Simultaneous First- and Second-Sphere Coordination. Organopalladium Metalloreceptors for Water, Ammonia, Amines, Hydrazine, and the Hydrazinium Ion

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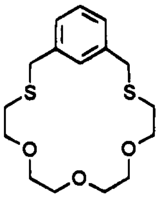
Received May 16, 1995[⊗]

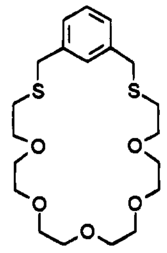
The complexes [Pd(L)(CH_3CN)][BF_4] (L^3 = 5,8,11-trioxa-2,14-dithia[15]-*m*-cyclophane and L^5 = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane) were prepared by palladation of the respective thiacyclophane employing [Pd(CH_3CN)$_4$][BF_4]$_2$. These metalloreceptors were reacted with various small substrates (H_2O, NH_3, NH_2R, NHR_2, NH_2NH_2, and $NH_2NH_3^+$) capable of simultaneously coordinating to the Pd center and hydrogen-bonding with the peripheral ether oxygens. [Pd(L^3)(NH_3)][BF_4] crystallized in the space group *Pbca* with a = 21.377(4) Å, b = 21.656(5) Å, c = 9.437(6) Å, V = 4368(2) Å^3, and Z = 8. The structure refined to R = 6.41% and R_w = 7.03% for 659 reflections with $F_o^2 > 3\sigma(F_o^2)$. [Pd(L^3)(NH_2NH_2)][BF_4] crystallized in the space group $P\bar{1}$ with a = 11.652(3) Å, b = 12.669(4) Å, c = 8.356(1) Å, α = 94.13(2)°, β = 94.34(2)°, γ = 117.21(1)°, V = 1090.3(5) Å^3, and Z = 2. The structure refined to R = 2.81% and R_w = 3.40% for 2709 reflections with $F_o^2 > 3\sigma(F_o^2)$. [Pd(L^5)(H_2O)][BF_4] crystallized in the space group $P\bar{1}$ with a = 11.076(3) Å, b = 15.147(5) Å, c = 8.586(2) Å, V = 1284(1) Å^3, and Z = 2. The structure refined to R = 3.14% and R_w = 4.06% for 2275 reflections with $F_o^2 > 3\sigma(F_o^2)$. [Pd(L^3)(NH_2NH_3)][CF_3SO_3]$_2$ crystallized in the space group $P2_1/c$ with a = 11.906(4) Å, b = 17.19(1) Å, c = 15.313(4) Å, β = 111.18(2)°, V = 2923(4) Å^3, and Z = 4. The structure refined to R = 3.13% and R_w = 4.25% for 2954 reflections with $F_o^2 > 3\sigma(F_o^2)$. [Pd(L^5)(NH_2NH_3)][BF_4]$_2$ crystallized in the space group $P\bar{1}$ with a = 9.391(3) Å, b = 18.292(5) Å, c = 9.107(2) Å, α = 94.46(3)°, β = 102.02(2)°, γ = 103.51(2)°, V = 1474.5(8) Å^3, and Z = 2. The structure refined to R = 3.69% and R_w = 4.58% for 3059 reflections with $F_o^2 > 3\sigma(F_o^2)$. Each complex shows evidence of hydrogen bonding between the Pd-bound substrate and the peripheral oxygen atoms. The major hydrogen-bonding sites are the oxygen atoms adjacent to the thioether atoms, while the extent of the hydrogen bonding is dependent on the size of the polyether ring and the orientation of the substrate. Controlling the number of hydrogen bonds formed results in selective binding of primary amines (two hydrogen bonds) over secondary amines (one hydrogen bond) and tertiary amines (no hydrogen bonds) as determined by competition reactions monitored by ^{1}H NMR spectroscopy.

Introduction

A substrate molecule or ancillary ligand may interact with a metal-containing receptor such that it occupies sites in *both* the first and second coordination spheres of the transition metal complex. This phenomenon is known as *simultaneous* first- and second-sphere coordination.[1] The first complexes in which this phenomenon was unambiguously identified by X-ray crystallography were not created by design and involved substrates such as water[2] and ammonia.[3] Recently, however, metalloreceptors were designed which employ this multiple-point binding scheme for the molecular recognition of DNA nucleobases,[4] barbiturates,[5] and amino acids.[6] As well, boron-containing receptors have been prepared which demonstrate complementary binding of amines *and* alcohols.[7]

Our work in this area has centered on a series of organopalladium metalloreceptors which employ σ-donation to a transition metal (Pd) and non-covalent second-sphere interaction such as hydrogen bonding and π-stacking to produce molecule recognition.[4] In this article, we report the synthesis, structural investigations, and binding properties of metalloreceptors based on the thiacyclophane ligands L^3 and L^5 (3 and 5 represent the number of ether oxygen atoms in the polyether ring). These complexes act as metalloreceptors for simple substrates such as H_2O, NH_3, NH_2R, NHR_2, NH_2NH_2, and $NH_2NH_3^+$ via


L^3


L^5

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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0020-1669/95/1334-5656$09.00/0

simultaneous first- and second-sphere coordination.[8] Preliminary results describing complexes with the hydazinium ion were the subject of a recent communication.[8]

Experimental Section

All starting materials, hexaethylene glycol, hydrazine hydrochloride, hydrazine hydrate, *n*-butylamine, *N*-methylbutylamine, *N,N*-dimethylbutylamine, allylamine, deuterated solvents, and anhydrous *N,N*-dimethylformamide (DMF) were purchased from Aldrich Chemicals and used without further purification, except acetonitrile, which was distilled from CaH_2 under $N_2(g)$. $[Pd(L^3)(CH_3CN)][BF_4]$ and $[PdCl(L^3)]$ were prepared as described previously.[4,9] All reactions were performed under an atmosphere of $N_2(g)$ using standard Schlenk or drybox techniques, and all solvents and liquid starting materials were degassed prior to use. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC300 spectrometer locked to the deuterated solvent at 300.1 and 75.5 MHz, respectively, and infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia.

Preparation of 1,17-Dichloro-3,6,9,12,15-pentaoxaheptadecane. To a solution of $SOCl_2$ (8.7 g, 73 mmol) in 100 mL of CH_2Cl_2 was added a solution of hexaethylene glycol (10.015 g, 35.5 mmol) and pyridine (5.9 g, 74 mmol) in CH_2Cl_2 (100 mL) over a 4 h period. The solvent was reduced to 75 mL, and the solution was washed with water (25 mL), 0.1 M HCl (25 mL), and water (25 mL) and then dried over $MgSO_4$ overnight. The solution was filtered, and the solvent was removed, leaving a yellow oil which was vacuum-distilled. Yield: 9.143 g (81%). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.73 (t, 4H, OCH_2), 3.64 (br s, 16 H, OCH_2), 3.60 (t, 4H, CH_2Cl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 71.45 (OCH_2), 70.77, 70.71 (OCH_2), 42.81 (CH_2Cl). Anal. Calcd for $C_{12}H_{24}Cl_2O_5$: C, 45.14; H, 7.59. Found: C, 45.08; H, 7.43.

Preparation of 5,8,11,14,17-Pentaoxa-2,20-dithia[21]-*m*-cyclophane, L^5. To a suspension of Cs_2CO_3 (7.718 g, 23.7 mmol) in DMF (500 mL), at 56 °C, was added a solution of *m*-xylene-α,α′-dithiol (1.977 g, 11.6 mmol) and 1,17-dichloro-3,6,9,12,15-pentaoxaheptadecane (3.705 g, 11.6 mmol) in DMF (115 mL) over 36 h. After the slow addition was complete, the DMF was removed *in vacuo*, leaving a brown oil and cesium salts. The residue was dissolved in CH_2Cl_2 (200 mL), and the solution was filtered, washed with 0.1 M NaOH (2 × 50 mL) and distilled water (50 mL), and then dried over anhydrous $MgSO_4$ overnight. The dried solution was then filtered and the CH_2Cl_2 evaporated to dryness *in vacuo*. Column chromatography using diethyl ether as eluent ($R_f = 0.30$) and 60 g of silica gel (70–230 mesh 60 Å) gave a clear oil upon evaporation of the solvent. Yield: 1.448 g (30%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.26–7.15 (m, 4H, aromatic), 3.74 (s, 4H, benzylic), 3.63–3.51 (m, 20H, OCH_2), 2.56 (m, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 138.81, 129.65, 128.91, 127.67 (aromatic), 71.10, 70.80, 70.45, 70.35 (OCH_2), 36.54 (benzylic), 30.50 (SCH_2). Anal. Calcd for $C_{20}H_{32}O_5S_2$: C, 57.65; H, 7.76. Found: C, 57.25; H, 7.56.

Preparation of $[Pd(L^5)(CH_3CN)][BF_4]$. $[Pd(CH_3CN)_4][BF_4]_2$ (0.116 g, 2.61×10^{-4} mol) and L^5 (0.108 g, 2.59×10^{-4} mol) were added to a Schlenk flask (100 mL) and dissolved in CH_3CN (40 mL) with stirring. Within 5–10 min, the solution changed color from orange to pale yellow. The solution was then refluxed for 12 h. Upon cooling, the solution was concentrated to 3–5 mL and the complex precipitated by the addition of diethyl ether to the solution. Yield of yellow semisolid: 0.129 g (82%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.91 (m, 3H, aromatic), 4.44 (m vbr, 4H, benzylic), 3.93 (br s, 4H, OCH_2), 3.71–3.58 (br m, 16 H, OCH_2), 3.30 (br s, 4H, SCH_2), 2.31 (s, 3H, CH_3CN). Anal. Calcd for $C_{22}H_{34}BF_4NO_5PdS_2$: C, 40.66; H, 5.28. Found: C, 40.12; H, 5.44.

Preparation of $[Pd(L^3)(NH_3)][BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.031 g, 55 μmol) was dissolved in acetonitrile (5.0 mL), and $NH_3(g)$ was passed over the solution for 10 min. The solution was stirred for 2 h at room temperature, after which the solvent was removed *in vacuo*. The resulting paste was recrystallized from acetonitrile/diethyl ether to give a pale yellow powder. Yield: 0.021 g (71%). ^{1}H NMR (CD_3CN): δ (ppm) 7.13 (br s, 3H, aromatic), 4.49 (br s, 4H, benzylic), 4.01 (br s, 4H, OCH_2), 3.75 (br s, 4H, OCH_2), 3.69 (br s, 4H, OCH_2), 3.5–3.2 (m, 4H, SCH_2), 2.54 (br s, 3H, NH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ (ppm) 148.56, 126.23, 123.36 (aromatic, Pd–C not observed), 71.06, 70.22, 68.86 (OCH_2), 47.07 (benzylic), 38.93 (SCH_2). Anal. Calcd for $C_{16}H_{26}BF_4NO_3PdS_2$: C, 35.73; H, 4.88. Found: C, 35.25; H, 4.66.

Preparation of $[Pd(L^3)(n\text{-}BuNH_2)][BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.023 g, 41 μmol) was dissolved in acetonitrile (3.0 mL), and *n*-butylamine (7 μL, 71 μmol) was added by syringe. The solution was stirred at room temperature for 4 h, the solvent removed, and the resulting paste triturated with diethyl ether for 12 h. The diethyl ether was decanted and the resulting pale yellow powder dried *in vacuo*. Yield: 0.023 g (95%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.97 (br m, 3H, aromatic), 4.47 (d, 2H, J = 14.8 Hz, benzylic), 4.33 (d, 2H, benzylic, J = 14.8 Hz), 3.99 (br s, 4H, OCH_2), 3.7–3.2 (m, 12H, OCH_2; 2H, NH_2), 2.66 (m, 2H, $N(\alpha)CH_2$), 1.55 (m, 2H, $N(\beta)CH_2$), 1.34 (m, 2H, $N(\gamma)CH_2$), 0.92 (t, 3H, $N(\delta)CH_3$). Anal. Calcd for $C_{20}H_{34}BF_4NO_3PdS_2$: C, 40.45; H, 5.78. Found: C, 40.34; H, 5.49.

Preparation of $[Pd(L^3)(n\text{-}Bu(Me)NH)][BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.030 g, 53 μmol) was dissolved in acetonitrile (3.0 mL), and *N*-methylbutylamine (7 μL, 59 μmol) was added by syringe. The solution was stirred at room temperature for 4 h, the solvent removed, and the resulting paste triturated with diethyl ether. The diethyl ether was decanted and the pale yellow powder dried *in vacuo*. Yield: 0.031 g (96%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.94 (br s, 3H, aromatic), 4.47–4.36 (m, 4H, benzylic), 4.14–3.88 (m, 6H, OCH_2), 3.71–3.25 (m, 6H, OCH_2; 4H, SCH_2), 2.73 (m, 2H, $N(\alpha)CH_2$), 1.74 (m, 2H, $N(\beta)CH_2$), 1.33 (m, 2H, $N(\gamma)CH_2$), 0.92 (t, 3H, $N(\delta)CH_3$). Anal. Calcd for $C_{21}H_{36}BF_4NO_3PdS_2$: C, 41.49; H, 5.98. Found: C, 41.03; H, 5.63.

Attempted Preparation of $[Pd(L^3)(n\text{-}Bu(Me)_2N)][BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.030 g, 53 μmol) was dissolved in acetonitrile (3.0 mL), and *N,N*-dimethylbutylamine (8 μL, 57 μmol) was added by syringe. The solution was stirred at room temperature for 4 h, the solvent removed, and the resulting paste triturated with diethyl ether for 12 h. The diethyl ether was decanted and the pale yellow powder dried *in vacuo*. The isolated material was shown by ^{1}H NMR spectroscopy to be the original metalloreceptor $[Pd(L^3)(CH_3CN)][BF_4]$.

Preparation of $[Pd(L^3)(allylamine)[BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.045 g, 80 μmol) was dissolved in chloroform (15 mL), and allylamine (9 μL, 122 μmol) was added by syringe. The solution was stirred overnight and the solvent removed *in vacuo*. The resulting yellow paste was recrystallized from chloroform/diethyl ether. Yield: 0.042 g (91%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.95 (m, 3H, aromatic), 5.96 (m, 1H, RCH=R), 5.23 (m, 2H, R=CH_2), 4.45 (d, 2H, ^2J = 14.8 Hz, benzylic), 4.31 (d, 2H, benzylic), 3.97 (br s, 4H, OCH_2), 3.68–3.50 (m, 8H, OCH_2; 2H, NH_2), 3.32–3.24 (m, 4H, SCH_2; 2H, NCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 157.39, 147.36, 125.64, 122.74 (aromatic), 136.07 (olefinic CH), 117.82 (olefinic CH_2), 70.37, 69.17, 68.39 (OCH_2), 47.44 (NCH_2), 46.71 (benzylic), 38.87 (SCH_2). Anal. Calcd for $C_{19}H_{30}BF_4NO_3PdS_2$: C, 39.49; H, 5.24. Found: C, 39.37; H, 5.21.

Preparation of $[Pd(L^5)(H_2O)][BF_4]$. Yellow crystals of $[Pd(L^5)(H_2O)][BF_4]$ were grown from a diffusion of diethyl ether into an acetonitrile solution of $[Pd(L^5)(CH_3CN)][BF_4]$. Trace amounts of water from the atmosphere were introduced into the system, resulting in replacement of the ancillary CH_3CN ligand by H_2O. ^{1}H NMR (CD_3CN): δ (ppm) 6.99 (m, 3H, aromatic), 4.48 (br m, 4H, benzylic), 3.86 (br s, 4H, OCH_2), 3.54 (br m, 18H, OCH_2, H_2O), 3.26 (br s, 4H, SCH_2). Anal. Calcd for $C_{20}H_{33}BF_4O_6PdS_2$: C, 38.32; H, 5.32. Found: C, 38.05; H, 5.18.

Preparation of $[Pd(L^3)(NH_2NH_2)][BF_4]$. $[Pd(L^3)(CH_3CN)][BF_4]$ (0.061 g, 110 μmol) and excess hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) were dissolved in acetonitrile (10 mL), and the solution was stirred overnight. The solvent was removed *in vacuo* and the complex recrystallized from acetonitrile/diethyl ether, resulting in a pale yellow powder. Yield: 0.048 g (80%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.96 (m, 3H, aromatic), 5.57 (s, 2H, $N(\alpha)H_2$), 5.05 (s, 2H, $N(\beta)H_2$), 4.39 (d, 2H, J = 14.2 Hz, benzylic), 4.25 (d, 2H, J = 14.2 Hz, benzylic), 4.03–3.57 (m, 12H, OCH_2; 2H, SCH_2), 3.22 (br d, 1H, J = 14 Hz, SCH_2), 3.07 (br d, 1H, J = 14 Hz, SCH_2). Anal. Calcd for $C_{16}H_{27}BF_4N_2O_3PdS_2$: C, 34.76; H, 4.93. Found: C, 34.50; H, 4.78.

Preparation of $[Pd(L^5)(NH_2NH_2)][BF_4]$. $[Pd(L^5)(CH_3CN)][BF_4]$ (4.0 mL, 25 mM, 100 μmol) and excess hydrazine hydrate were

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Table 1. Summary of X-ray Crystallographic Data Collection, Solution, and Refinement Parameters

compd	$[Pd(L^3)(NH_3)][BF_4]$	$[Pd(L^5)(H_2O)][BF_4]$	$[Pd(L^3)(NH_2NH_2)][BF_4]$	$[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$	$[Pd(L^5)(NH_2NH_3)][BF_4]_2$
formula	$C_{16}H_{26}BF_4NO_3PdS_2$	$C_{20}H_{33}BF_4O_6PdS_2$	$C_{16}H_{27}BF_4N_2O_3PdS_2$	$C_{18}H_{28}F_6N_2O_9PdS_4$	$C_{20}H_{36}BF_4N_2O_5PdS_2$
fw	537.71	626.8	552.72	765.06	728.64
a, Å	21.377(4)	11.076(3)	11.652(3)	11.906(4)	9.391(3)
b, Å	21.656(5)	15.147(5)	12.669(4)	17.192(14)	18.292(5)
c, Å	9.437(6)	8.586(2)	8.356(1)	15.313(4)	9.107(2)
α, deg		92.42(2)	94.13(2)		94.46(3)
β, deg		112.12(2)	92.34(2)	111.18(2)	102.02(2)
γ, deg		74.58(2)	117.21(1)		103.51(2)
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2/c$ (No. 14)	$P\bar{1}$ (No. 2)
V, Å^3	4368(2)	1283.5(12)	1090.3(5)	2923(4)	1474.5(8)
ρ, g cm^{-3}	1.64	1.62	1.68	1.74	1.64
Z	8	2	2	4	2
μ, cm^{-1}	10.91	9.48	10.96	10.07	8.55
λ, Å	0.7017	0.7017	0.7017	0.7017	0.7017
T, °C	23	23	23	23	23
goodness of fit	1.95	1.27	1.54	1.54	1.52
$R(F_o)$,[a] %	6.41	3.14	2.81	3.13	3.69
$R_w(F_o)$,[b] %	7.03	4.06	3.40	4.25	4.58

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

dissolved in acetonitrile (10 mL), and the mixture was stirred under N_2 overnight. The solution was filtered, and the solvent was reduced to 1−2 mL. Diffusion of diethyl ether into this solution gave a pale yellow powder. Yield: 0.022 g (34%). ^1H NMR ($CDCl_3$): δ (ppm) 6.95 (m, 3H, aromatic), 5.6 (br s, NH_2NH_2), 4.6−3.9 (br, 8H, benzylic, OCH_2), 3.8−3.6 (m, 16H, OCH_2), 3.4−3.1 (br s, 4H, SCH_2). Anal. Calcd for $C_{20}H_{35}BF_4N_2O_5PdS_2$: C, 37.48; H, 5.52. Found: C, 37.23; H, 5.46.

Preparation of $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$. $[AgCF_3SO_3]$ (0.062 g, 230 μmol), $NH_2NH_2{\cdot}HCl$ (0.009 g, 130 μmol), and $[PdCl(L^3)]$ (0.0534 g, 115 μmol) were stirred and warmed in acetonitrile. The AgCl was filtered off, and the solvent was removed *in vacuo* to give a yellow solid, which was recrystallized from acetonitrile/diethyl ether. Yield: 0.053 g (60%). Th BF_4^- salt of this compound was prepared by the addition of 1 equiv of $AgBF_4$ to hydrazine hydrochloride and the receptor $[Pd(L^3)(CH_3CN)][BF_4]$. The ^1H NMR spectrum of the dication is independent of the anion. ^1H NMR ($CDCl_3$): δ (ppm) 7.10−6.75 (d, t, d, 3H, aromatic), 4.65 (br s, 4H, benzylic), 4.21−3.61 (m, 12H, OCH_2; 5H, NH_2NH_3), 3.34 (br s, 4H, SCH_2). Anal. Calcd for $C_{18}H_{28}F_6N_2O_9PdS_4$: C, 28.25; H, 3.70. Found: C, 28.15; H, 3.67.

Preparation of $[Pd(L^5)(NH_2NH_3)][BF_4]_2$. $[Pd(L^5)(CH_3CN)][BF_4]$ (4.0 mL, 25 mM) and $[NH_2NH_3][BF_4]$ (2.0 mL, 52 mM, 100 μM) were stirred at room temperature for 1 h in acetonitrile (5 mL), after which the solvent was reduced to 1 mL. Diethyl ether was diffused into the solution, yielding yellow crystals. Yield: 0.037 g (51%). ^1H NMR (CD_3COCD_3): δ (ppm) 7.00 (br s, 3H, aromatic), 4.57 (vbr s, 4H, benzylic), 4.2−3.9 (br m, 8H, OCH_2), 3.72- 3.31 (br m, 21H, OCH_2, SCH_2, NH_2NH_3). Anal. Calcd for $C_{20}H_{36}B_2F_8N_2O_5PdS_2$: C, 32.96; H, 5.00. Found: C, 32.78; H, 4.80.

X-ray Diffraction Data Collection, Solution, and Refinement. Pale yellow to yellow crystals of $[Pd(L^3)(NH_3)][BF_4]$, $[Pd(L^5)(H_2O)][BF_4]$, $[Pd(L^3)(NH_2NH_2)][BF_4]$, $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$, and $[Pd(L^5)(NH_2NH_3)][BF_4]_2$ were grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell constants and orientation matrices for data collection were obtained from 25 centered reflections (15° < 2θ < 35°). Machine parameters, crystal data, and data collection parameters are summarized in Table 1 and in the Supporting Information. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. The intensity data were collected using the $\omega-2\theta$ scan technique, in four shells (2θ < 30, 40, 45, 50°). Absorption coefficients were calculated and corrections applied to the data. The data were processed using the TEXSAN software[10] package running on an SGI Challenge XL computer. The positions of the palladium atoms were determined by conventional Patterson methods. For each compound, the remaining non-hydrogen atoms were located from a series of difference Fourier map calculations. Refinements were carried out with full-matrix least-squares techniques on F by minimizing the function $\sum w(F_o - F_c)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[11] and anomalous dispersion terms[12,13] were taken from the usual sources. In the final cycles of refinement, all non-H atoms were assigned anisotropic thermal parameters except for the carbon atoms of $[Pd(L^3)(NH_3)][BF_4]$, which were refined isotropically, and the BF_4^- anion of $[Pd(L^3)(NH_3)][BF_4]$, which was refined as a rigid group with individual isotropic thermal parameters for each atom. In each compound, the hydrogen atoms involved in hydrogen bonding were treated as rigorously as possible. For $[Pd(L^3)(NH_3)][BF_4]$, the data were of too poor quality to locate the H atoms. The NH_3 H atoms were input at calculated positions and refined as a rigid rotor. For $[Pd(L^5)(H_2O)][BF_4]$, $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$, and $[Pd(L^5)(NH_2NH_3)][BF_4]_2$, the H atoms of the water and hydrazinium groups were located and input as fixed contributions at these experimentally determined positions. For $[Pd(L^3)(NH_2NH_2)][BF_4]$, the hydrazine H atoms were located and input as isotropic atoms and their positions refined. Fixed H atom contributions were included for all carbon atoms with C−H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameters of the bonded C atoms. These H atoms were not refined, but all values were updated as refinement continued. Selected atomic positional parameters, selected bonding parameters, a full listing of atomic positional parameters, nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as Supporting Information.

Results

Synthesis and Characterization of L^5 and $[Pd(L^5)(CH_3CN)][BF_4]$. The thiacyclophane L^5 was prepared by a straightforward, three-step process employing commercially available materials as outlined in Scheme 1. The final ring closure step involves the reaction between the dithiol and dichloride employing Kellogg's Cs^+-mediated method in DMF solution.[14] This relatively straightforward synthetic route produces L^5 as a colorless oil in 30% yield after chromatography. The ^1H NMR spectrum of L^5 contains well-separated sets of resonances attributable to OCH_2, SCH_2, benzylic, and aromatic protons with the proton at the 2-position assigned to a singlet slightly downfield of the other three aromatic protons. The $^{13}C\{^1H\}$ NMR spectrum for this ligand shows well-resolved peaks for all carbon atoms, and a full spectral interpretation was straightforward.

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(10) teXsan Structure Analysis Package, Molecular Structure Corp. (1985).

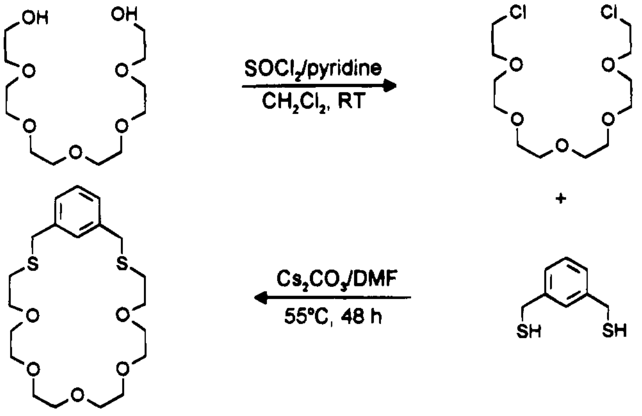
(11) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(12) Ibers, J. A.; Hamilton. W. C. *Acta Crystallogr.* **1974**, *17*, 781.

(13) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

(14) (a) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481−4486. (b) Buter, J.; Kellogg, R. M. *Org. Synth.* **1987**, *65*, 150−152.

Scheme 1



Introduction of a palladium atom into the receptor was achieved by palladation of the 2-position of the aromatic ring employing $[Pd(CH_3CN)_4][BF_4]_2$ in acetonitrile.[4] The resulting metalloreceptor complex $[Pd(L^5)(CH_3CN)][BF_4]$ could only be isolated as a pasty solid after repeated attempts at recrystallization; however, all spectroscopic and analytical data are consistent with the formula. In particular, the ^1H NMR spectrum shows the changes usually observed for palladated thiacyclophanes in this series, most notably the lack of a proton resonance at *ca.* 7.1 ppm and separate resonances for two sets of benzylic protons due to the formation of the chelate rings.[4] The synthesis, spectral characterization, and X-ray structure of $[Pd(L^3)(CH_3CN)][BF_4]$ were described in a previous publication.[4]

Synthesis and Characterization of $[Pd(L^3)(NH_3)][BF_4]$. The initial application of $[Pd(L^3)(CH_3CN)][BF_4]$ and $[Pd(L^5)(CH_3CN)][BF_4]$ as metalloreceptors involved the reaction of $[Pd(L^3)(CH_3CN)][BF_4]$ with ammonia. CPK models suggested that a primary amine, NH_2R, or ammonia, NH_3, could form a Pd−N bond accompanied by two N−H• • •O hydrogen bonds to ether oxygen atoms adjacent to the thioether sulfur atoms. The ^1H NMR spectrum of $[Pd(L^3)(NH_3)][BF_4]$, at room temperature, shows a broad singlet at 2.49 ppm for the ammine protons. The approximately 2 ppm downfield shift of this resonance in $[Pd(L^3)(NH_3)][BF_4]$ ($CDCl_3$), in comparison to that for free ammonia (CD_3CN), is consistent with the substrate being bonded to the palladium atom. If hydrogen bonding is present, there must be rapid rotation about the Pd−N bond which would interchange NH protons on the NMR time scale. At low temperature (213 K), this rotation is slowed and separate peaks are observed at 2.60 and 2.49 ppm which integrate in a 2:1 ratio, indicative of two hydrogen-bonded NH protons and one free NH proton.

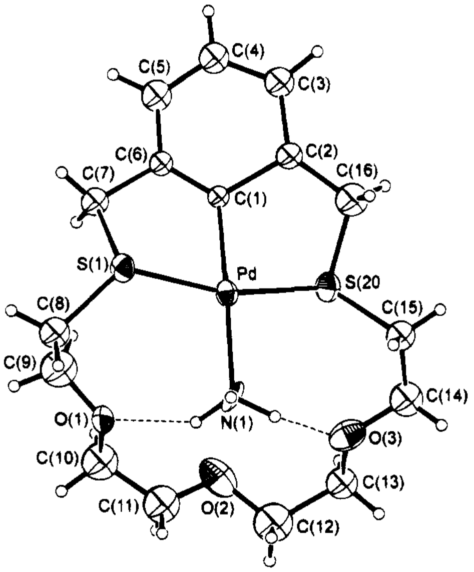


Figure 1. Structure of the $[Pd(L^3)(NH_3)]^+$ cation showing the atom-numbering scheme and hydrogen bonds to the metalloreceptor only.

Table 2. Selected Positional Parameters for $[Pd(L^3)(NH_3)][BF_4]$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Pd	0.2876(1)	0.1042(1)	0.0134(3)	4.3(1)
S(1)	0.3489(4)	0.1914(4)	0.014(1)	5.1(6)
S(2)	0.2103(6)	0.0347(5)	0.055(1)	5.7(6)
O(1)	0.445(1)	0.074(1)	0.119(3)	7(2)
O(2)	0.394(1)	−0.049(2)	0.142(3)	9(2)
O(3)	0.287(2)	−0.071(1)	−0.030(3)	8(2)
N(1)	0.350(1)	0.046(1)	−0.105(3)	5(2)
C(1)	0.231(1)	0.162(2)	0.115(4)	3.5(9)
C(2)	0.157(2)	0.144(2)	0.123(4)	5(1)
C(3)	0.117(2)	0.191(2)	0.195(4)	6(1)
C(4)	0.146(2)	0.239(2)	0.261(5)	7(1)
C(5)	0.210(2)	0.251(2)	0.260(4)	7.1(8)
C(6)	0.250(2)	0.212(2)	0.183(4)	4(1)
C(7)	0.320(2)	0.228(2)	0.184(4)	6(1)
C(8)	0.433(2)	0.182(2)	0.055(4)	7(1)
C(9)	0.444(3)	0.132(3)	0.168(6)	10(1)
C(10)	0.467(3)	0.028(2)	0.215(6)	10(1)
C(11)	0.450(3)	−0.034(3)	0.164(6)	10(1)
C(12)	0.386(3)	−0.102(3)	0.058(6)	11(1)
C(13)	0.315(2)	−0.117(2)	0.053(4)	7(1)
C(14)	0.224(2)	−0.081(2)	−0.047(5)	9(1)
C(15)	0.194(2)	−0.023(2)	−0.085(4)	7(1)
C(16)	0.142(2)	0.085(2)	0.046(5)	8(1)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

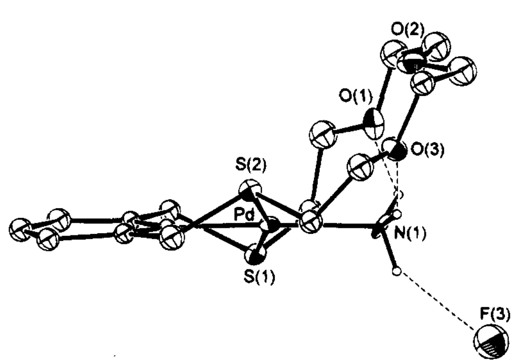


Figure 2. Alternative view of the $[Pd(L^3)(NH_3)]^+$ cation emphasizing the orientation of the polyether ring to the substrate and showing the substrate interaction with F(3) of the BF_4^- anion.

The proposed solution conformation is also that observed in the X-ray crystal structure. The unit cell is orthorhombic and contains eight $[Pd(L^3)(NH_3)]^+$ cations and eight BF_4^- anions. A perspective view of the cation with the atom-numbering scheme is shown in Figure 1. The palladium atom is in a square planar environment with the palladated S_2C fragment occupying three sites and the ammonia nitrogen atom occupying the fourth site on the metal: Pd−S(1) 2.299(9), Pd−S(2) 2.269(10), Pd−N(1) 2.15(3), and Pd−C(1) 1.98(3) Å. The angles at palladium are S(1)−Pd−C(1) 80.1(11) and S(2)−Pd−C(1) 83.6(11)° for the five-membered chelate rings, S(1)−Pd−N(1) 97.3(8) and S(2)−Pd−N(1) 99.0(8)° for the external angles, and N(1)−Pd−C(1) 176.6(10) and S(1)−Pd−S(2) 163.6(4)° for the *trans* angles. From Figure 2, it can be seen that the metal-bound NH_3 substrate is "nested" into the partial crown created by the polyether chain of the macrocycle. Since this is a relatively poor-quality structure, the hydrogen atoms were not located. However, the rigid-rotor positions calculated for the NH_3 hydrogen atoms place two of the hydrogen atoms in positions for linear hydrogen bonding to O(1) and O(3): H(N1A)• • •O(1) and H(N1B)• • •O(3) distances of 2.16(3) and 2.09(3) Å and N(1)−H(N1A)• • •O(1) and N(1)−H(N1B)• • •O(3) angles of 147(2) and 151(2)°, respectively. The third NH_3 hydrogen atom is directed away from the macrocyclic cavity, as predicted by

Table 3. Selected Bonding Parameters for $[Pd(L^3)(NH_3)][BF_4]$

Distance (Å)			
Pd−S(1)	2.299(9)	Pd−S(2)	2.269(10)
Pd−N(1)	2.15(3)	Pd−C(1)	1.98(3)
S(1)−C(7)	1.89(4)	S(1)−C(8)	1.85(4)
S(2)−C(15)	1.86(4)	S(2)−C(16)	1.82(5)
O(1)−C(9)	1.33(7)	O(1)−C(10)	1.42(6)
O(2)−C(11)	1.25(6)	O(2)−C(12)	1.41(7)
O(3)−C(13)	1.40(5)	O(3)−C(14)	1.37(6)
C(1)−C(2)	1.64(5)	C(1)−C(6)	1.33(5)
C(2)−C(3)	1.49(6)	C(2)−C(16)	1.51(6)
C(3)−C(4)	1.35(6)	C(4)−C(5)	1.40(6)
C(5)−C(6)	1.40(6)	C(6)−C(7)	1.54(5)
C(8)−C(9)	1.54(7)	C(10)−C(11)	1.48(8)
C(12)−C(13)	1.55(7)	C(14)−C(15)	1.45(6)
Angles (deg)			
S(1)−Pd−S(2)	163.6(4)	S(1)−Pd−N(1)	97.3(8)
S(1)−Pd−C(1)	80.1(11)	S(2)−Pd−N(1)	99.0(8)
S(2)−Pd−C(1)	83.6(11)	N(1)−Pd−C(1)	176.6(10)
C(7)−S(1)−C(8)	100(2)	C(15)−S(2)−C(16)	102(2)
C(9)−O(1)−C(10)	117(4)	C(11)−O(2)−C(12)	115(4)
C(13)−O(3)−C(14)	112(3)	C(2)−C(1)−C(6)	117(3)
C(1)−C(2)−C(3)	115(3)	C(1)−C(2)−C(16)	112(3)
C(3)−C(2)−C(16)	133(4)	C(2)−C(3)−C(4)	118(4)
C(3)−C(4)−C(5)	126(4)	C(4)−C(5)−C(6)	120(4)
C(1)−C(6)−C(5)	124(4)	C(1)−C(6)−C(7)	118(3)
C(5)−C(6)−C(7)	118(3)	S(1)−C(7)−C(6)	103(2)
S(1)−C(8)−C(9)	112(3)	O(1)−C(9)−C(8)	115(4)
O(1)−C(10)−C(11)	111(4)	O(2)−C(11)−C(10)	121(5)
O(2)−C(12)−C(13)	108(4)	O(3)−C(13)−C(12)	106(4)
O(3)−C(14)−C(15)	110(4)	S(2)−C(15)−C(14)	108(3)
S(2)−C(16)−C(2)	109(3)		

CPK models and observed by ^1H NMR spectroscopy, but in the solid state is involved in further hydrogen bonding to the anion through a NH$\cdots$F$^-$ interaction: H(N1C)$\cdots$F(3) 2.42(2) Å and N(1)−H(N1C)$\cdots$F(3) 147(2)°.

Interaction of $[Pd(L^3)(CH_3CN)][BF_4]$ with Amines. In reactions with *n*-butylamine (*n*-$BuNH_2$), *N*-methylbutylamine (*n*-Bu(Me)NH), and *N,N*-dimethylbutylamine (*n*-$Bu(Me)_2N$), $[Pd(L^3)(CH_3CN)][BF_4]$ formed 1:1 adducts with only the primary and secondary amines. In the ^1H NMR spectra of $[Pd(L^3)(n\text{-}BuNH_2)][BF_4]$ and $[Pd(L^3)(n\text{-}Bu(Me)NH)][BF_4]$, the nitrogen-bonded CH_2 resonances of both substrates and the CH_3 resonance for *N*-methylbutylamine undergo additional coupling to the amino NH proton(s) that is not observed in the spectra of the free substrates. The CH_2 resonances at 2.66 and 2.73 ppm for $[Pd(L^3)(n\text{-}BuNH_2)][BF_4]$ and $[Pd(L^3)(n\text{-}Bu(Me)NH)][BF_4]$, respectively, appear as multiplets, and the CH_3 resonance for *N*-methylbutylamine at 2.59 ppm is split into a doublet. The benzylic resonances for the receptor appear at 4.4 ppm and are split into two sets of doublets, and the aliphatic portion of the macrocycle exhibits sharpened resonances. The NH resonances for $[Pd(L^3)(n\text{-}BuNH_2)][BF_4]$ and $[Pd(L^3)(n\text{-}Bu(Me)NH)][BF_4]$ are shifted downfield and included in the group of resonances ranging from 3.3 to 3.7 ppm.

In a substrate competition experiment between *n*-$BuNH_2$ and *n*-Bu(Me)NH for $[Pd(L^3)(CH_3CN)][BF_4]$ in $CDCl_3$, a 1:1 mixture of *n*-$BuNH_2$ and *n*-Bu(Me)NH was mixed with 1 equiv of $[Pd(L^3)(CH_3CN)][BF_4]$ in $CDCl_3$ and the extent of complexation determined by ^1H NMR spectroscopy. The result was a high selectivity for *n*-$BuNH_2$, as $[Pd(L^3)(n\text{-}BuNH_2)][BF_4]$ was formed exclusively, leaving the *N*-methylbutylamine uncoordinated. As the secondary amine would be expected to be a stronger Lewis base, the primary amine must compete successfully for the palladium coordination site as a result of two factors: (i) the primary amine (*n*-$BuNH_2$) is able to form one more hydrogen bond with the receptor than the secondary amine (*n*-Bu(Me)NH) and (ii) *n*-$BuNH_2$ is less sterically hindered than *n*-Bu(Me)NH.

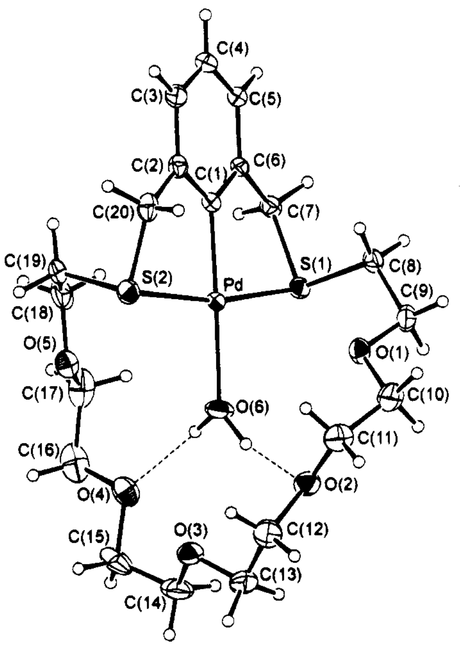


Figure 3. Structure of the $[Pd(L^5)(H_2O)]^+$ cation showing the atom-numbering scheme and hydrogen-bonds to the metalloreceptor.

Allyl halides and allyl Grignard reagents are known to form η^3 complexes with transition metals.[15] In the hope of using hydrogen bonding to induce proton transfer from CH_2 to NH_2 in allylamine and form a Pd−allyl complex, $[Pd(L^3)(CH_3CN)][BF_4]$ was reacted with allylamine in a 1:1 ratio. The substrate was shown by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy to be bonded to the palladium atom via the NH_2 group rather than a π-donor group. This was evidenced by only minor changes in the chemical shifts and splitting patterns for the three olefinic hydrogen atoms and no change in the aliphatic CH_2 resonances upon coordination to the metal, whereas the NH_2 hydrogens are shifted downfield by 2.2 ppm.

Structure of $[Pd(L^5)(H_2O)][BF_4]$. In an attempt to grow crystals of $[Pd(L^5)(CH_3CN)][BF_4]$ employing vapor diffusion of diethyl ether into an acetonitrile solution of the complex, crystals of the Pd−aqua complex were isolated and the crystal structure was determined. The unit cell is triclinic and contains two $[Pd(L^5)(H_2O)]^+$ cations and two BF_4^- anions. A perspective view of the cation with the atom-numbering scheme is shown in Figure 3. The palladium atom is in a square planar environment with the S_2C bracket occupying three sites and the oxygen atom of the water molecule occupying the fourth site on the metal: Pd−S(1) 2.326(2), Pd−S(2) 2.309(2), Pd−C(1) 1.968(7), and Pd−O(6) 2.149(5) Å. The angles at the palladium atom are S(1)−Pd−C(1) 84.9(2) and S(2)−Pd−C(1) 83.8(2)° for the five-membered chelate rings and S(1)−Pd−O(6) 95.3(2) and S(2)−Pd−O96) 95.9(2)° to the nonchelating water ligand. The C(1)−Pd−O(6) 178.3(3)° angle is very close to linear while the S(1)−Pd−S(2) angle of 168.36(8)° shows more distortion from linearity, which is typical for these systems.[4] The large polyether chain of the receptor loops around the water molecule with the S(1)−C(8) and S(2)−C(19) bonds oriented on opposite sides of the aromatic ring (Figure 4). The two hydrogen atoms of the bound water molecule were located in a difference Fourier map and input in these locations for the final model. These positions result in two linear hydrogen bonds with the water substrate at distances of H(O6A)$\cdots$O(2) 2.014(5) and H(O6B)$\cdots$O(4) 2.036(5) Å and angles of O(6)−H(O6A)$\cdots$O(2) 145.9(4) and O(6)−H(O6B)$\cdots$O(4) 161.9(3)°.

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(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. J. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Table 4. Selected Positional Parameters for $[Pd(L^5)(H_2O)][BF_4]$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Pd	0.22961(7)	0.18082(5)	0.23884(8)	2.98(3)
S(1)	0.1206(2)	0.2411(1)	0.4198(2)	3.3(1)
S(2)	0.3333(3)	0.0930(2)	0.0744(3)	5.0(1)
O(1)	0.3677(5)	0.3118(4)	0.5038(6)	4.1(3)
O(2)	0.3657(6)	0.4263(4)	0.2371(7)	4.8(3)
O(3)	0.1834(6)	0.4564(4)	−0.1157(7)	4.8(3)
O(4)	−0.0262(6)	0.3775(4)	−0.2065(7)	5.3(4)
O(5)	0.0385(6)	0.1825(4)	−0.1762(7)	5.0(4)
O(6)	0.1951(5)	0.3108(4)	0.1154(6)	5.3(4)
C(1)	0.2565(8)	0.0612(5)	0.3465(8)	3.2(4)
C(2)	0.3519(7)	−0.0173(5)	0.3295(9)	3.3(4)
C(3)	0.3699(8)	−0.1012(5)	0.410(1)	4.2(5)
C(4)	0.2939(9)	−0.1057(5)	0.504(1)	4.4(5)
C(5)	0.1993(8)	−0.0301(5)	0.5184(9)	3.6(4)
C(6)	0.1796(7)	0.0543(5)	0.4400(8)	2.9(4)
C(7)	0.0724(7)	0.1379(5)	0.4471(8)	3.5(4)
C(8)	0.2557(8)	0.2379(5)	0.6241(9)	3.8(4)
C(9)	0.3204(8)	0.3150(6)	0.636(1)	4.3(5)
C(10)	0.4512(9)	0.3711(6)	0.525(1)	5.6(6)
C(11)	0.4822(9)	0.3761(6)	0.371(1)	5.4(6)
C(12)	0.395(1)	0.4511(7)	0.098(1)	6.3(7)
C(13)	0.271(1)	0.5104(6)	−0.026(1)	6.6(7)
C(14)	0.051(1)	0.5100(6)	−0.202(1)	6.5(7)
C(15)	−0.035(1)	0.4518(7)	−0.309(1)	6.4(6)
C(16)	−0.118(1)	0.3259(9)	−0.294(1)	7.3(7)
C(17)	−0.089(1)	0.2411(9)	−0.188(1)	6.8(7)
C(18)	0.062(1)	0.0962(8)	−0.103(1)	7.1(8)
C(19)	0.204(1)	0.0439(6)	−0.069(1)	7.2(7)
C(20)	0.4297(8)	−0.0049(6)	0.226(1)	4.6(5)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

Table 5. Selected Bonding Parameters for $[Pd(L^5)(H_2O)][BF_4]$

Distances (Å)			
Pd−S(1)	2.326(2)	Pd−S(2)	2.309(2)
Pd−O(6)	2.149(5)	Pd−C(1)	1.968(7)
S(1)−C(7)	1.831(7)	S(1)−C(8)	1.820(7)
S(2)−C(19)	1.82(1)	S(2)−C(20)	1.818(9)
O(1)−C(9)	1.416(9)	O(1)−C(10)	1.412(9)
O(2)−C(11)	1.414(9)	O(2)−C(12)	1.438(9)
O(3)−C(13)	1.42(1)	O(3)−C(14)	1.40(1)
O(4)−C(15)	1.42(1)	O(4)−C(16)	1.41(1)
O(5)−C(17)	1.42(1)	O(5)−C(18)	1.39(1)
C(1)−C(2)	1.409(9)	C(1)−C(6)	1.397(9)
C(2)−C(3)	1.40(1)	C(2)−C(20)	1.50(1)
C(3)−C(4)	1.38(1)	C(4)−C(5)	1.37(1)
C(5)−C(6)	1.394(9)	C(6)−C(7)	1.506(9)
C(8)−C(9)	1.50(1)	C(10)−C(11)	1.50(1)
C(12)−C(13)	1.46(1)	C(14)−C(15)	1.50(1)
C(16)−C(17)	1.49(1)	C(18)−C(19)	1.47(1)
O(6)−H(O6A)[a]	0.894(5)	O(6)−H(O6B)[a]	0.907(5)
Angles (deg)			
S(1)−Pd(1)−S(2)	168.36(8)	S(1)−Pd(1)−O(6)	95.3(2)
S(1)−Pd(1)−C(1)	84.9(2)	S(2)−Pd(1)−O(6)	95.9(2)
S(2)−Pd(1)−C(1)	83.8(2)	O(6)−Pd(1)−C(1)	178.3(3)
C(7)−S(1)−C(8)	100.2(3)	C(19)−S(2)−C(20)	99.0(4)
C(9)−O(1)−C(10)	111.9(6)	C(11)−O(2)−C(12)	113.2(7)
C(13)−O(3)−C(14)	112.1(8)	C(15)−O(4)−C(16)	112.3(8)
C(17)−O(5)−C(18)	111.8(8)	C(2)−C(1)−C(6)	119.8(7)
C(1)−C(2)−C(3)	119.3(7)	C(1)−C(2)−C(20)	116.9(7)
C(3)−C(2)−C(20)	123.9(7)	C(2)−C(3)−C(4)	119.6(7)
C(3)−C(4)−C(5)	121.5(7)	C(4)−C(5)−C(6)	120.0(7)
C(1)−C(6)−C(5)	119.8(7)	C(1)−C(6)−C(7)	118.6(6)
C(5)−C(6)−C(7)	121.5(7)	S(1)−C(7)−C(6)	109.3(5)
S(1)−C(8)−C(9)	112.2(5)	O(1)−C(9)−C(8)	109.1(6)
O(1)−C(10)−C(11)	110.0(7)	O(2)−C(11)−C(10)	110.3(7)
O(2)−C(12)−C(13)	109.2(8)	O(3)−C(13)−C(12)	109.3(8)
O(3)−C(14)−C(15)	110.5(8)	O(4)−C(15)−C(14)	109.0(7)
O(4)−C(16)−C(17)	109.7(8)	O(5)−C(17)−C(16)	108.4(8)
O(5)−C(18)−C(19)	109.3(9)	S(2)−C(19)−C(18)	116.0(7)
S(2)−C(20)−C(2)	110.0(6)	H(O6A)−O(6)−H(O6B)[a]	95.9(5)

[a] H(O6A) and H(O6B) were positioned in located positions but not refined.

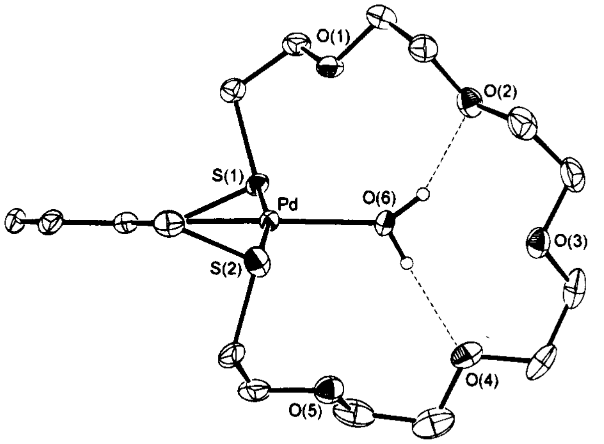

Figure 4. Alternative view of the $[Pd(L^5)(H_2O)]^+$ cation emphasizing the orientation of the polyether ring to the substrate.

Synthesis and Characterization of the Hydrazine Complexes $[Pd(L^3)(NH_2NH_2)][BF_4]$ and $[Pd(L^5)(NH_2NH_2)][BF_4]$. The two receptor molecules were reacted with excess $NH_2NH_2{\cdot}H_2O$ in acetonitrile at room temperature, and the complexes were isolated as pale yellow, hygroscopic powders. The ^{1}H NMR spectrum of $[Pd(L^3)(NH_2NH_2)][BF_4]$ shows splitting of the benzylic resonances centered at 4.32 ppm into two slightly broad doublets and sharpening of the aliphatic resonances consistent with coordination of the hydrazine substrate to the palladium center. In addition, resonances for the hydrazine substrate are observed at 5.59 ppm for the coordinating NH_2 and 5.07 ppm for the noncoordinating amine group; both resonances integrate to two hydrogens. The ^{1}H NMR spectrum of $[Pd(L^5)(NH_2NH_2)][BF_4]$ is broader than, and not quite as diagnostic as, that for the smaller receptor. The only resonance observed for the hydrazine substrate appears as a broad peak at 5.61 ppm, indicating that the nature of the receptor−substrate interaction is quite fluxional on the NMR time scale.

In addition to the NMR evidence observed for $[Pd(L^3)(NH_2NH_2)][BF_4]$, X-ray-quality crystals of this complex were isolated and the crystal structure was determined. The unit cell is triclinic and contains two $[Pd(L^3)(NH_2NH_2)]^+$ cations and two BF_4^- anions. A perspective view of the cation with the atom-numbering scheme is shown in Figure 5. The palladium atom is in a square planar environment with the S_2C bracket occupying three sites and a nitrogen atom of hydrazine occupying the fourth site on the metal: Pd−S(1) 2.299(1), Pd−S(2) 2.289(1), Pd−N(1) 2.137(5), and Pd−C(1) 1.988(5) Å. The angles at the palladium atom are S(1)−Pd−C(1) 82.1(1) and S(2)−Pd−C(1) 83.2(1)° for the five-membered chelate rings and S(1)−Pd−N(1) 98.7(1) and S(2)−Pd−N(1) 96.0(1)° to the hydrazine ligand. The *trans* angle N(1)−Pd−C(1) 178.6(2)° is essentially linear, with the S(1)−Pd−S(2) 165.15(5)° angle showing a deviation characteristic of these complexes. In much the same way as described for the receptor complex of ammonia, Figure 6 shows that the metal-bound substrate is nested into the receptor to form two linear hydrogen bonds with the substrate. The hydrogen-bonding distances are H(N1A)· · ·O(1) 2.16(5) and H(N1B)· · ·O(3) 2.13(7) Å, and the angles are N(1)−H(N1A)· · ·O(1) 159(5) and N(1)−H(N1B)· · ·O(3) 155(7)°. In addition, there is also interaction between the noncoordinated NH_2 group of the hydrazine ligand and the BF_4^- anion in the solid state (Figure 6): H(N2C)· · ·F(4) 2.620(4) Å and N(2)−H(N2C)· · ·F(4) 129.1(3)°.

Synthesis and Characterization of the Hydrazinium Complexes $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$ and $[Pd(L^5)(NH_2NH_3)][BF_4]_2$. The receptors were reacted with a previously prepared $CF_3SO_3^-$ or BF_4^- salt of the hydrazinium cation $NH_2NH_3^+$ in a 1:1 ratio in acetonitrile to give the complexes in moderate yields. It was not possible to identify specific hydrogen-bonding

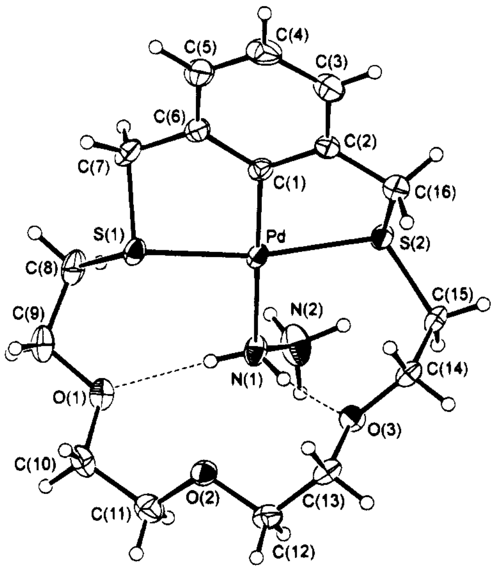

Figure 5. Structure of the $[Pd(L^3)(NH_2NH_2)]^+$ cation showing the atom-numbering scheme and hydrogen bonds to the metalloreceptor only. Note: H atoms of the uncomplexed NH_2 group are shown as a disordered NH_3 with each H atom having a 0.667 occupancy.

Table 6. Selected Positional Parameters for $[Pd(L^3)(NH_2NH_2)][BF_4]$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Pd	0.03232(4)	0.21615(4)	0.39624(5)	2.83(2)
S(1)	0.1300(1)	0.2652(1)	0.6542(1)	3.24(5)
S(2)	−0.1110(1)	0.1369(1)	0.1723(2)	3.67(5)
O(1)	0.3575(3)	0.4778(3)	0.5707(4)	4.2(2)
O(2)	0.2115(3)	0.5839(3)	0.4462(4)	3.8(1)
O(3)	0.0167(3)	0.4406(3)	0.1927(4)	3.4(1)
N(1)	0.1884(5)	0.3423(5)	0.2774(6)	3.8(2)
N(2)	0.2177(5)	0.2993(5)	0.1290(5)	6.0(2)
C(1)	−0.1156(5)	0.1004(4)	0.5048(6)	3.0(2)
C(2)	−0.2414(5)	0.0491(4)	0.4305(6)	3.5(2)
C(3)	−0.3450(6)	−0.0292(5)	0.5091(7)	4.9(3)
C(4)	−0.3233(7)	−0.0543(5)	0.6635(7)	5.7(3)
C(5)	−0.1991(7)	−0.0065(5)	0.7351(6)	4.9(3)
C(6)	−0.0960(5)	0.0689(4)	0.6562(6)	3.6(2)
C(7)	0.0406(6)	0.1195(5)	0.7290(6)	4.0(2)
C(8)	0.2970(6)	0.2909(5)	0.6697(6)	4.6(3)
C(9)	0.3828(5)	0.4221(6)	0.6990(7)	5.0(3)
C(10)	0.3881(5)	0.5987(5)	0.6172(7)	4.7(2)
C(11)	0.3470(5)	0.6479(5)	0.4816(7)	4.6(2)
C(12)	0.1665(5)	0.6298(4)	0.3215(6)	4.0(2)
C(13)	0.0273(5)	0.5473(5)	0.2733(6)	3.5(2)
C(14)	−0.1138(5)	0.3586(5)	0.1452(6)	3.6(2)
C(15)	−0.1202(5)	0.2475(5)	0.0543(6)	4.0(2)
C(16)	−0.2632(5)	0.0809(5)	0.2671(7)	4.6(2)

[a] $B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

interactions in solution, since well-resolved ^{1}H NMR spectra for $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$ or $[Pd(L^5)(NH_2NH_3)[BF_4]_2$ could not be obtained in weakly hydrogen-bonding solvents such as CD_2Cl_2 and $CDCl_3$ due to limited solubility. However, spectra in CD_3CN and $(CD_3)_2CO$, although highly fluxional, were consistent with the formation of a 1:1 complex, and poorly resolved ^{1}H and $^{13}C\{^1H\}$ NMR spectra of $[Pd(L_3)(NH_2NH_3)][CF_3SO_3]_2$ in $CDCl_3$ provided some general information. For example, the $^{13}C\{^1H\}$ NMR spectrum contains six separate peaks in the aromatic region rather the three expected for a symmetric receptor−substrate complex. This asymmetry is presumably due to the presence of the hydrazinium cation and reflects an asymmetric binding mode in solution.

Table 7. Selected Bonding Parameters for $[Pd(L^3)(NH_2NH_2)][BF_4]$

Distances (Å)

Pd−S(1)	2.299(1)	Pd−S(2)	2.289(1)
Pd−N(1)	2.137(5)	Pd−C(1)	1.988(5)
S(1)−C(7)	1.829(5)	S(1)−C(8)	1.817(5)
S(2)−C(15)	1.810(5)	S(2)−C(16)	1.822(6)
O(1)−C(9)	1.417(6)	O(1)−C(10)	1.424(6)
O(2)−C(11)	1.412(6)	O(2)−C(12)	1.421(6)
O(3)−C(13)	1.416(5)	O(3)−C(14)	1.413(6)
N(1)−N(2)	1.435(6)	C(1)−C(2)	1.397(7)
C(1)−C(6)	1.395(6)	C(2)−C(3)	1.391(7)
C(2)−C(16)	1.495(7)	C(3)−C(4)	1.392(7)
C(4)−C(5)	1.376(8)	C(5)−C(6)	1.377(7)
C(6)−C(7)	1.498(7)	C(8)−C(9)	1.491(8)
C(10)−C(11)	1.494(7)	C(12)−C(13)	1.491(7)
C(14)−C(15)	1.519(7)	N(1)−H(N1A)[a]	0.81(6)
N(1)−H(N1B)[a]	0.84(5)		

Angles (deg)

S(1)−Pd−S(2)	165.15(5)	S(1)−Pd−N(1)	98.7(1)
S(1)−Pd−C(1)	82.1(1)	S(2)−Pd−N(1)	96.0(1)
S(2)−Pd−C(1)	83.2(1)	N(1)−Pd−C(1)	178.6(2)
C(8)−S(1)−C(7)	103.8(3)	C(15)−S(2)−C(16)	101.9(2)
C(9)−O(1)−C(10)	112.4(4)	C(11)−O(2)−C(12)	112.5(4)
C(14)−O(3)−C(13)	111.3(4)	N(2)−N(1)−Pd	117.0(4)
C(6)−C(1)−C(2)	118.8(5)	C(3)−C(2)−C(1)	120.2(5)
C(3)−C(2)−C(16)	120.6(5)	C(1)−C(2)−C(16)	119.2(5)
C(2)−C(3)−C(4)	119.7(6)	C(5)−C(4)−C(3)	120.1(5)
C(4)−C(5)−C(6)	120.3(5)	C(5)−C(6)−C(1)	120.8(5)
C(5)−C(6)−C(7)	121.5(5)	C(1)−C(6)−C(7)	117.7(5)
C(6)−C(7)−S(1)	106.5(3)	C(9)−C(8)−S(1)	108.2(4)
O(1)−C(9)−C(8)	108.7(4)	O(1)−C(10)−C(11)	109.4(4)
O(2)−C(11)−C(10)	110.1(4)	O(2)−C(12)−C(13)	109.4(4)
O(3)−C(13)−C(12)	108.9(4)	O(3)−C(14)−C(15)	109.5(4)
C(14)−C(15)−S(2)	117.4(3)	C(2)−C(16)−S(2)	108.3(4)
H(N1A)−N(1)−H(N1B)[a]	121(6)		

[a] H(N1A) and H(N1B) of the coordinated NH_2 group were located and refined.

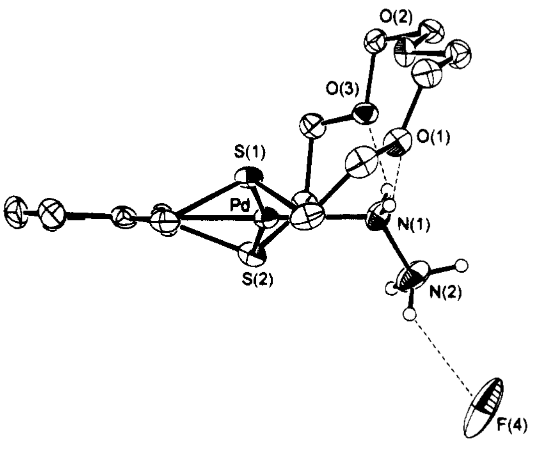

Figure 6. Alternative view of the $[Pd(L^3)(NH_2NH_2)]^+$ cation emphasizing the orientation of the polyether ring to the substrate and showing the substrate interaction with F(4) of the BF_4^- anion. Note: H atoms of the uncomplexed NH_2 group are shown as a disordered NH_3 with each H atom having a 0.667 occupancy.

In addition to the spectroscopic evidence observed for the structures of $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$ and $[Pd(L^5)(NH_2NH_3)][BF_4]_2$, X-ray-quality crystals of both complexes were isolated and the structures determined. For $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$, the unit cell is monoclinic and contains four $[Pd(L^3)(NH_2NH_3)]^{2+}$ cations and eight $CF_3SO_3^-$ anions. A perspective view of the cation with the atom-numbering scheme is shown in Figure 7. The palladium atom is in a square planar environment with the S_2C bracket occupying three sites and the NH_2 nitrogen atom of the substrate occupying the fourth site on the metal: Pd−S(1) 2.315(2), Pd−S(2) 2.290(2), Pd−N(1) 2.180(5), and Pd−C(1) 1.989(6) Å. The angles at palladium are S(1)−Pd−C(1) 83.9(2) and S(2)−Pd−C(1) 83.1(2)° for the five-membered chelate rings and S(1)−Pd−N(1) 98.5(1) and S(2)−Pd−N(1) 94.4(1)° to the nonchelating substrate. The N(1)−Pd−C(1) angle is essentially linear at 177.4-

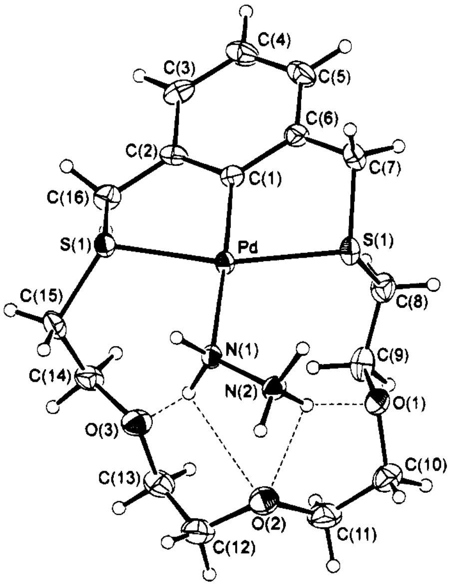

Figure 7. Structure of the $[Pd(L^3)(NH_2NH_3)]^{2+}$ cation showing the atom-numbering scheme and hydrogen bonds to the metalloreceptor only.

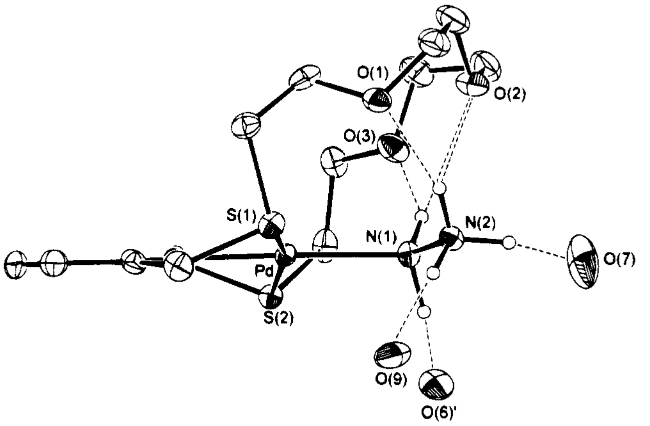

Figure 8. Alternative view of the $[Pd(L^3)(NH_2NH_3)]^{2+}$ cation emphasizing the orientation of the polyether ring to the substrate and showing the substrate interactions with O(7), O(9), and O(6)′ of the two separate triflate anions and a symmetry-related anion, respectively.

Table 8. Selected Positional Parameters for $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Pd	0.65812(4)	0.00194(4)	0.31914(3)	2.56(2)
S(1)	0.6152(2)	0.1322(1)	0.3289(1)	3.55(8)
S(2)	0.7449(2)	−0.1188(1)	0.3365(1)	3.08(7)
O(1)	0.3574(4)	0.1095(3)	0.2663(3)	4.2(2)
O(2)	0.2584(4)	−0.0323(3)	0.1851(4)	5.0(3)
O(3)	0.4414(4)	−0.1471(3)	0.2663(4)	4.9(3)
N(1)	0.5257(4)	−0.0222(3)	0.1804(3)	3.1(2)
N(2)	0.4492(5)	0.0389(3)	0.1290(4)	3.3(3)
C(1)	0.7831(6)	0.0198(4)	0.4451(4)	2.8(3)
C(2)	0.8403(6)	−0.0436(4)	0.5007(5)	3.2(3)
C(3)	0.9307(6)	−0.0299(5)	0.5881(5)	4.2(4)
C(4)	0.9587(7)	0.0447(5)	0.6203(5)	4.6(4)
C(5)	0.9037(7)	0.1072(5)	0.5674(6)	4.5(4)
C(6)	0.8167(6)	0.0955(4)	0.4777(6)	3.7(4)
C(7)	0.7609(7)	0.1599(4)	0.4132(6)	4.6(4)
C(8)	0.5271(7)	0.1354(4)	0.4029(5)	4.4(4)
C(9)	0.4148(7)	0.0891(4)	0.3641(5)	4.5(4)
C(10)	0.2301(7)	0.0960(5)	0.2279(6)	5.4(4)
C(11)	0.1977(7)	0.0132(6)	0.2296(6)	6.0(5)
C(12)	0.2383(7)	−0.1138(6)	0.1909(6)	5.8(5)
C(13)	0.3271(8)	−0.1516(5)	0.2744(6)	5.5(4)
C(14)	0.5302(7)	−0.1917(4)	0.3357(5)	4.3(4)
C(15)	0.6393(7)	−0.1985(4)	0.3092(5)	4.2(3)
C(16)	0.8073(6)	−0.1234(4)	0.4640(5)	3.7(3)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

Table 9. Selected Bonding Parameters for $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$

	Distances (Å)		
Pd−S(1)	2.315(2)	Pd−S(2)	2.290(2)
Pd−N(1)	2.180(5)	Pd−C(1)	1.989(6)
S(1)−C(7)	1.813(7)	S(1)−C(8)	1.801(7)
S(2)−C(15)	1.804(7)	S(2)−C(16)	1.823(7)
O(1)−C(9)	1.446(8)	O(1)−C(10)	1.432(8)
O(2)−C(11)	1.398(9)	O(2)−C(12)	1.430(9)
O(3)−C(13)	1.412(8)	O(3)−C(14)	1.422(8)
N(1)−N(2)	1.427(6)	C(1)−C(2)	1.399(9)
C(1)−C(6)	1.398(8)	C(2)−C(3)	1.402(9)
C(2)−C(16)	1.480(9)	C(3)−C(4)	1.37(1)
C(4)−C(5)	1.36(1)	C(5)−C(6)	1.405(9)
C(6)−C(7)	1.473(9)	C(8)−C(9)	1.48(1)
C(10)−C(11)	1.48(1)	C(12)−C(13)	1.48(1)
C(14)−C(15)	1.50(1)	N(1)−H(N1A)[a]	0.969(5)
N(1)−H(N1B)[a]	1.100(5)	N(2)−H(N2A)[a]	0.959(5)
N(2)−H(N2B)[a]	1.033(5)	N(2)−H(N2C)[a]	1.021(5)
	Angles (deg)		
S(1)−Pd−S(2)	166.02(7)	S(1)−Pd−N(1)	98.5(1)
S(1)−Pd−C(1)	83.9(2)	S(2)−Pd−N(1)	94.4(1)
S(2)−Pd−C(1)	83.1(2)	N(1)−Pd−C(1)	177.4(2)
C(7)−S(1)−C(8)	99.7(4)	C(15)−S(2)−C(16)	101.3(3)
C(9)−O(1)−C(10)	114.8(6)	C(11)−O(2)−C(12)	113.0(7)
C(13)−O(3)−C(14)	112.7(6)	Pd−N(1)−N(2)	119.4(4)
C(2)−C(1)C−(6)	119.6(6)	C(1)−C(2)−C(3)	119.2(7)
C(1)−C(2)−C(16)	119.2(6)	C(3)−C(2)−C(16)	121.6(7)
C(2)−C(3)−C(4)	120.2(7)	C(3)−C(4)−C(5)	121.5(7)
C(4)−C(5)−C(6)	119.6(7)	C(1)−C(6)−C(5)	119.8(7)
C(1)−C(6)−C(7)	117.3(7)	C(5)−C(6)−C(7)	122.8(7)
S(1)−C(7)−C(6)	111.3(5)	S(1)−C(8)−C(9)	112.2(5)
O(1)−C(9)−C(8)	107.7(6)	O(1)−C(10)−C(11)	113.1(7)
O(2)−C(11)−C(10)	110.3(7)	O(2)−C(12)−C(13)	113.6(7)
O(3)−C(13)−C(12)	108.0(7)	O(3)−C(14)−C(15)	108.9(6)
S(2)−C(15)−C(14)	118.5(5)	S(2)−C(16)−C(2)	108.4(5)
H(N1A)−N(1)−H(N1B)[a]	112.3(4)	H(N2A)−N(2)−H(N2B)[a]	109.1(5)
H(N2A)−N(2)−H(N2C)[a]	112.3(5)	H(N2B)−N(2)−H(N2C)[a]	104.8(5)

[a] H(N1A), H(N1B), H(N2A), H(N2B), and H(N2C) of the hydrazinium ion were placed in located positions but not refined.

(2)°, while the S(1)−Pd−S(2) angle of 166.02(7)° is distorted similar to those of the other metalloreceptor−substrate complexes.

For $[Pd(L^5)(NH_2NH_3)][BF_4]_2$, the unit cell is triclinic and contains two $[Pd(L^5)(NH_2NH_3)]^{2+}$ cations and four BF_4^- anions. A perspective view of the cation with the atom-numbering scheme is shown in Figure 9. The palladium atom is in a square planar environment with the S_2C bracket occupying three sites and the NH_2 nitrogen atom of the substrate occupying the fourth site on the metal: Pd−S(1) 2.312(2), Pd−S(2) 2.306(2), Pd−N(1) 2.172(5), and Pd−C(1) 1.972(7) Å. The angles at the palladium atom are S(1)−Pd−C(1) 85.1(2) and S(2)−Pd−C(1) 85.7(2)° for the five-membered chelate rings and S(1)−Pd−N(1) 98.0(1) and S(2)−Pd−N(1) 91.2(1)° to the nonchelating substrate. The N(1)−Pd−C(1) angle is almost linear at 176.8(3)°, while the S(1)−Pd−S(2) 170.76(7)° angle shows a slight distortion.

For $[Pd(L^3)(NH_2NH_3)]^{2+}$, the hydrazinium substrate is too large to nest in the macrocycle so it "perches" on the crown ether ring with one hydrogen atom from each nitrogen directed toward the receptor. The result is an array of seven hydrogen-bonding interactions as illustrated in Figure 8. Four of these hydrogen-bonding interactions are between receptor and substrate. Two are linear (H(N1A)···O(3) 1.993(4) Å, N(1)−H(N1A)···O(3) 151.4(3)° and H(N2A)···O(1) 2.044(4) Å, N(2)−H(N2A)···O(1) 159.0(3)°) and two are bifurcated (H(N1A)···O(2) 1.882(5) Å, N(1)−H(N1A)···O(2) 120.4(3)° and H(N2A)···O(2) 1.854(4) Å, N(2)−H(N2A)···O(2) 117.4(3)°). The remaining three interactions are between the hydrazinium substrate and the triflate anions: H(N1B)···O(6)′

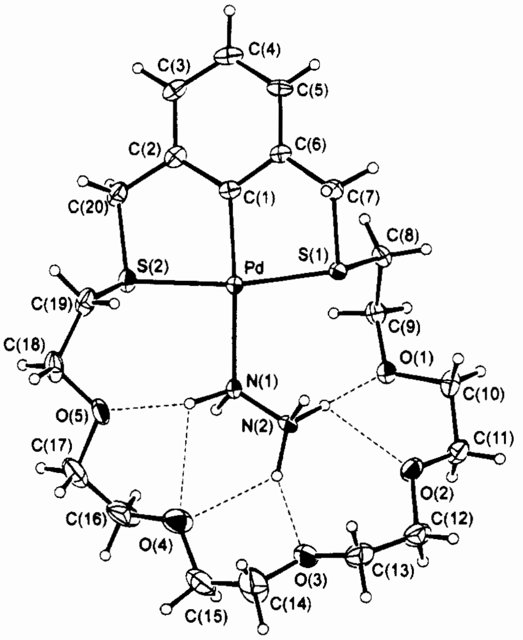

Figure 9. Structure of the $[Pd(L^5)(NH_2NH_3)]^{2+}$ cation showing the atom-numbering scheme and hydrogen bonds to the metalloreceptor only.

Table 10. Selected Positional Parameters for $[Pd(L^5)(NH_2NH_3)][BF_4]_2$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Pd	0.47148(7)	0.18260(3)	0.11481(7)	2.64(2)
S(1)	0.4155(2)	0.1820(1)	0.3502(2)	2.95(7)
S(2)	0.5472(2)	0.1684(1)	−0.1086(2)	3.47(8)
O(1)	0.0929(5)	0.1810(3)	0.2301(5)	3.9(2)
O(2)	0.0965(6)	0.3272(3)	0.3211(6)	4.8(3)
O(3)	0.1460(7)	0.4236(4)	0.0948(7)	6.3(3)
O(4)	0.2887(8)	0.3913(4)	−0.1390(7)	7.1(3)
O(5)	0.5130(7)	0.3192(3)	−0.1822(6)	5.4(3)
N(1)	0.3440(6)	0.2613(3)	0.0281(6)	3.5(3)
N(2)	0.2749(7)	0.2991(3)	0.1254(7)	3.7(3)
C(1)	0.5917(7)	0.1113(4)	0.1834(8)	3.0(3)
C(2)	0.6540(8)	0.0734(4)	0.0842(8)	3.3(3)
C(3)	0.7278(8)	0.0187(4)	0.130(1)	3.8(3)
C(4)	0.7398(9)	0.0011(4)	0.276(1)	4.6(4)
C(5)	0.6862(8)	0.0412(4)	0.3789(9)	3.9(3)
C(6)	0.6133(7)	0.0951(4)	0.3334(8)	2.9(3)
C(7)	0.5642(8)	0.1434(4)	0.4458(7)	3.4(3)
C(8)	0.2556(8)	0.1011(4)	0.3299(8)	3.8(3)
C(9)	0.1226(8)	0.1092(4)	0.2139(8)	3.7(3)
C(10)	0.0441(9)	0.1997(5)	0.363(1)	4.9(4)
C(11)	−0.017(1)	0.2667(5)	0.347(1)	4.9(4)
C(12)	0.051(1)	0.3963(5)	0.311(1)	6.0(5)
C(13)	0.152(1)	0.4500(5)	0.246(1)	6.9(5)
C(14)	0.217(2)	0.4768(6)	0.017(2)	13.0(9)
C(15)	0.204(2)	0.4423(8)	−0.137(1)	12.3(9)
C(16)	0.296(1)	0.3611(6)	−0.281(1)	8.5(6)
C(17)	0.449(1)	0.3597(6)	−0.294(1)	7.5(5)
C(18)	0.648(1)	0.3040(5)	−0.207(1)	5.9(4)
C(19)	0.697(1)	0.2538(5)	−0.093(1)	5.1(4)
C(20)	0.6420(9)	0.0933(4)	−0.073(1)	4.4(4)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i{}^*a_j{}^*\cdot\vec{a}_i\vec{a}_j$.

Table 11. Selected Bonding Parameters for $[Pd(L^5)(NH_2NH_3)][BF_4]_2$

	Distances (Å)		
Pd−S(1)	2.312(2)	Pd−S(2)	2.306(2)
Pd−N(1)	2.172(5)	Pd−C(1)	1.972(7)
S(1)−C(7)	1.805(7)	S(1)−C(8)	1.811(7)
S(2)−C(19)	1.813(8)	S(2)−C(20)	1.819(8)
O(1)−C(9)	1.407(8)	O(1)−C(10)	1.426(8)
O(2)−C(11)	1.416(9)	O(2)−C(12)	1.432(9)
O(3)−C(13)	1.41(1)	O(3)−C(14)	1.38(1)
O(4)−C(15)	1.36(1)	O(4)−C(16)	1.39(1)
O(5)−C(17)	1.42(1)	O(5)−C(18)	1.41(1)
N(1)−N(2)	1.427(7)	C(1)−C(2)	1.397(9)
C(1)−C(6)	1.403(9)	C(2)−C(3)	1.39(1)
C(2)−C(20)	1.50(1)	C(3)−C(4)	1.38(1)
C(4)−C(5)	1.39(1)	C(5)−C(6)	1.370(9)
C(6)−C(7)	1.512(9)	C(8)−C(9)	1.503(9)
C(10)−C(11)	1.47(1)	C(12)−C(13)	1.45(1)
C(14)−C(15)	1.46(2)	C(16)−C(17)	1.47(1)
C(18)−C(19)	1.51(1)	N(1)−H(N1A)[a]	1.028(5)
N(1)−H(N1B)[a]	1.166(6)	N(2)−H(N2A)[a]	1.104(5)
N(2)−H(N2B)[a]	1.053(6)	N(2)−H(N2C)[a]	1.065(6)
	Angles (deg)		
S(1)−Pd−S(2)	170.76(7)	S(1)−Pd−N(1)	98.0(1)
S(1)−Pd−C(1)	85.1(2)	S(2)−Pd−N(1)	91.2(1)
S(2)−Pd−C(1)	85.7(2)	N(1)−Pd−C(1)	176.8(3)
C(7)−S(1)−C(8)	99.9(3)	C(19)−S(2)−C(20)	105.3(4)
C(9)−O(1)−C(10)	115.9(6)	C(11)−O(2)−C(12)	113.0(7)
C(13)−O(3)−C(14)	114.9(9)	C(15)−O(4)−C(16)	115.8(8)
C(17)−O(5)−C(18)	112.6(7)	Pd−N(1)−N(2)	119.8(4)
C(2)−C(1)−C(6)	117.8(7)	C(1)−C(2)−C(3)	121.0(7)
C(1)−C(2)−C(20)	119.0(7)	C(3)−C(2)−C(20)	120.0(7)
C(2)−C(3)−C(4)	119.8(7)	C(4)−C(5)−C(6)	120.2(7)
C(1)−C(6)−C(5)	121.1(7)	C(1)−C(6)−C(7)	117.7(6)
C(5)−C(6)−C(7)	121.0(7)	S(1)−C(7)−C(6)	110.6(5)
S(1)−C(8)−C(9)	110.9(5)	O(1)−C(9)−C(8)	114.1(6)
O(1)−C(10)−C(11)	109.5(7)	O(2)−C(11)−C(10)	108.7(7)
O(2)−C(12)−C(13)	110.7(7)	O(3)−C(13)−C(12)	111.5(9)
O(3)−C(14)−C(15)	109(1)	O(4)−C(15)−C(14)	111(1)
O(4)−C(16)−C(17)	114(1)	O(5)−C(17)−C(16)	110.3(8)
O(5)−C(18)−C(19)	108.1(6)	S(2)−C(19)−C(18)	110.1(6)
S(2)−C(20)−C(2)	113.0(5)	H(N1A)−N(1)−H(N1B)[a]	86.5(4)
H(N2A)−N(2)−H(N2B)[a]	123.6(5)	H(N2A)−N(2)−H(N2C)[a]	117.4(5)
H(N2B)−N(2)−H(N2C)[a]	92.4(4)		

[a] H(N1A), H(N1B), H(N2A), H(N2B), and H(N2C) of the hydrazinium ion were placed in located positions but not refined.

1.854(4) Å, N(1)−H(N1B)···O(6)′ 150.6(3)°; H(N2B)···O(7) 1.882(5) Å, N(2)−H(N2B)···O(7) 145.2(4)°; and H(N2C)···O(9) 1.854(4) Å, N(2)−H(N2C)···O(9) 162.0(3)°.

For $[Pd(L^5)(NH_2NH_3)]^{2+}$, the fit of receptor and substrate is quite remarkable. The polyether chain wraps around the $NH_2NH_3^+$ ion which is nested inside the larger crown ether cavity. There are six internal receptor-substrate hydrogen bonds accompanying the Pd−N σ-bond and three additional substrate−anion interactions. In the hydrogen-bonding array involving the polyether sites, there are three linear hydrogen bonds (H(N1A)···O(5) 1.867(5) Å, N(1)−H(N1A)···O(5) 158.2(4)°; H(N2A)···O(3) 1.838(6) Å, N(2)−H(N2A)···O(3) 146.5(3)°; and H(N2B)···O(1) 1.735(5) Å, N(2)−H(N2B)···O(1) 178.7(3)°) and three bifurcated (H(N1A)···O(4) 2.469(6) Å, N(1)−H(N1A)···O(4) 111.9(3)°; H(N2A)···O(4) 2.268(6) Å, N(2)−H(N2A)···O(4) 126.2(3)°; and H(N2B)···O(2) 2.403(6) Å, N(2)−H(N2B)···O(2) 99.9(3)°). As Figure 10 shows, in the solid state, the cationic receptor−substrate complex is sandwiched between sets of BF_4^- anions, resulting in additional hydrogen-bonding interactions: H(N1B)···F(6)′ 2.133(6) Å, N(1)−H(N1B)···F(6)′ 157.7(3)°; H(N2C)···F(2) 1.831(5) Å, N(2)−H(N2C)···F(2) 147.2(3)°; and H(N1B)···F(7) 2.118(6) Å, N(1)−H(N1B)···F(7) 122.7(3)°.

Discussion

The complexes $[Pd(L^3)(CH_3CN)][BF_4]$ and $[Pd(L^5)(CH_3CN)][BF_4]$ were designed as metalloreceptors to coordinate a substrate molecule via σ-donation to the Pd center while simultaneously undergoing hydrogen bonding to the peripheral ether oxygen atoms. A previous study[4b] describing the synthesis and X-ray structure of $[Pd(L^3)(CH_3CN)][BF_4]$ showed that these first- and second-sphere binding sites are oriented in the same direction, allowing for simultaneous interactions with a substrate. Relevant to this current study, CPK models suggested that primary interaction at the Pd center employing a donor atom containing hydrogen atoms would allow for the formation of

Table 12. Summary of Hydrogen Bonding Interactions

acceptor (type)	distance (Å)		angle (deg)	
		$[Pd(L^5)(NH_3)][BF_4]$		
receptor (linear)	H(N1A)···O(1)	2.16(3)	N(1)−H(N1A)···O(1)	147(2)
receptor (linear)	H(N1B)···O(3)	2.09(3)	N(1)−H(N1B)···O(3)	151(2)
anion (linear)	H(N1C)···F(3)	2.42(2)	N(1)−H(N1C)···F(3)	147(2)
		$[Pd(L^5)(H_2O)][BF_4]$		
receptor (linear)	H(O6A)···O(2)	2.014(5)	O(6)−H(O6A)···O(2)	145.9(4)
receptor (linear)	H(O6B)···O(4)	2.036(5)	O(6)−H(O6B)···O(4)	161.9(3)
		$[Pd(L^3)(NH_2NH_2)][BF_4]$		
receptor (linear)	H(N1A)···O(1)	2.16(5)	N(1)−H(N1A)···O(1)	159(5)
receptor (linear)	H(N1B)···O(3)	2.13(7)	N(1)−H(N1B)···O(3)	155(7)
anion (bifurcated)	H(N2C)···F(4)	2.620(4)	N(2)−H(N2C)···F(4)	129.1(3)
		$[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$		
receptor (linear)	H(N1A)···O(3)	1.993(4)	N(1)−H(N1A)···O(3)	151.4(3)
receptor (bifurcated)	H(N1A)···O(2)	1.882(5)	N(1)−H(N1A)···O(2)	120.4(3)
receptor (linear)	H(N2A)···O(1)	2.044(4)	N(2)−H(N2A)···O(1)	159.0(3)
receptor (bifurcated)	H(N2A)···O(2)	1.854(4)	N(2)−H(N2A)···O(2)	117.4(3)
anion (linear)	H(N1B)···O(6)′	1.854(4)	N(1)−H(N1B)···O(6)′	150.6(3)
anion (linear)	H(N2B)···O(7)	1.882(5)	N(2)−H(N2B)···O(7)	145.2(4)
anion (linear)	H(N2C)···O(9)	1.854(4)	N(2)−H(N2C)···O(9)	162.0(3)
		$[Pd(L^5)(NH_2NH_3)][BF_4]_2$		
receptor (linear)	H(N1A)···O(5)	1.867(5)	N(1)−H(N1A)···O(5)	158.2(4)
receptor (bifurcated)	H(N1A)···O(4)	2.469(6)	N(1)−H(N1A)···O(4)	111.9(3)
receptor (linear)	H(N2A)···O(3)	1.838(6)	N(2)−H(N2A)···O(3)	146.5(3)
receptor (bifurcated)	H(N2A)···O(4)	2.268(6)	N(2)−H(N2A)···O(4)	126.2(3)
anion (linear)	H(N1B)···F(6)′	2.133(6)	N(1)−H(N1B)···F(6)′	157.7(3)
anion (bifurcated)	H(N1B)···F(7)	2.118(6)	N(1)−H(N1B)···F(7)	122.7(3)
receptor (linear)	H(N2B)···O(1)	1.735(5)	N(2)−H(N2B)···O(1)	178.7(3)
receptor (bifurcated)	H(N2B)···O(2)	2.403(6)	N(2)−H(N2B)···O(2)	99.9(3)
anion (linear)	H(N2C)···F(2)	1.831(5)	N(2)−H(N2C)···F(2)	147.2(3)

linear hydrogen bonds to the two ether oxygen atoms adjacent to the thioether donors, $-SCH_2CH_2O-$. In order to test this model, ammonia and simple amines were used as substrates with $[Pd(L^3)(CH_3CN)][BF_4]$. The NMR and X-ray data correlate, showing that these hydrogen bonds are indeed formed and can be used as a source of discrimination among primary amines, which can form two hydrogen bonds, secondary amines, which can form one hydrogen bond, and tertiary amines, which have no NH protons for hydrogen-bond formation. Although there are certainly steric factors to be taken into account in the described competition reactions, the selectivity is impressive and must be attributed in part to the second-sphere hydrogen bonding designed into these systems.

Experiments employing larger nitrogen-based substrates, such as hydrazine derivatives, show that the degree of second-sphere coordination depends in large part on the ability of a substrate to penetrate the crown ether cavity and the number of ether oxygen atoms available for hydrogen bonding. A lesser effect, which appears to have some importance, is the arrangement of cation and anion in the lattice, as the anions tend to engage in hydrogen bonding to most of the remaining hydrogen atoms on the substrate. In the case of the hydrazinium ion, it is noteworthy that the receptor and the substrate are *both* cationic, and despite the electrostatic repulsion that must be present between the two entities, there is both solution and solid state evidence for complex formation. These compounds emphasize that an effective receptor−substrate interaction can be a subtle interplay of covalent, electrostatic, and non-covalent forces, which does not always give intuitive results.

In summary, this work demonstrates that binding of a substrate *via* first- and second-sphere coordination can be designed into a receptor and tuned to fit a particular molecule or ion.

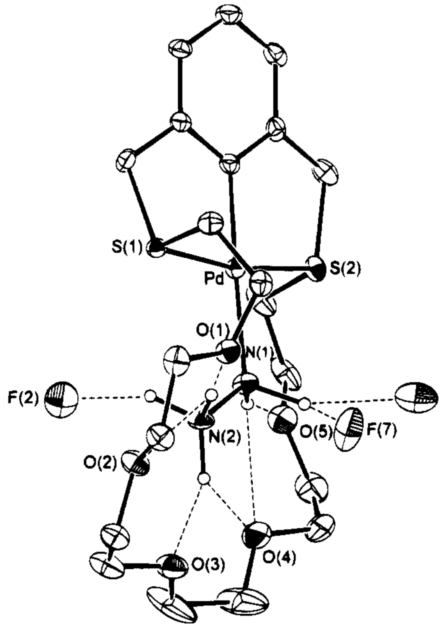

Figure 10. Alternative view of the $[Pd(L^5)(NH_2NH_3)]^{2+}$ cation emphasizing the orientation of the polyether ring to the substrate and showing the substrate interactions with F(2) of one BF_4^- anion and F(6) and F(7) of the other.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research. J.E.K. is grateful for the award of an Ontario Graduate Scholarship.

Supporting Information Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bonding parameters, and hydrogen atom parameters (26 pages). Ordering information is given on any current masthead page.

IC9506062