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"Swollen" Macrocycles: Palladium(II)-Directed Template Syntheses of Pendant-Arm 14-, 16-, and 18-Membered Macrocycles

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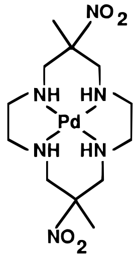
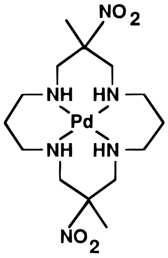
The bis(diamine)palladium(II) cations (diamine = ethane-1,2-diamine, propane-1,3-diamine, or butane-1,4-diamine) all undergo condensation reactions with formaldehyde and nitroethane to produce macromonocycles where each pair of *cis*-disposed primary amines has been converted to a $-NH-CH_2-C(CH_3)(NO_2)-CH_2-NH-$ strap. The 14-membered-ring macrocycle has been previously prepared by condensation around copper(II) and nickel(II), but this does not permit synthesis of the larger ring macrocycles. The macrocyclic complex (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)palladium(II) perchlorate crystallizes in the triclinic space group $P\bar{1}$, $a = 8.105(3)$ Å, $b = 8.370(2)$ Å, $c = 9.437(4)$ Å, $\alpha = 69.04(3)°$, $\beta = 68.60(3)$, $\gamma = 71.53(3)°$. Complexes of the 16- and 18-membered macrocycles (3,11-dimethyl-3,11-dinitro-1,5,9,13-tetraazacyclohexadecane)palladium(II) perchlorate and (3,12-dimethyl-3,12-dinitro-1,5,10,14-tetraaazacyclooctadecane)palladium(II) perchlorate crystallize in the monoclinic space group $P2_1/c$, with $a = 8.391(2)$ Å, $b = 12.816(3)$ Å, $c = 23.925(9)$ Å, and $\beta = 93.18(2)°$, and the triclinic space group $P\bar{1}$, with $a = 7.746(5)$ Å, $b = 9.912(5)$ Å, $c = 18.96(2)$ Å, $\alpha = 91.76(6)°$, $\beta = 101.73(7)°$, and $\gamma = 112.83(5)°$ respectively. The larger macrocycles are "swollen" by incorporating longer methylene chains, "swelling" leading to an increase in Pd−N distance and in tetrahedral distortion, with the dominant geometric isomer apparently changing with macrocycle size from *anti*-disposed nitro pendants (14-membered) to the *syn* isomer (16-, 18-membered). An irreversible $Pd^{II/IV}$ oxidation occurs at ca +1 V (vs Ag/AgCl), varying slightly with ring size, with a multi-electron nitro group reduction observed near −0.8 V in each case. Electronic spectra also vary slightly with ring size.

Introduction

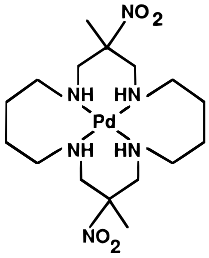
The metal template reaction of bis(ethane-1,2-diamine)copper(II) with formaldehyde and the carbon acid nitroethane in basic solution proceeds readily to produce a substituted cyclam (1,4,8,11-tetraazacyclotetradecane) macrocycle, which is the copper(II) analogue of **I**.[3] The same product is obtained following cyclization around a nickel(II) metal ion template.[4] Despite the facility of these particular reactions around at least copper(II), the outcome is altered significantly by introducing substituents on, or varying the chelate ring size of, the precursor diamine. For example, the yield of macrocycle drops to <1% upon introduction of *gem*-dimethyl substituents on the ethane-1,2-diamine (en) precursor, whereas with propane-1,3-diamine (tn) there is no macrocycle formed.[5] Significantly lower stability of the complex with six-membered chelate rings, which leads to decomposition in the basic conditions of the reaction, presumably defines the outcome in the latter case, but not the former. The nickel(II) complex of propane-1,3-diamine does not yield macrocyclic products either under the basic conditions of the reaction. Copper(II) complexes of 18-membered macrocyclic tetraamines incorporating butane-1,4-diamine (bn) units have been prepared by nontemplate means,[6] so it is clear that large chelate rings do not limit stable complex formation with macrocyclic ligands, supporting the instability of the precursors as the primary cause of failure of the condensation reactions with larger chelate ring diamines.



I



II



III

Diamine complexes of palladium(II) exhibit markedly greater kinetic and thermodynamic stability than the copper(II) and nickel(II) systems and offer a potential starting point for condensation reactions. We have observed earlier that reaction of a dinuclear palladium(II) complex of the tridentate ligand 1,5-diaminopentane-3-thiolate with formaldehyde and nitroethane yields a macrocyclic product encapsulating the two palladium ions, where six-membered chelate rings are present in the precursor and product.[7] The palladium(II) complex of a linear tetraamine has been shown to undergo a Schiff base condensation with 1,1-diacetyl-2,2′-biimidazole to yield a diamagnetic macrocyclic complex.[8] Although not prepared by template means, stable palladium(II) complexes of saturated macrocyclic polyamines are well-known, including mono-, bi-,

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(3) Comba, P.; Curtis, N. F.; Lawrance, G. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1986**, *25*, 4260.

(4) Curtis, N. F.; Gainsford, G. J.; Siriwardena, A.; Weatherburn, D. C. *Aust. J. Chem.* **1993**, *46*, 755.

(5) Rossignoli, M.; Lawrance, G. A.; Maeder, M.; Skelton, B. W.; White, A. H. *Aust J. Chem.*, submitted.

(6) Hay, R. W.; Pujari, M. P. *Inorg. Chim. Acta* **1986**, *121*, 57.

(7) Lawrance, G. A.; Maeder, M.; Manning, T. M.; O'Leary, M. A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1990**, 2491.

(8) Kandil, S. S.; Collier, H. L. *Inorg. Chem.* **1988**, *27*, 4542.

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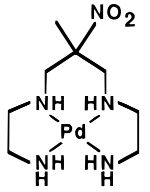
and trinuclear complexes depending on macrocycle ring size and number of amine donors.[9,10]

We set out to examine the prospect of employing bis(diamine)palladium(II) complexes as precursors for formaldehyde/carbon acid condensation reactions leading to macrocyclic tetraamines carrying methyl and nitro groups as substituents. The facility of the reaction was established by employing bis(ethane-1,2-diamine)palladium(II), which replicates the chemistry observed around the labile copper(II) template to produce a 14-membered macrocyclic complex, **I**. Importantly, the reaction is also successful when employing both propane-1,3-diamine and butane-1,4-diamine analogues, producing 16- and 18-membered macrocyclic complexes **II** and **III**, respectively, "swollen" around the center as five-membered chelate rings are replaced by six- and seven-membered rings in turn. Details of the syntheses and characterization, including X-ray crystal structure determinations for isomers of all three macrocycles, are reported herein.

Results and Discussion

Effective syntheses of $[Pd(en)_2]^{2+}$ and $[Pd(tn)_2]^{2+}$ have been reported previously[11] and can be adapted to allow synthesis of the $[Pd(bn)_2]^{2+}$ analogue. Reaction of a concentrated aqueous solution of $[PdCl_4]^{2-}$ with 1 molar equiv of the required diamine around pH 10 readily yields the relatively insoluble yellow $[Pd(diamine)Cl_2]$ compounds. When reaction is carried out with excess diamine, pink to brown $[Pd(diamine)_2][PdCl_4]$ forms first. Heating and stirring a suspension of either with excess diamine drive the reaction toward essentially colorless $[Pd(diamine)_2]^{2+}$. Although the isolated bis(diamine)palladium(II) precursor can be employed in condensation reactions, it is possible to generate the bis(diamine) in situ and proceed with a successful condensation. The range of possibilities is illustrated by commencing with $[PdCl_4]^{2-}$ (with bn), $[Pd(diamine)Cl_2]$ (with en), and $[Pd(diamine)_2]^{2+}$ (with tn) in the syntheses reported herein. In each case, a colorless macrocyclic palladium(II) complex was obtained. Yields were excellent with en and tn, but reduced somewhat with the longer chain bn; however, the method developed in the latter case starting from $[PdCl_4]^{2-}$ could be optimised by purification of the bis(diamine) intermediate, although this is difficult to isolate. Nevertheless, we have separately observed successful condensation reactions around palladium(II) with mixed en and decane-1,10-diamine chelates, indicating that the method can be extended to yet larger ring macrocycles.[12]

Macrocyclization is defined by the appearance of characteristic infrared resonances associated with the introduced nitro group pendants near 1550 and 1345 cm^{-1}, as well as the appearance of a multielectron irreversible reduction of the nitro groups observed near −0.8 V (versus Ag/AgCl) in voltammetry of the products. Further, the strong infrared resonances in the region 1560−1600 cm^{-1} associated with the primary amine deformation modes in the precursors are replaced by weak resonances associated with only secondary amine bands in the macrocycles. This behavior mirrors that observed with condensation around a copper(II) template.[3] The condensation reactions are driven toward the macrocyclic product by employing an excess of formaldehyde and nitroethane reagents. When limited amounts of these reagents are employed, reaction can be intercepted at the "half-built" stage, with the acyclic molecule **IV** characterized in the case of the reaction based on en. The presence of primary amines in this molecule is clear in the infrared, but the most obvious characterization comes from proton-decoupled ^{13}C NMR spectroscopy. The crystallized macrocyclic product **I** exhibits only four resonances (27.6, 57.9, 59.0, 94.1 ppm), assigned to the pendant methyl, two types of ring methylenes, and tertiary carbon, respectively. The crystallized acyclic product **IV** is of lower symmetry, and five resonances are predicted and observed (25.5, 44.7, 56.4, 57.9, 92.1 ppm), the additional resonance near 45 ppm assigned to the carbons adjacent to the primary amines. Acyclic molecules are generally avoided in the syntheses described by judicious use of appropriate amounts of condensation reagents and by control of pH. Macrocyclic products of high analytical purity crystallized reasonably readily in the presence of perchlorate ion, crystals of X-ray quality being produced upon recrystallization from water.



IV

Ion chromatography on Sephadex cation exchange resin was employed in an attempt to separate different products and isomers, with the eluate monitored spectrophotometrically in the region 250−300 nm. This permitted separation of cyclic products from some minor amounts of acyclic and neutral molecules, but we were not successful in separating the two potential geometric isomers known to form with at least copper(II) as the templating metal. The presence and separation of *syn* (nitro groups on the same side of the macrocyclic plane) and *anti* (nitro groups on opposite sides of the plane) isomers were inferred from earlier work with the copper(II)-templated analogue of **I**, although separation and characterization had to await zinc−acid reduction of the nitro groups to pendant amines, with complexation of isomers of the free ligand to several metal ions, permitting their structural characterization. In the case of **I**, only the *anti* isomer was isolated in high yield, inferring a small percentage of *syn* isomer forms. This stereoselectivity parallels the behavior in the analogous copper(II)-based chemistry for this reaction.[3] In the case of **II** and **III**, the more readily crystallized and dominant product is the *syn* isomer, although NMR spectroscopy of eluate solutions indicates that the reaction is again stereoselective rather than stereospecific. Nevertheless, there appears to be a trend from a preference for *anti* to *syn* isomer with increasing ring size. The stereochemistry of the precursor presumably plays a role in directing the stereochemical outcome. With a pair of six-membered chelate rings both adopting chair conformations on the same side of the donor plane in the precursor, for example, the condensation chemistry should be directed to the other side, leading to preferentially a *syn* isomer.

Cyclic voltammetric (gold working electrode) examination of the macrocyclic complexes in aqueous solution permitted identification of an irreversible oxidation near +1 V (versus Ag/AgCl) assigned to a Pd(II)/Pd(IV) couple. The position of the couple varied only slightly with ring size, with E_{pa} observed at +0.96 V [14-membered], +0.93 V [16-membered], and +1.10 V [18-membered]. A reduction wave was observed on the return sweep near 0 V, presumably associated with reduction

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[9] Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-España, E.; Paoletti, P.; Paoli, P.; Ramirez, J. A.; Rodriguez, A. *Inorg. Chem.* **1993**, *32*, 1204.

[10] McAuley, A.; Whitcombe, T. W.; Zaworotko, M. J. *Inorg. Chem.* **1991**, *30*, 3513.

[11] Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1970**, *9*, 1800.

[12] Rossignoli, M.; Lawrance, G. A.; Maeder, M. Unpublished results.

Table 1. Summary of Crystal Data for Complexes **I**−**III**

	I	II	III
formula	$PdC_{12}H_{26}N_6Cl_2O_{12}$	$PdC_{14}H_{30}N_6Cl_2O_{14}$	$PdC_{16}H_{32}N_6Cl_2O_{14}$
fw	623.69	683.74	709.78
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	8.105(3)	8.391(2)	7.746(5)
b, Å	8.370(2)	12.816(3)	9.912(5)
c, Å	9.437(4)	23.925(9)	18.96(2)
α, deg	69.04(3)	90	91.76(1)
β, deg	68.60(3)	93.18(2)	101.73(1)
γ, deg	71.53(3)	90	112.83(5)
V, Å^3	543.7(3)	2568.9	1304(2)
Z	1	4	2
ρ_{calc}, g/cm^3	2.003	1.768	1.808
ρ_{obs}, g/cm^3	2.01	1.75	1.82
λ, Å	0.710 69	0.710 69	0.710 69
T, K	294	294	294
μ, mm^{-1}	1.173	1.007	0.996
R1^a	0.0351	0.0614	0.0713
wR2^b	0.1154	0.1905	0.2061

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **I**

	x	y	z	U(eq)^a
Pd	0	0	0	28(1)
N(1)	2745(4)	−682(4)	−849(4)	34(1)
C(1)	3219(5)	−2624(5)	−515(6)	44(1)
C(2)	3565(5)	189(6)	−2525(5)	45(1)
N(2)	163(4)	−2591(4)	1186(4)	35(1)
C(3)	−1055(6)	−2969(5)	2828(5)	44(1)
C(4)	2101(6)	−3354(5)	1123(6)	45(1)
C(5)	3055(6)	2170(5)	−3011(5)	41(1)
N(3)	3710(4)	2873(4)	−2045(4)	40(1)
O(5)	3413(7)	4430(5)	−2304(5)	75(1)
O(6)	4501(6)	1854(5)	−1109(5)	72(1)
C(6)	4123(7)	2851(8)	−4737(5)	60(1)
Cl(1)	730(2)	1896(2)	2719(1)	49(1)
O(1)	684(6)	3303(5)	1287(4)	72(1)
O(2)	1392(9)	2336(7)	3642(6)	113(2)
O(3)	−960(8)	1488(10)	3420(8)	136(3)
O(4)	1935(11)	328(8)	2342(7)	126(2)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **II**

	x	y	z	U(eq)
Pd(1)	3034(1)	7915(1)	3564(1)	47(1)
N(1)	2092(8)	8518(5)	4276(3)	74(2)
N(2)	4062(8)	6671(6)	3975(3)	77(2)
N(3)	3875(7)	7263(5)	2851(2)	62(2)
N(4)	1929(8)	9175(5)	3174(3)	67(2)
C(1)	1996(15)	7858(9)	4780(4)	94(3)
C(3)	3539(10)	6318(7)	4504(4)	75(2)
C(2)	1929(8)	6698(8)	4673(3)	68(2)
C(4)	5714(9)	6541(8)	3890(4)	84(3)
C(5)	6311(10)	6555(13)	3345(4)	111(4)
C(6)	5586(10)	7139(7)	2876(4)	76(2)
C(7)	3252(10)	7572(9)	2308(3)	76(2)
C(8)	1693(8)	8175(7)	2271(3)	62(2)
C(9)	1810(11)	9208(7)	2569(4)	80(2)
C(10)	2647(13)	10208(7)	3419(5)	97(3)
C(11)	2395(15)	10340(8)	4002(6)	109(4)
C(12)	2831(14)	9555(9)	4399(5)	103(3)
C(13)	1511(13)	6111(11)	5202(4)	112(4)
C(14)	1194(12)	8311(12)	1642(4)	104(3)
N(5)	604(10)	6420(9)	4259(3)	96(3)
O(1)	880(13)	5694(9)	3937(4)	147(4)
O(2)	−570(10)	6904(11)	4245(5)	170(6)
N(6)	359(9)	7518(9)	2494(3)	84(2)
O(3)	−841(8)	7989(8)	2625(4)	126(3)
O(4)	532(11)	6603(9)	2509(4)	137(3)
Cl(1)	2304(3)	4824(2)	1149(1)	96(1)
O(11)	2516(22)	5803(9)	1013(6)	218(7)
O(12)	1345(12)	4376(15)	730(7)	267(11)
O(13)	3731(13)	4396(16)	1267(10)	288(12)
O(14)	1499(14)	4726(23)	1592(7)	316(15)
Cl(2)	3846(3)	13303(2)	3971(1)	93(1)
O(21)	3101(13)	12978(10)	3501(4)	166(6)
O(22)	2912(17)	13456(12)	4395(5)	188(5)
O(23)	4977(13)	12468(10)	4118(6)	160(4)
O(24)	4884(15)	14106(8)	3917(6)	179(5)
O(1′)	3431(17)	4884(8)	2703(6)	202(6)
O(2′)	6270(32)	8212(20)	4834(11)	327(13)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of the palladium(IV) complex formed. Irreversibility and wide separation of the forward and reverse waves are associated with rapid conversion from four-coordination to six-coordination and the reverse in the oxidation and reduction steps, respectively. For all complexes, dc polarography characterized a multielectron reduction at −0.71 V [14-membered], −0.78 V [16-membered], and −0.88 V [18-membered], assigned to reduction of the nitro groups to hydroxylamine groups in neutral solution. The trend in reduction potential may reflect a differing electronic influence of the metal ion with increase in ring size (and Pd−N bond length), as well as effects related to conversion of the form of the complex from an *anti* to a *syn* isomer. The electronic spectra also change with ring size from 275 nm [14-membered] to 293 nm [16-membered] and 291 nm [18-membered]. The structural similarities of **II** and **III**, described below, may account for their similar spectra, whereas **I** is an *anti* isomer with a more compressed coordination sphere. Previously, a correlation between M−N distance and electronic maxima was observed.[13] The increasing molar absorptivity with increasing ring size (508 to 593 to 615 M^{-1} cm^{-1} from 14- to 16- to 18-membered) correlates with the increasing tetrahedral distortion of the square planar geometry observed at least in the structural studies reported below, such distortion relaxing selection rules.

The three macrocyclic species were characterized finally by X-ray crystal structure analyses. A summary of crystal data appears in Table 1, with atomic coordinates and equivalent isotropic displacement parameters given in Tables 2−4. Details of the palladium environments in **I**−**III** appear in Table 5. The structure of the complex cation of **I**, which contains a 14-membered macrocycle with substituents in *anti* dispositions, is shown in Figure 1. Half of the molecule is symmetry generated, as the palladium lies at the center of symmetry and the metal and nitrogen donors are necessarily coplanar. The complex exhibits square-planar coordination, with oxygens of perchlorates located above the axial sites too far away (at 3.264 and 3.750 Å) to say they occupy those positions. The pendants are in an arrangement where each nitro group is axial and each methyl group equatorial, attached to central carbon atoms of six-membered chelate rings which adopt chair conformations. The four secondary amines exhibit *RRSS* stereochemistries whereby pairs of protons on amines linked by the six-membered chelate rings lie on opposite sides of the macrocyclic plane. The structure can be compared with that of the palladium(II) complex of the nitro-reduced analogue (6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine, diammac).[14] The Pd−N distances in the diammac structure [2.036(3), 2.044(3) Å] are the same within experimental error as those observed in

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(13) Bernhardt, P. V.; Lawrance, G. A. *Coord. Chem. Rev.* **1990**, *93*, 297.

(14) Bernhardt, P. V.; Lawrance, G. A.; Patalinghug, W. C.; Skelton, B. W.; White, A. H.; Curtis, N. F.; Siriwardena, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2853.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **III**

	x	*y*	*z*	*U*(eq)
Pd(1)	774(1)	2500(1)	2500(1)	38(1)
N(1)	1965(9)	4772(7)	2542(4)	45(1)
N(2)	28(11)	2306(9)	1374(4)	56(2)
N(3)	−348(9)	232(7)	2462(4)	46(1)
N(4)	1380(10)	2699(9)	3620(4)	57(2)
C(1)	1364(13)	5431(9)	1907(5)	56(2)
C(2)	−674(11)	4595(10)	1457(5)	51(2)
C(21)	−1175(15)	5561(12)	911(6)	70(3)
N(5)	−2025(13)	4398(16)	1970(6)	97(4)
O(51)	−1553(18)	5377(20)	2455(8)	158(6)
O(52)	−3450(22)	3437(24)	1826(10)	236(11)
C(3)	−1068(18)	3147(11)	1068(6)	80(3)
C(4)	1496(27)	2158(22)	1046(11)	62(1)
C(4′)	−578(27)	1084(21)	930(11)	62(1)
C(5)	2474(27)	1283(21)	1385(11)	62(1)
C(5′)	1006(26)	403(22)	974(11)	62(1)
C(6)	1195(29)	−296(22)	1497(11)	62(1)
C(6′)	2144(28)	432(23)	1707(11)	62(1)
C(7)	941(16)	−423(11)	2257(6)	65(2)
C(8)	−974(13)	−421(9)	3089(5)	54(2)
C(9)	−1722(12)	409(10)	3545(5)	51(2)
C(91)	−2633(15)	−561(12)	4093(6)	71(3)
N(6)	−3416(17)	580(16)	3026(6)	93(3)
O(61)	−4387(18)	−371(19)	2547(7)	152(6)
O(62)	−3669(36)	1602(26)	3175(11)	256(13)
C(10)	−293(17)	1842(11)	3937(6)	76(3)
C(11)	3277(26)	2841(22)	3966(11)	62(1)
C(11′)	2428(26)	3937(21)	4084(11)	62(1)
C(12)	4816(26)	3708(21)	3605(11)	62(1)
C(12′)	4635(26)	4600(22)	4028(11)	62(1)
C(13)	4993(27)	5316(22)	3516(11)	62(1)
C(13′)	5024(27)	4581(23)	3305(11)	62(1)
C(14)	4114(12)	5426(11)	2743(6)	67(3)
Cl(1)	5305(4)	7878(6)	795(2)	105(1)
O(11)	6209(19)	7531(14)	1407(6)	121(4)
O(12)	5856(18)	7629(15)	195(6)	129(4)
O(13)	3460(13)	7702(15)	715(6)	121(4)
O(14)	6348(22)	9544(14)	974(13)	236(11)
Cl(2)	1634(6)	7124(6)	4205(2)	107(1)
O(21)	2265(16)	7471(14)	3593(6)	119(4)
O(22)	3040(16)	7360(15)	4806(6)	128(4)
O(23)	51(16)	7306(15)	4284(6)	120(4)
O(24)	771(30)	5432(14)	4017(12)	218(10)
O(1)	2954(49)	9738(77)	4206(14)	585(50)
O(2)	3976(48)	5143(77)	789(14)	582(47)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Palladium Environments in **I**−**III**

Palladium Environemnt in **I**

atom	*r*	N(1#)	N(2#)	N(2)
N(1)	2.034(3)	180.0	94.79(12)	85.21(12)
N(2)	2.040(3)	94.79(12)	180.0	
N(2#)	2.040(3)	85.21(12)		
N(1#)	2.034(3)			

Palladium Environment in **II**

atom	*r*	N(4)	N(3)	N(2)
N(1)	2.067(7)	84.3(3)	177.3(3)	93.8(3)
N(2)	2.047(7)	177.8(3)	85.9(3)	
N(3)	2.058(6)	96.0(3)		
N(4)	2.062(6)			

Palladium Environment in **III**

atom	*r*	N(4)	N(3)	N(2)
N(1)	2.069(6)	89.8(3)	178.6(2)	90.0(3)
N(2)	2.078(7)	177.0(3)	85.83(3)	
N(3)	2.065(6)	90.0(3)		
N(4)	2.066(7)			

[a] *r* is the palladium−donor atom distance (Å); # defines a symmetry-generated atom; the other entries in the matrix are the angles (degrees) subtended at the palladium by the relevant atoms at the head of the row and column.

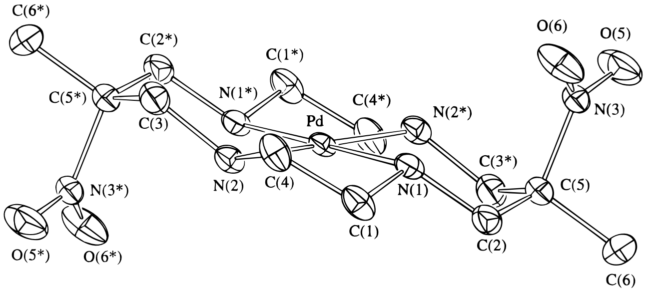

Figure 1. ORTEP drawing of the cation of **I** showing the crystallographic numbering (50% probability ellipsoids shown; hydrogen atoms omitted).

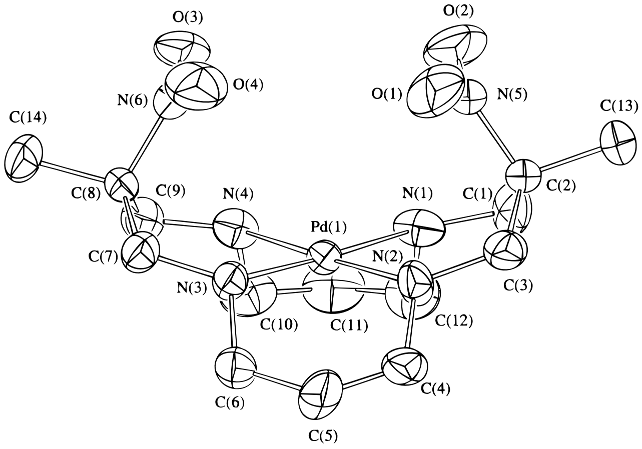

Figure 2. ORTEP drawing of the cation of **II** showing the crystallographic numbering (50% probability ellipsoids shown; hydrogen atoms omitted).

the present structure [2.034(3), 2.040(3) Å], despite the change from nitro pendants in the latter to ammonio pendants in the former. However, there is a shift from the pendant methyl being equatorial in **I** to axial in diammac. The Pd−N distances are slightly shorter than in the Pd(II) complex of cyclam [2.044(7), 2.057(7) Å][15] and shorter still than in complexes of cyclic amines such as 1,4,7-triazacyclononane where the amine acts as a simple chelate [average 2.056(6) Å][16] .

The crystal structure of **II** identified a molecular cation as well as two perchlorate and two water molecules in the unit cell for a solution in the $P2_1/c$ space group. The structure exhibits significant disorder, but an alternate solution in the $P2_1$ space group did not provide any improvement. Disorder in the propyl chains evident from the large thermal ellipsoids could not be resolved. A view of the complex cation of **II** shown in Figure 2 confirms the *syn* configuration of the pendants and the formation of a sixteen-membered macrocycle. The complex ion adopts a "nest" type of geometry where the two nitro groups lie symmetrically opposite above the PdN_4 plane as axial substituents on six-membered chelate rings of boat conformation directed above the donor plane. The other opposite pairs of unsubstituted six-membered chelate rings also adopt boat conformations directed below the donor plane. This arrangement leads to all the amine protons lying on the same side of the ring as the nitro pendants (*RSRS* stereochemistry), forming

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(15) Toriumi, K.; Yamashita, M.; Ito, H.; Ito, T. *Acta Crystallogr., Sect. C* **1986**, *42*, 963.

(16) Blake, A. J.; Gordon, L. M.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1452.

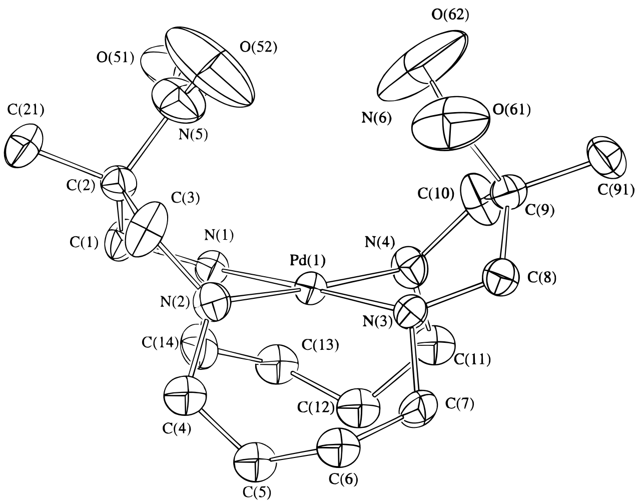

Figure 3. ORTEP drawing of the cation of **III** showing the crystallographic numbering (50% probability ellipsoids shown; hydrogen atoms omitted).

part of the "nest" framework. The two water molecules are involved in a number of hydrogen-bonding interactions, mainly with perchlorate oxygens, although several hydrogen-bonding interactions with the amines exist [e.g. O(1′)···HN(1) 2.261 Å].

The synthesis and structure of the unsubstituted 16-membered macrocycle 1,5,9,13-tetraazacyclohexadecane as the free amine have been reported previously.[17] Interestingly, this metal-free macrocycle adopts the same geometry for the macrocycle framework as that observed in **II**, with adjacent trimethylene groups folded toward opposite sides of the nitrogen plane. The nitrogens adopt a square-planar arrangement in the free ligand with a deviation (average 0.019 Å) similar to that found in **II**, with an average edge length for the square of 2.925(4) Å, compared with an average 2.908(10) Å in the complex described here. The free ligand displays S_4 point group symmetry, also approximated in **II** if pendants are ignored. Excluding the amine hydrogens and substituents, both macrocyclic compounds display nearly D_{2d} symmetry with the trimethylene units bisected by dihedral mirror planes and the nitrogen atoms on 2-fold axes. The common structure suggests that this is a low-energy conformation, favored even in the presence of a bound metal ion.

For **III**, the longer diaminobutyl chains in the precursor lead to an 18-membered macrocycle which exhibits disorder in the long chains. This disorder has been resolved, but only one conformation is shown in the drawing of the complex cation in Figure 3. One carbon atom (C(7) and C(14), depending on the chain considered) is common to both conformations, i.e. the butyl chain is disordered over only three of the four carbon atoms. The *syn* disposition of pendants is obvious in the figure, but whereas the two pendants in **II** are symmetrically disposed opposite each other attached to symmetric six-membered boat chelate rings, in the structure of **III** the two boats are skewed, and the nitro groups thus twisted, in opposite directions. One oxygen on each nitro group [O(52) and O(62)] approaches one on the other to within 3.179 Å and also approaches the palladium more closely than do the other two nitro oxygens [Pd−O(52) 3.773 Å, Pd−O(62) 3.708 Å, and Pd−O(51) 3.951 Å, Pd−O(61) 3.926 Å]. The seven-membered chelate rings are folded down on the opposite side of the PdN_4 plane to the six-membered rings. Apart from the increase in the ring size in **III**, this leads to a structure similar to that observed in the 16-membered macrocycle complex **II**. Deviation of atoms from the PdN_4 least-squares plane is observed, with opposite pairs of nitrogens displaced in the same direction but the opposed direction to the other pair [N(1), N(3) −0.039 Å and N(2), N(4) +0.040 Å] in a tetrahedral distortion. The Pd is also displaced from the plane (−0.014 Å), and the Pd−N distances vary from 2.065 to 2.078 Å. A similar but smaller tetrahedral distortion (deviations ±0.015 Å) is observed in the smaller 16-membered **II**, but there is necessarily no deviation observable in the 14-membered **I**. For the series of macrocycles, the average Pd−N distance increases from 2.040 Å (14-membered) to 2.058 Å (16-membered) to 2.070 Å (18-membered). Thus there is an increase in both Pd−N bond distance and tetrahedral distortion as the macrocyclic ring swells.

Most studies of palladium(II) binding to 18-membered macrocycles have involved molecules with more than four donors. For example 1,4,7,10,13,16-hexaazacyclooctadecane binds two palladium ions, each bound to three amines and a chloride or bromide ion.[10,18] The two tridentate units of the macrocycle are oriented *trans* with respect to the Pd−Pd vector, and the two Pd atoms are separated by only 3.02−3.04 Å. Larger rings with six or eight donors also readily accommodate two palladium(II) atoms.[9,10,18] The only way two palladium ions could be accommodated in the present case is by each palladium binding a pair of amines and two halogen ions; the synthetic method employed prohibits such an outcome. However, with the prospect of extending the chemistry to larger rings and rings with additional donors, the method may provide a synthetic route to macrocycles capable of encapsulating two metal ions. The present series of "swollen" macrocycles indicate how transfer of the metal-directed carbon acid/formaldehyde condensation chemistry from a labile copper(II) template to a much more inert palladium(II) template can extend the applicability of the method to the facile synthesis of larger ring macrocycles.

Experimental Section

Synthesis. *Caution!* Metal perchlorate compounds present a potential explosive hazard. Although we detected no problems with the compounds described below, due care should be taken.

(5-Methyl-5-nitro-3,7-diazanonane-1,9-diamine)palladium(II)Perchlorate Hemihydrate, [Pd(nolin)](ClO_4)$_2$·0.5H_2O, (IV). The precursor [Pd(en)Cl_2] was prepared as described previously.[11] To a suspension of [Pd(en)Cl_2] (1.0 g) in water (130 mL) was added a solution of ethane-1,2-diamine (0.3 mL) in water (20 mL). After 20 min of stirring and heating (60 °C), the resulting colorless solution was filtered, the filtrate treated with formaldehyde (4 mL, 37% aqueous solution) and nitroethane (2 mL), and the pH raised to 10 with dilute NaOH solution. Stirring at room temperature for 10 days produced a bright yellow solution, which was filtered to remove traces of Pd metal, the filtrate was diluted to 2 L with water, and the solution was sorbed onto a column of Sephadex SP-C25 cation exchange resin. The column was washed with water, and elution was commenced with 0.2 M $NaClO_4$ solution. A minor yellow band was eluted first, and discarded. The slower elution of the major product was followed spectrophotometrically using a flow-through spectrophotometer cell in the region 280−300 nm. The eluate was concentrated on a rotary evaporator to ca. 5 mL, precipitating a small amount (0.03 g) of a fine white powder identified following collection as the macrocyclic product **I** described in an optimized synthesis below. To the filtrate was added ethanol and diethyl ether, and the solution was refrigerated overnight. A fine white powder formed and was collected, washed with ethanol and diethyl ether, and dried (0.19 g). Anal. Calcd for $C_8H_{22}Cl_2N_5O_{10.5}Pd$: C, 18.1; H, 4.2; N, 13.2. Found: C, 18.0; H, 4.0; N, 13.1. Electronic spectrum (water): λ_{max} 282 (ϵ 542 M^{-1} cm^{-1}), 221 nm (ϵ 1990). IR spectrum (KBr disk): 1549, 1349 cm^{-1} (−NO_2), 1594, 1616 cm^{-1} (−NH_2). NMR

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(17) Smith, W. L.; Ekstrand, J. D.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 3539.

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

spectra (DMSO-d_6): ^{1}H δ 1.60 (s, 3H), 2.5−3.3 (m, 18H); ^{13}C (^{1}H-decoupled) δ 25.5, 44.7, 56.4, 57.9, 92.1.

(6,13-Dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)palladium(II) Perchlorate, [Pd(dino[14]mac)](ClO_4)$_2$, (I). [Pd(en)Cl_2] was prepared as described previously.[11] To a suspension of [Pd(en)Cl_2] (1.0 g) in water (150 mL) was added ethane-1,2-diamine (0.3 mL). The mixture was stirred and heated (60°C) until a colorless solution resulted. Heating was discontinued, and the solution was allowed to cool to room temperature. Nitroethane (2 mL) and formaldehyde (4 mL, 37% aqueous solution) were added, and the pH was adjusted to 11 with dilute NaOH solution. The resulting mixture was stirred at room temperature for 2.5 days, and a moderate amount of white precipitated macrocyclic product was present after that time. Heating (35 °C) and stirring were initiated and continued for 6 days, with the levels of nitroethane and formaldehyde supplemented twice during this period (1 mL and 2 mL, respectively), the solution slowly turning bright yellow. On cooling, more white powder precipitated and was collected, washed with ethanol and then diethyl ether, and air-dried. The product was recrystallized from hot water, with addition of solid $NaClO_4$ to aid in the reprecipitation of **I** as the perchlorate salt (0.76 g). The filtrate was diluted to 1.5 L with water, and the solution was sorbed onto a column (15 × 3 cm) of Sephadex SP-C25 cation exchange resin. Elution with 0.2 M NaCl removed the product, the eluate being monitored spectrophotometrically in the region 250−300 nm. The colorless eluate was concentrated on a rotary evaporator to a small volume, and $NaClO_4$ was added to precipitate the product. Recrystallization was performed as with the first batch, with which it was identical (total 1.7 g, 66%). Anal. Calcd for $C_{12}H_{26}Cl_2N_6O_{12}Pd$: C, 23.1; H, 4.2; N, 13.5. Found: C, 23.05; H, 4.2; N, 13.5. Electronic spectrum (water): λ_{max} 275 (ϵ 508 M^{-1} cm^{-1}), 220 nm (ϵ 2200). IR spectrum (KBr disk): 1555, 1346 cm^{-1} ($-NO_2$). NMR spectra (DMSO-d_6): ^{1}H δ 1.60 (s, 6H), 2.5−3.1 (m, 16H); ^{13}C (^{1}H-decoupled) δ 27.6, 57.9, 59.0, 94.1. Slow evaporation of a solution of [Pd(dino[14]mac)](ClO_4)$_2$ in water afforded colorless crystals of the perchlorate salt suitable for X-ray analysis.

(3,11-Dimethyl-3,11-dinitro-1,5,9,13-tetraazacyclohexadecane)palladium(II) Perchlorate Hydrate, [Pd(dino[16]mac)](ClO_4)$_2$·H_2O (II). The precursor [Pd(tn)$_2$](ClO_4)$_2$ was prepared as described previously.[11] To a solution of [Pd(tn)$_2$](ClO_4)$_2$ (1.48 g) in water (50 mL) were added nitroethane (2 mL) and formaldehyde (4 mL, 37% aqueous solution), and the pH was adjusted to 9.5 with dilute NaOH solution. The resulting mixture was stirred at room temperature for 3 days and then allowed to stand for another 4 days. The solution was filtered, the filtrate was diluted to 3 L with water, and the solution was sorbed onto a column (15 × 3 cm) of Sephadex SP-C25 cation exchange resin. Following washing with water, elution with 0.2 M $NaClO_4$ removed the product, the major portion of eluate collected exhibiting a band near 290 nm. The eluate was concentrated on a rotary evaporator to a small volume, and off-white flakes of the product precipitated and were collected, washed with ethanol and diethyl ether, and air-dried (0.84 g). Further crops were produced on prolonged standing (0.56g, total yield 64%). Anal. Calcd for $C_{14}H_{32}Cl_2N_6O_{13}Pd$: C, 25.1; H, 4.8; N, 12.55. Found: C, 24.8; H, 4.8; N, 12.5. Electronic spectrum (water): λ_{max} 292 (ϵ 577 M^{-1} cm^{-1}), 225 nm (ϵ 1790). IR spectrum (KBr disk): 1550, 1346 cm^{-1} ($-NO_2$). NMR spectra (DMSO-d_6): ^{1}H δ 1.5 (s, 6H); 1.6−2.0 (m, 4H), 2.4−3.1 (m, 16H). ^{13}C (^{1}H-decoupled) δ 24.3, 25.5, 50.5, 54.0, 88.6. Slow evaporation of a solution of [Pd(dino[16]mac)](ClO_4)$_2$ in water afforded colorless crystals of the perchlorate salt suitable for X-ray analysis.

(3,12-Dimethyl-3,12-dinitro-1,5,10,14-tetraazacyclooctadecane)palladium(II) Perchlorate Dihydrate, [Pd(dino[18]mac)](ClO_4)$_2$·2H_2O (III). To a solution of $K_2[PdCl_4]$ (0.5 g) in water (50 mL) was added a solution of butane-1,4-diamine dihydrogen chloride (0.49 g) in water (20 mL). The pH was adjusted to 7 with 0.1 M NaOH solution, and heating (60 °C) and stirring were continued until a very pale yellow solution resulted. After cooling, nitroethane (0.5 mL) and formaldehyde (1 mL, 37% aqueous solution) were added and the pH was adjusted to 8 with NaOH solution. Stirring at room temperature was continued for 8 days. Filtration removed traces of palladium metal, the filtrate was diluted to 1 L with water, and the solution was sorbed onto a column (15 × 3 cm) of Sephadex SP-C25 cation exchange resin. Following washing with water, elution with 0.2 M $NaClO_4$ removed the product. The eluate was concentrated on a rotary evaporator to ca. 10 mL volume, and a very pale yellow powder precipitated on standing and was collected, washed with ethanol and diethyl ether, and air-dried (0.17g, 16%). Anal. Calcd for $C_{16}H_{38}Cl_2N_6O_{14}Pd$: C, 26.85; H, 5.35; N, 11.75. Found: C, 26.7; H, 5.3; N, 11.8. Electronic spectrum (water): λ_{max} 291 (ϵ 613 M^{-1} cm^{-1}) 230 (ϵ 3050). IR spectrum (KBr disk): 1553, 1347 cm^{-1} ($-NO_2$). NMR spectra (DMSO-d_6): ^{1}H δ 1.4−1.9 (m, 14H), 2.3−2.8 (m, 16H); ^{13}C (^{1}H-decoupled) δ 23.8, 24.8, 52.8, 56.6, 90.6. Slow evaporation of a solution of [Pd(dino[18]mac)](ClO_4)$_2$ in water afforded near-colorless crystals of the perchlorate salt suitable for X-ray analysis.

Physical Methods. Electronic spectra were measured on a Hitachi 150-20 UV−vis spectrophotometer. Infrared spectra were measured on a Bio-Rad FT-IR spectrometer with samples being dispersed in KBr disks. Cyclic voltammetry was performed with a BAS CV-27 controller employing a gold working electrode, a silver/silver chloride reference electrode, and a platinum counter electrode. Polarography employed a Metrohm 663VA static mercury drop unit. All aqueous solutions were 0.1 M in $NaClO_4$ and were purged with nitrogen. The NMR spectra were recorded on a JEOL FX-90Q spectrometer in DMSO-d_6, with the shifts cited versus TMS.

Structure Analyses. For the structures of the three Pd macrocyclic complexes, lattice parameters at 294 K were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation. Intensity data were collected in the range $1 < \theta < 25°$ by using a $\omega-2\theta$ scan mode. Data reduction, polarization, and numerical Gaussian absorption corrections were carried out with the Enraf-Nonius Structure Determination Package.[19] Crystallographic data are summarized in Table 1.

The structures were solved by direct methods (**II**) and Patterson methods (**I** and **III**) according to the computer program SHELXS-86[20] and refined by difference-Fourier methods with the SHELXL-93[21] program. All non-hydrogen atoms with the exception of minor sites of C(ligand) disorder were refined anisotropically. Hydrogen atoms were placed at geometrically calculated sites according to the recommended specifications of the SHELXL-93 program and refined with respect to the atoms to which they were attached. Scattering factors and anomalous dispersion corrections were taken from ref 22. Plots were drawn using ORTEP.[23] Non-hydrogen atom coordinates are listed in Tables 2-4, and selected distances and angles around the palladium appear in Tables 5. Views of the molecular cations (Figures 1−3) also show the atom-numbering schemes adopted.

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(19) *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1985.
(20) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(21) Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.
(22) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(23) Johnson, C. K. *ORTEP: A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.