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Thermodynamic and Structural Properties of Palladium(II) Polynuclear Complexes of Azamacrocycles. Crystal Structure of the $[Pd_2([24]aneN_8)](ClO_4)_4$ Complex

Andrea Bencini,[1a] Antonio Bianchi,[*,1a] Paolo Dapporto,[1b] Enrique Garcia-España,[*,1c] Piero Paoletti,[*,1a] Paola Paoli,[1b] José Antonio Ramirez,[1c] and Agustin Rodriguez[1d]

Department of Chemistry, University of Florence, Via Maragliano 75/77, 50144 Florence, Italy, Department of Energetics, University of Florence, Santa Marta, Florence, Italy, Department of Inorganic Chemistry, University of Valencia, C/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain, and Department of Inorganic Chemistry, University of La Laguna, Tenerife, Canary Islands, Spain

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The formation of Pd^{2+} complexes of [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane), [21]aneN_7 (1,4,7,10,13,16,19-heptaazacyclohenicosane), and [24]aneN_8 (1,4,7,10,13,16,19,21-octaazacyclotetracosane) in solution has been studied by microcalorimetry and ^{1}H and ^{13}C NMR. As previously reported (Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-España, E.; Micheloni, M.; Paoletti, P.; Paoli, P. *J. Chem. Soc., Chem. Commun.* **1990**, 1382) [18]aneN_6 and [21]aneN_7 form both mono- and binuclear complexes, while [21]aneN_7 forms also a trinuclear complex $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$ in which an amino group of the ligand deprotonates bridging two Pd^{2+} ions. In the present work only the formation of a binuclear complex of [24]aneN_8 has been observed. These complexes are very stable due to favorable enthalpic and entropic contributions. The crystal structure of $[Pd_2([24]aneN_8)](ClO_4)_4$ (*Pcab*, $a = 15.874(8)$ Å, $b = 13.070(16)$ Å, $c = 16.454(7)$ Å, $V = 3414(5)$ Å^3, $Z = 4$, $R = 0.082$, $R_w = 0.066$) has been solved by X-ray analysis. In the centrosymmetric $[Pd_2([24]aneN_8)]^{4+}$ complex cation the two palladium ions, located 5.447(4) Å apart, are coordinated by four nitrogen atoms of the macrocycle in a distorted squared geometry. The palladium ions are 0.145(1) Å out of the donor atoms' mean plane. NMR data suggest that the rigidity observed in this crystal structure, as well as in that of $[Pd_2([18]aneN_6)Cl_2](ClO_4)_2$, is almost maintained in solution. In the case of the complex $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$, signals at ca. 70 ppm, which could be diagnostic for the deprotonation of an amino group in this type of compounds, have been observed.

Introduction

Macrocyclic ligands have been widely used to prepare and study polynuclear metal compounds.[2,3] The recognition that several biological functions need multisite metal complexes[4–14] has given impulse to the study of polynuclear macrocyclic complexes as model systems.[4–9,14,15] Among these ligands, polyazacycloalkanes are particularly efficient to form polynuclear metal centers with transition metal ions.[3]

Although Pd^{2+} has shown some interest as a Pt^{2+} substitute in amine complexes, which exhibit antitumoral properties,[4] thermodynamic data for the binding of Pd^{2+} in aqueous solution by amine ligands are rare.[3]

In recent papers[16,17] we have reported the synthesis and some thermodynamic and structural properties of Pd^{2+} complexes of [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane) and [21]aneN_7 (1,4,7,10,13,16,19-heptaazacyclohenicosane).

[18]aneN_6 and [21]aneN_7 form both mono- and binuclear Pd^{2+} complexes characterized by high thermodynamic stability. [21]aneN_7 is also able to bind a third Pd^{2+} ion forming a tripalladium(II) species in which deprotonation of an amino group of the heptaaza ligand occurs. The crystal structures of the two complexed cations $[Pd_2([18]aneN_6)Cl_2]^{2+}$ and $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$ in the solid state were determined by X-ray analysis.[16,17]

The structure observed in $[Pd_2([18]aneN_6)Cl_2]^{2+}$ was confirmed for the analogous bromide compound $[Pd_2([18]aneN_6)Br_2]^{2+}$.[18] In that work the crystal structure of the $[Pd_2([20]aneN_6)Br_2]^{2+}$ ([20]aneN_6 = 1,4,7,11,14,17-hexaazacycloicosane) was also reported as well as some results on structural studies in solution and kinetics of substitution of the coordinated bromide ions. In the present paper we consider the thermodynamic,

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(1) (a) Department of Chemistry, University of Florence. (b) Department of Energetics, University of Florence. (c) Department of Inorganic Chemistry, University of Valencia. (d) Department of Inorganic Chemistry, University of La Laguna.

(2) Izatt, R. M., Christensen, J. J., Eds. *Synthetic Multidentate Macrocyclic Ligands*; Academic Press: New York, 1978. Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979. Christensen, J. J., Izatt, R. M., Eds. *Synthesis of Macrocycles, the Design of Selective Complexing Agents*; Wiley: New York, 1987. Lindoy, L. F., Ed. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge Univ. Press: Cambridge, U.K., 1989.

(3) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721. Bianchi, A.; Micheloni, M.; Paoletti, P. *Coord. Chem. Rev.* **1991**, *110*, 17.

(4) Hughes, M. N. *The Inorganic Chemistry of Biological Processes*; Wiley: New York, 1981; and references therein.

(5) Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley: New York, 1981, p 41 and references therein.

(6) Ibers, J. A.; Holm, R. H. *Science* **1980**, *209*, 223.

(7) Himmelwright, R. S.; Eickman, N. C.; Lubien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378.

(8) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206.

(9) Richardson, J. S.; Thomas, K. A.; Rubin, B. H.; Richardson, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1349.

(10) Melbye, S. W.; Carpenter, F. H. *J. Biol. Chem.* **1971**, *246*, 2459. Jurnak, F.; Rich, A.; Van Loon-Klassen, L.; Bloemendal, H.; Taylor, A.; Carpenter, F. H. *J. Mol. Biol.* **1977**, *112*, 149.

(11) Plocke, D. J.; Levinthal, C.; Vallee, B. L. *Biochemistry* **1962**, *1*, 373. Plocke, D. J.; Vallee, B. L. *Biochemistry* **1962**, *1*, 1039. Simpson, R. T.; Vallee, B. L. *Biochemistry* **1968**, *7*, 4343.

(12) Benkovic, A.; Caperelli, C. A.; de Maine, M.; Benkovic, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 2185.

(13) Pedrosa, F. O.; Pontremol, S.; Horecker, B. L. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 2742.

(14) Strothkamp, K. G.; Lippard, S. J. *Acc. Chem. Res.* **1982**, *10*, 318.

(15) Agnus, Y. L. Synthetic Model Compound for Type 3 Copper Proteins. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; and references therein.

(16) Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-España, E.; Micheloni, M.; Paoletti, P.; Paoli, P. *J. Chem. Soc., Chem. Commun.* **1990**, 1382.

(17) Bencini, A.; Bianchi, A.; Micheloni, M.; Paoletti, P.; Dapporto, P.; Paoli, P.; Garcia-España, E. *J. Incl. Phenom.* **1992**, *12*, 291.

(18) McAuley, A.; Whitcombe, T. W.; Zaworotko, M. J. *Inorg. Chem.* **1991**, *30*, 3513.

0020-1669/93/1332-1204$04.00/0

Table I. Crystallographic Data for $[Pd_2([24]aneN_8)](ClO_4)_2$

chem formula	$C_{16}H_{40}N_8Cl_4Pd_2O_{16}$	D_{calcd}, g cm^{-3}	1.86
fw	955.14	*T*, °C	25
space group	*Pcab*	radiation (λ, Å)	Mo Kα, graphite monochromated (0.7107)
a, Å	15.874(8)		
b, Å	13.070(16)	μ, cm^{-1}	14.3
c, Å	16.454(7)	transm coeff	0.62–0.71
V, Å^3	3414(5)	*F*(000)	1920
Z	4	R^a	0.082
		$R_w{}^b$	0.066

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

spectroscopic, and structural properties of the dipalladium(II) complex of the octaaza ligand $[24]aneN_8$ (1,4,7,10,13,16,19,21-octaazacyclotetracosane). We also report the results of the microcalorimetric determination of the enthalpic contribution to the formation of the binuclear Pd^{2+} complexes with $[18]aneN_6$ and $[21]aneN_7$, as well as the NMR study of all the polynuclear complexes formed by these ligands in solution. The crystal structure of the compound $[Pd_2([24]aneN_8)](ClO_4)_4$, obtained by single-crystal X-ray analysis, will be presented.

Experimental Section

Materials. $[21]aneN_7$ and $[24]aneN_8$ were synthesized as previously reported,[19] while $[18]aneN_6$ was purchased from Fluka. Crystals of $[Pd_2([24]aneN_8)](ClO_4)_4$ were prepared by slow evaporation of a solution containing Na_2PdCl_4, $[24]aneN_8$, and $NaClO_4$ in stoichiometric ratios at neutral pH. Once separated from the mother liquor, these crystals crack without apparent change of color and elemental analysis.

All the solutions of the complexes here employed were prepared in NaCl (Merck suprapure grade) media. All other products were reagent grade.

NMR Spectroscopy. The 200.0-MHz ^1H NMR and 50.32-MHz ^{13}C spectra were recorded in Varian Gemini and Bruker AC-200 spectrometers in D_2O solutions with dioxane as reference standard (δ = 67.4 ppm).

Spectrophotometric Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 instrument.

Microcalorimetry. The enthalpy changes for the reactions of $PdCl_4{}^{2-}$ ions with $[18]aneN_6$, $[21]aneN_7$, and $[24]aneN_8$ were determined in 0.5 mol dm^{-3} NaCl solution by means of a LKB Batch Model 10700-2 microcalorimeter by following a procedure already described.[19]

X-ray Structure Analysis. Prismatic very pale yellow crystals of $[Pd_2([24]aneN_8)](ClO_4)_4$ were obtained by slow evaporation from an aqueous solution. Because they were not stable in air, a crystal of approximate dimensions 0.2 × 0.3 × 0.5 mm was sealed into a fiber glass with some drops of solvent to preserve it from damage and mounted on a four-circle Enraf-Nonius CAD4 automatic diffractometer. The compound crystallizes in an orthorhombic crystal system, space group *Pcab* (Z = 4), with lattice constants a = 15.874(8), b = 13.070(16), and c = 16.454(7) Å, as determined by 25 accurately centered reflections. During data collection three standard reflections were monitored to check the stability of the crystal and of the diffractometer: no loss of intensity was recognized. A total of 4379 intensity data were collected up to $2\theta = 50°$, by using Mo Kα graphite-monochromated radiation, and corrected for Lorentz and polarization effects; an absorption correction was applied once the structure has been solved by using the DIFABS[20] program. A summary of the crystallographic data is reported in Table I.

Structure Solution and Refinement. The structure was solved by means of the heavy-atom method that gave the position of the palladium atom. Successive Fourier syntheses showed all the non-hydrogen atoms. The 2033 reflections having $I > 3\sigma(I)$ were used in the structure refinement which was carried out by means of a full-matrix least-square technique. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = a/\sigma^2(F)$, where a is an adjustable parameter. Some degree of disorder was found for the oxygen atoms of a perchlorate anion, and therefore, in the final model two positions with population parameters of 0.5 were assigned to some oxygen atoms. All non-hydrogen atoms were refined anisotropically, except the disordered oxygen atoms which were treated isotropically. The hydrogen atoms were introduced in calculated position, with U = 0.05 Å, and their positional parameters were refined accordingly to the corresponding linked atoms. The final convergence factors were R = 0.082 and R_w = 0.066. All calculations were performed on an IBM PS2/80 computer with the SHELX-76[21] set of programs that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 22. Table II reports the list of the final atomic coordinates for the non-hydrogen atoms and their thermal parameters. The molecular plots were produced by the program ORTEP.[23]

Table II. Atomic Coordinates (×10^4) and Isotropic or Equivalent Thermal Parameters (×10^3) with Their Esd's in Parentheses

atom[a]	*x/a*	*y/b*	*z/c*	*U*, Å^2
Pd	1022(1)	1434(1)	685(1)	24(1)
Cl1	2874(2)	1211(3)	−832(2)	43(2)
Cl2	−831(3)	1617(4)	2309(2)	66(3)
O1	3518(7)	1068(12)	−1400(6)	88(9)
O2	2160(9)	683(14)	−1143(9)	132(14)
O3	2640(11)	2244(14)	−664(12)	153(16)
O4	3142(10)	872(14)	−78(9)	138(15)
O5	−1063(11)	1893(14)	1522(7)	135(14)
O6	−1408(19)	947(20)	2848(22)	305(35)
O7*	−139(19)	644(28)	2429(18)	111(10)
O8*	−60(13)	1507(19)	2499(12)	60(6)
O9*	−1181(22)	2681(33)	2687(21)	144(12)
O10*	−1357(16)	1643(24)	2889(16)	69(7)
N1	1399(5)	−104(8)	619(5)	23(5)
N2	1598(6)	1404(9)	1750(6)	29(6)
N3	993(8)	2949(8)	829(6)	41(7)
N4	503(6)	1678(9)	−433(6)	37(7)
C1	1852(8)	−305(12)	1396(8)	39(9)
C2	2221(8)	664(11)	1734(8)	38(9)
C3	1833(11)	2528(15)	2025(10)	72(13)
C4	1807(10)	3219(15)	1306(11)	81(13)
C4	895(9)	3467(12)	53(8)	48(9)
C6	224(9)	2891(12)	−382(8)	44(9)
C7	−99(7)	1165(9)	−842(7)	25(7)
C8	−868(7)	965(10)	−323(7)	35(8)

[a] An asterisk indicates an atom with occupancy factor 0.5.

Results and Discussion

Description of the Structure. In the crystal packing there are $[Pd_2([24]aneN_8)]^{4+}$ complex cations (see Figure 1a) and perchlorate anions. Bond lengths and angles in the coordination polyhedron, as calculated with the PARST program,[24] are reported in Table III.

The macrocyclic molecule, which is located around a symmetry center, behaves as two tetradentate ligands: each palladium ion is surrounded by four nitrogen atoms in a distorted square-planar coordination. The distances Pd–N, ranging from 1.98(1) to 2.10(1) Å, are within the expected values. The macrocycle forms five-membered chelate rings in the gauche conformation: the N–C–C–N dihedral angles vary from 44(2) to 56(1)°. The N4–C7–C8–N1′ chain, which joins the two symmetry-related coordination moieties, shows a nearly trans conformation (−159(1)°), imposing an overall "chair" conformation to the dinuclear complex (Figure 1b).

The arrangement of the donor atoms around the metal ion results in a mean plane where the N3 atom shows the largest deviation (0.10(1) Å); the palladium atom is located 0.145(1) Å out of this plane. The two palladium ions, which are 5.447(4) Å apart, are oriented toward the plane passing through the symmetry center parallel to the coordinating N_4 mean planes

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(19) Bianchi, A.; Mangani, S.; Micheloni, M.; Nanini, V.; Orioli, P.; Paoletti, P.; Seghi, B. *Inorg. Chem.* **1985**, *24*, 1182. Micheloni, M.; Paoletti, P.; Bianchi, A. *Inorg. Chem.* **1985**, *24*, 3702.

(20) Walker, N.; Stuart, D. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(21) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(22) *International Tables for X-ray Crystallography*, Kynoch: Birmingham, England, 1974; Vol. IV.

(23) Johnson, C. K. *ORTEP*; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(24) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(25) Ryhl, T. *Acta Chem. Scand.* **1972**, *26*, 2961.

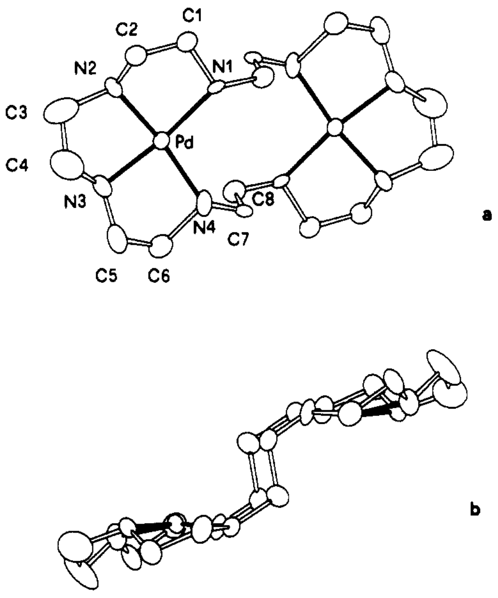


Figure 1. Top view (a) and lateral view (b) of the crystal structure of the complex cation $[Pd_2([24]aneN_8)]^{4+}$.

Table III. Bond Distances (Å) and Angles (deg) Related to the Coordination Sphere with Esd's in Parentheses

	Bond Distances		
Pd-N1	2.10(1)	Pd-N3	1.99(1)
Pd-N2	1.98(1)	Pd-N4	2.04(1)
	Bond Angles		
N3-Pd-N4	86.7(4)	N1-Pd-N4	102.6(4)
N2-Pd-N4	171.4(5)	N1-Pd-N3	164.4(4)
N2-Pd-N3	85.7(5)	N1-Pd-N2	84.0(4)

Table IV. ^1H NMR Parameters for $[Pd_2([24]aneN_8)]^{4+}$ and $[Pd_2([18]aneN_6)Cl_2]^{2+}$ in D_2O[a]

	$[Pd_2([24]aneN_8)]^{4+}$
ABCD	$\delta_A = 2.60, \delta_B = 2.71, \delta_C = 3.02, \delta_D = 3.16$ $J_{AB} = 3.95, J_{AC} = -12.98, J_{AD} = 13.22,$ $J_{BC} = 0.16, J_{BD} = -12.74, J_{CD} = 3.86$
EE′FF′	$\delta_E = \delta_{E'} = 3.10, \delta_F = \delta_{F'} = 3.31$ $J_{EE'} = J_{FF'} = 5.16, J_{EF} = J_{E'F'} = -13.02,$ $J_{EF'} = J_{E'F} = 7.59$
G_4	$\delta_G = 3.16$
	$[Pd_2([18]aneN_6)Cl_2]^{2+}$
AA′BB′	$\delta_A = \delta_{A'} = 2.53, \delta_B = \delta_{B'} = 3.46$ $J_{AB} = J_{A'B'} = -16.35, J_{AA'} = J_{BB'} = 10.49,$ $J_{AB'} = J_{A'B} = 2.02$

[a] Chemical shifts are in ppm and coupling constants are in Hz.

Table V. Thermodynamic Data Obtained at 298.15 K in 0.5 mol dm^{-3} NaCl Solution for the Formation of Dipalladium(II) Complexes of $[18]aneN_6$, $[21]aneN_7$, and $[24]aneN_8$

reacn	$-\Delta H°$
$2PdCl_4^{2-} + [18]aneN_6 = [Pd_2([18]aneN_6)Cl_2]^{2+} + 6Cl^-$	26.5(5)[a]
$2PdCl_4^{2-} + [21]aneN_7 = [Pd_2([21]aneN_7)Cl]^{3+} + 7Cl^-$	28.5(5)
$2PdCl_4^{2-} + [24]andN_8 = [Pd_2([24]aneN_8)]^{4+} + 8Cl^-$	28.4(3)
$2Pd^{2+} + [18]aneN_6 + 2Cl^- = [Pd_2([18]aneN_6)Cl_2]^{2+}$	49.7[b]
$2Pd^{2+} + [21]aneN_7 + Cl^- = [Pd_2([21]aneN_7)Cl]^{3+}$	51.7[b]
$2Pd^{2+} + [24]aneN_8 = [Pd_2([24]aneN_8)]^{4+}$	51.6[b]

[a] Values in parentheses are standard deviation on the last significant figure. [b] Calculated by considering the literature $\Delta H°$ value (-11.6 kcal mol^{-1})[25] for the reaction $Pd^{2+} + 4Cl^- = PdCl_4^{2-}$.

(Figure 1b), and the two complexed moieties are staggered, the Pd–Pd vector forming an angle of 119.5(2)° with each N_4 unit of the ligand. Similar values for the displacement of the Pd^{2+} ion from the mean plane of the coordinating atoms have been recognized in the analogous $[Pd_2([18]aneN_6)X_2]^{2+}$ (X = Cl, Br)[16-18] and $[Pd_2([20]aneN_6)Br_2]^{2+}$ [18] complexes. In all these species the two complexed moieties are cofacially disposed and the two metal ions, which point toward each other, are closer together than the donor atoms mean planes. The internal Pd–Pd distances span from 3.018 and 3.04 Å for the $[Pd_2([18]aneN_6)X_2]^{2+}$ (X = Cl, Br) complexes to 5.039 Å for $[Pd_2([20]aneN_6)Br_2]^{2+}$, with the Pd–Pd vector approximately orthogonal to each N_3X coordinating subunit.

Some intramolecular strain is present in the macrocyclic framework of the $[Pd_2([24]aneN_8)]^{4+}$ complex cation as provided by the angular values around the nitrogen atoms connecting the chelate rings (C2–N2–C3 = 119(1)° and C4–N3–C5 = 115(1)°), which are significantly larger than their classical value. This ligand strain, together with the observed displacement of the Pd^{2+} ion from the mean plane passing through the nitrogen atoms, could be ascribed to some difficulty in hosting the two metal ions, inside the macrocyclic cavity, in a square coordination mode.

Finally, in the crystal lattice exist several hydrogen-bond interactions between the oxygen atoms of the perchlorate anions and the hydrogen atoms of the secondary nitrogens.

Thermodynamic Data. Palladium(II) complexes of polyamines present a very high thermodynamic stability. As a matter of fact equilibrium data on the formation of palladium(II) complexes of azamacrocycles are almost unknown.[3] The determination of the stability of such complexes is further complicated by some kinetic inertness in the formation reactions.

We have previously reported the equilibrium constants of the mononuclear Pd^{2+} complexes of $[18]aneN_6$ and $[21]aneN_7$ and of the binuclear complex of $[18]aneN_6$.[16,17] It was observed that the ability of these macrocycles to form mononuclear Pd^{2+} complexes decreases with increasing number of donor atoms in the ligands, while the stability of binuclear complexes increases. Accordingly with these results, just the formation of a very highly stable dipalladium(II) complex of $[24]aneN_8$ has been observed, in the present work, in the pH range (2–12) useful for pH-metric determinations.

The enthalpy changes, experimentally determined by direct microcalorimetry, for the reaction of $PdCl_4^{2-}$ with the three macrocycles here considered to form the binuclear complexes $[Pd_2([18]aneN_6)Cl_2]^{2+}$, $[Pd_2([21]aneN_7)Cl]^{3+}$, and $[Pd_2([24]aneN_8)]^{4+}$ are reported in Table V. As can be seen, the increasing stability observed for the binuclear complexes of $[18]aneN_6$ and $[21]aneN_7$ is followed by an increasing enthalpic contribution. On the other hand, the enthalpy change for the reaction of two $PdCl_4^{2-}$ with the octaaza ligand $[24]aneN_8$, which removes all the chloride ions from both complex anions, is equal, within the experimental error, to the enthalpy change obtained for the analogous reaction of the heptaaza $[21]aneN_7$. Namely, from an enthalpic point of view, the eight nitrogen atoms of $[24]aneN_8$ and the seven donors of $[21]aneN_7$ plus a chloride anion give similar contributions to the stability of $[Pd_2([24]aneN_8)]^{4+}$ and $Pd_2([21]aneN_7)Cl]^{3+}$, respectively (Table V). It is worth noting also that along with the favorable enthalpic contribution the entropic one, at least in the case of $[18]aneN_6$ ($T\Delta S° = 21$ kcal mol^{-1} for $2Pd^{2+} + L + 2Cl^- = Pd_2LCl_2^{2+}$), is of great importance in determining the very high stability of these dipalladium(II) complexes.

Nuclear Magnetic Resonance. The ^{13}C NMR spectra for $[Pd_2([24]aneN_8)]^{4+}$, $[Pd_2([21]aneN_7)Cl]^{3+}$, and $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$ in D_2O are shown in Figure 2. While the spectra for the binuclear complexes of $[18]aneN_6$ and $[24]aneN_8$ display simple patterns, three and four signals respectively, those for the bi- and trinuclear complexes of $[21]aneN_7$ are rather complicated, the number of signals being higher than the overall number of carbon atoms present in the molecules.

The ^{13}C NMR spectrum of $[Pd_2([18]aneN_6)Cl_2]^{2+}$ is almost identical to that reported in the literature[18] for the analogous cation $[Pd_2([18]aneN_6)Br_2]^{2+}$. The only difference would be a

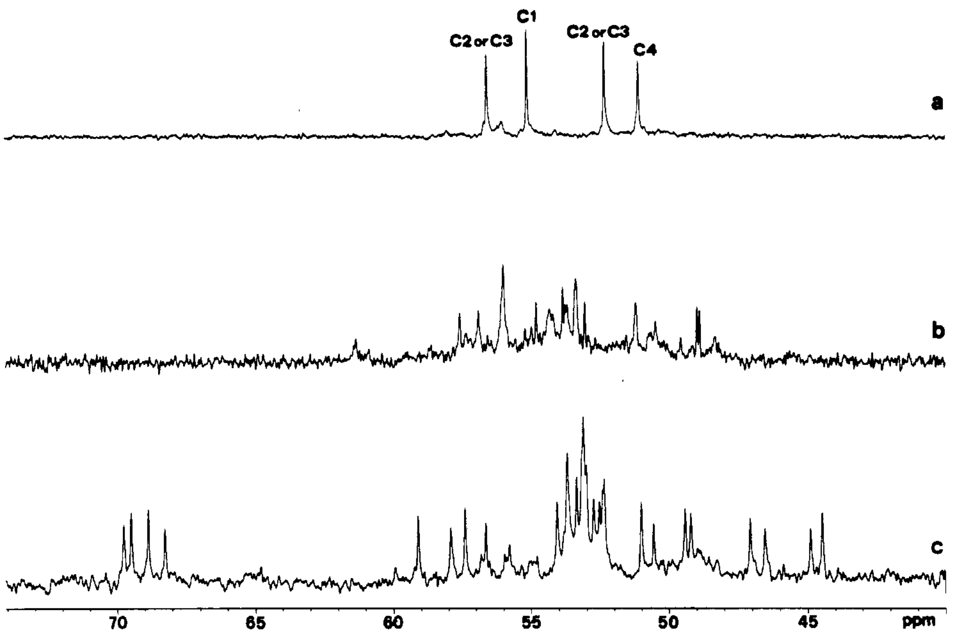


Figure 2. ^{13}C NMR spectra for $[Pd_2([24]aneN_8)]^{4+}$ (a), $[Pd_2([21]aneN_7)Cl]^{3+}$ (b), and $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$ (c) in D_2O.

Chart I

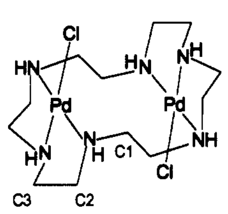
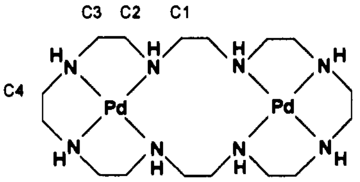


Chart II



slight downfield shift (ca. 0.5 ppm) of all the signals which appear at 46.5, 54.1, and 55.0 ppm. These peaks correspond to the three different carbon atoms present in the molecule: the bridging methylenes (C1) and the two different carbon atoms within the chelate ring (C2, C3) (Chart I).

The ^{13}C NMR spectrum of $[Pd_2([24]aneN_8)]^{4+}$ presents a similar pattern with four signals at 51.19, 52.42, 55.19, and 56.63 ppm (Figure 2a) corresponding to the bridging methylenes (C1) and to the three different carbon atoms within the chelate rings (C2, C3, C4) (Chart II). It should be noted that the signal at 46.5 ppm for $[Pd_2([18]aneN_6)Cl_2]^{2+}$, which can be tentatively attributed to the carbon atoms of the bridging methylenes (C1), is considerably downfield shifted for $[Pd_2([24]aneN_8)]^{4+}$.

As previously mentioned, the spectra for the bi- and trinuclear complexes of $[21]aneN_7$ (Figure 2b,c) are extremely complicated and are not amenable to analysis. However, the set of signals at ca. 70 ppm (Figure 2c) in the $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$ ^{13}C spectrum can surely be assigned to carbon atoms attached to the deprotonated amino group. Therefore, such signals could be diagnostic for the deprotonation of an amino group in this type of compounds. On the other hand, the large number of signals in these spectra suggested the presence of different conformers in solution.

The ^1H NMR spectrum of $[Pd_2([18]aneN_6)Cl_2]^{2+}$ consists of two subspectra with ABCD and EE′FF′ spin systems. The integral of the ABCD protons is twice that of the EE′FF′ ones. Therefore, and similarly to $[Pd_2([18]aneN_6)Br]^{2+}$, the ABCD pattern can be assigned to the protons of the chelating ethylenic chains and the EE′FF′ to the bridging ethylene groups. The ^1H NMR spectrum of $[Pd_2([24]aneN_8)]^{4+}$ displays similar features but in this case three subspecta are found: ABCD, EE′FF′ and G_4. Again, the double intensity of the ABCD pattern allows one to assign it to the ethylenic chain next to the bridging one (C2, C3) (Chart II). On the other hand, 2D ^1H–^1H homonuclear (Figure 3) and 2D ^1H–^{13}C heteronuclear (Figure 4) correlations permit one to establish that the ^{13}C peak at 51.19 ppm corresponds to the singlet G_4 in the ^1H spectrum, those at 52.42 and 56.63 ppm to the protons of the ethylenic chains displaying ABCD pattern, and that at 55.19 ppm to the protons of the EE′FF′ spin system. The simulated spectroscopic parameters for the AA′BB′ spin system of $[Pd_2([18]aneN_6)Cl_2]^{2+}$ and all the spin systems of $[Pd_2([24]aneN_8)]^{4+}$ are presented in Table IV. Within the ABCD pattern of $[Pd_2([24]aneN_8)]^{4+}$, it is of interest to note the large coupling constant found for two vicinal protons, $J_{AD} = 13.22$ Hz, indicating protons roughly located 180° apart. This feature was also observed within the ABCD spin system of $[Pd_2([18]aneN_6)Br_2]^{2+}$.[18] The NMR parameters indicate rigid conformations for two out of the three different ethylenic chains. While the values of the coupling constants within the ABCD spin system are in agreement with a gauche disposition of the ethylenic chains, the closer values for the coupling constants within the EE′FF′ pattern (Table IV) indicate trans disposition of these ethylenic chains. Thus, according to the solid-state data, it could be suggested that the EE′FF′ spin system corresponds to the bridging ethylenic chains (C1) while the G_4 pattern would correspond to the middle chelate rings (C4) (Chart II).

Addition of excess NaOD to the dipalladium(II) complexes of these ligands yields ^1H and ^{13}C NMR spectra much poorer resolved. In the case of the analogous complexes $[Pd_2([18]aneN_6)Br_2]^{2+}$ and $[Pd_2([20]aneN_6)Br_2]^{2+}$ it was suggested that a similar loss of coupling is most likely due to deprotonation of a nitrogen resulting in a coordinated amide.[18] However, unlike $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$, no ^{13}C signals at ca. 70 ppm are observed for these complexes, and therefore, it does not seem that deprotonation of ligand's amino groups is at the origin of such a spectral feature. Instead, some equilibria involving the binuclear complexes and OH^-, like in chloride or nitrogen replacement from the palladium(II) coordination sphere and hydroxide addition to form five-coordinated species, could be responsible for the dynamic process observed in presence of considerable

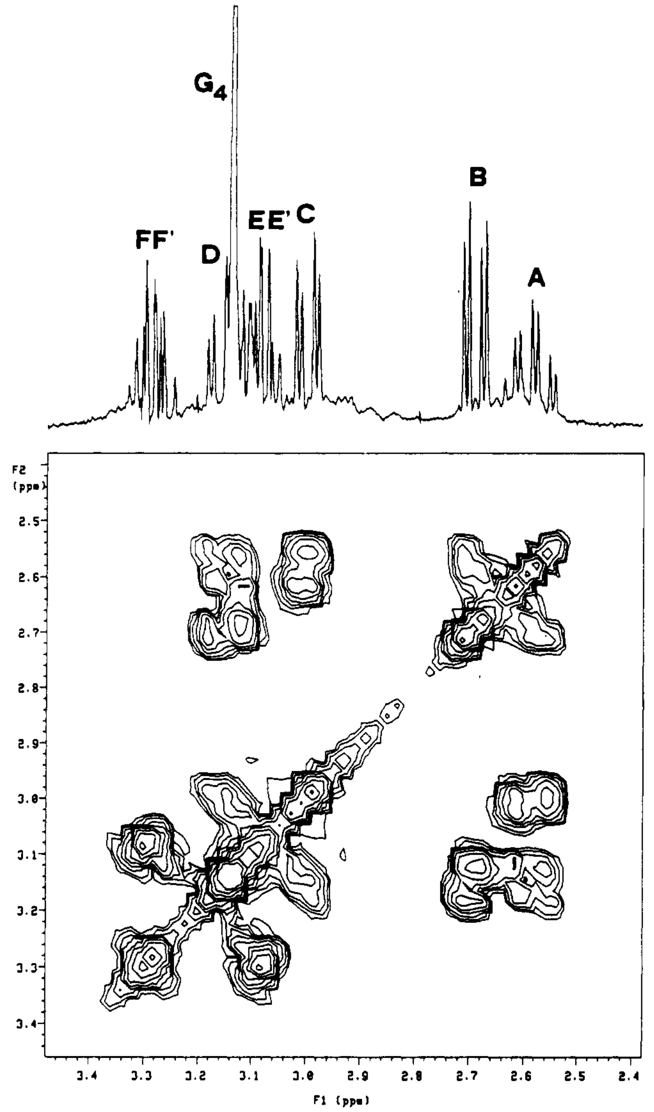


Figure 3. Correlated $^1H-^1H$ NMR spectrum for $[Pd_2([24]aneN_8)]^{4+}$ in D_2O.

amounts of OH^- anion. In fact, it is well-known that a rapid equilibrium (on the NMR time scale) between four- and five-coordinate species is present for the complex $[Pd(trenMe_6)Cl]^+$ ($trenMe_6 = N(CH_2CH_2N(CH_3)_2)_3$) in solution; this equilibrium affects the resolution of the ^1H NMR spectra.[26] Furthermore, the competitive character of OH^- in the binding of the Pd^{2+} ions is easily observed for the complex $[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$, for which in alkaline solution precipitation of palladium(II) hydroxide and formation of the binuclear complex occur.

UV/Vis Spectral Data. The electronic spectra of the polynuclear palladium(II) complexes of $[18]aneN_6$, $[21]aneN_7$, and

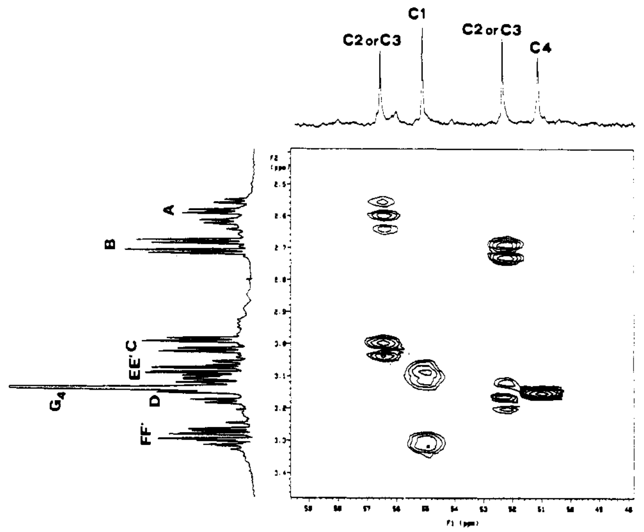


Figure 4. Correlated $^1H-^{13}C$ NMR spectrum for $[Pd_2([24]aneN_8)]^{4+}$ in D_2O.

Table VI. Electronic Spectral Data for Palladium(II) Complexes of $[18]aneN_6$, $[21]aneN_7$, and $[24]aneN_8$

	λ_{max} (ϵ)[a]	
complex	neutral pH	1 mol dm^{-3} NaOH
$[Pd_2([18]aneN_6)Cl_2]^{2+}$	342 (1330)[b]	313 (1370)
$[Pd_2([18]aneN_6)Br_2]^{2+}$	355 (1500)[c]	
$[Pd_2([18]aneN_6)I_2]^{2+}$	382 (2300)[c]	
$[Pd_2([21]aneN_7)Cl]^{3+}$	301 (1490)	327 (2351)
$[Pd_3([21]aneN_7\text{-}H)Cl_3]^{2+}$	377 (2400)[b]	
$[Pd_2([24]aneN_8)]^{4+}$	298 (2030)	325 (2090)

[a] λ_{max} given in nm, ϵ in dm^3 mol^{-1} cm^{-1}. [b] From refs 16 and 17. [c] From ref 18.

$[24]aneN_8$ in solution are characterized by single peaks whose λ_{max} values are reported in Table VI. A few general trends can be outlined: (i) At neutral pH the λ_{max} value experiences a shift toward lower values as the number of chloride ions coordinated to the metal decreases, while in 1 mol dm^{-3} NaOH solution no important changes are observed. (ii) For the $[Pd_2([18]aneN_6)X_2]^{2+}$ (X = Cl, Br, I) complexes the λ_{max} value increases with the increasing soft character of the coordinated halogen ($Cl^- < Br^- < I^-$).

Furthermore, we can observe that, from the spectroscopical data reported in Table VI for neutral and very alkaline solutions, no features diagnostic for the deprotonation of amino groups in this type of compounds are present.

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Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters for the hydrogen atoms, complete bond lengths and angles, and intermolecular hydrogen bonds (4 pages). Ordering information is given on any current masthead page.

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(26) Senoff, C. V. *Inorg. Chem.* **1978**, *17*, 2329. Bhattacharya, S. N.; Senoff, C. V. *Inorg. Chim. Acta* **1980**, *41*, 67. Walker, F. S.; Bhattacharya, S. N.; Senoff, C. V. *Inorg. Synth.* **1982**, *21*, 129.