slowness is indicative of inclusion we may conclude that $(\text{H}_9[27]\text{aneN}_9)^{9+}$ is the smallest receptor able to incorporate PdCl_4^{2-} inside the cavity. For $(\text{H}_{11}[33]\text{aneN}_{11})^{11+}$ a faster reaction was observed; this can be explained in terms of the greater cavity size allowing the anion to be included more snugly.

4. Conclusions

Polyazacycloalkanes have been shown to be good receptors both for transition metal ions and anionic species. In the present paper we have presented the case of a substrate (PdCl_4^{2-}) able, as a function of pH, to interact with these receptors providing either covalent or non-covalent interactions. The second sphere coordination takes place for those acid pH values where the macrocyclic nitrogens do not compete with the chloride anions for the direct coordination to the metal. When the pH is raised, the nitrogen donors of the macrocycle remove, at least partially, the chloride anions from the first coordination sphere to interact directly with the Pd^{2+} ions. For the first time, the inclusion of a complex anion inside the cavity of a macrocyclic receptor has been undoubtedly provided by X-ray analysis. On the other hand, the matching between a metal ion presenting rigid stereochemical requirements and ligands constrained by their cyclic topology results in some rare chemical events such as the deprotonation of an amine group to bridge two metal ions, that has been observed for the first time.

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