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Macrocyclic and Lantern Complexes of Palladium(II) with Bis(amidopyridine) Ligands: Synthesis, Structure, and Host–Guest Chemistry

Nancy L. S. Yue, Dana J. Eisler, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

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The reactions of $[PdCl_2(NCPh)_2]$ in a 1:1 ratio with the bis(amidopyridine) ligands LL = C_6H_3(5-R)(1,3-CONH-3-$C_5H_4N)_2$ with R = H (**1a**) or R = *t*-Bu (**1b**) give the corresponding neutral dipalladium(II) macrocycles *trans*,*trans*-$[Pd_2Cl_4(\mu\text{-LL})_2]$, **2a** and **2b**, which crystallize from dimethylformamide with one or two solvent molecules as macrocycle guests. The reaction of $[PdCl_2(NCPh)_2]$ with LL in a 1:2 ratio gave the cationic lantern complex $[Pd_2(\mu\text{-LL})_4]Cl_4$, **3c** (LL = **1b**), and the reaction in the presence of AgO_2CCF_3 gave the corresponding trifluoroacetate salts $[Pd_2(\mu\text{-LL})_4](CF_3CO_2)_4$, **3a** (LL = **1a**) and **3b** (LL = **1b**). These lantern complexes exhibit a remarkable host–guest chemistry, as they can encapsulate cations, anions, and water molecules by interaction of the guest with either the electrophilic NH or the nucleophilic C═O substituents of the amide groups, which can be directed toward the center of the lantern through easy conformational change. The structures of several of these host–guest complexes were determined, and it was found that the cavity size and shape vary according to the ligand conformation, with Pd···Pd separations in the range from 9.45 to 11.95 Å. Supramolecular ordering of the lanterns was observed in the solid state, through either hydrogen bonding or secondary bonding to the cationic palladium(II) centers. The selective inclusion by the lantern complexes of alkali metal ions in the sequence $Na^+ \gg K^+ \gg Li^+$ was observed by ESI-MS.

Introduction

The design, synthesis, and study of inorganic host molecules that can accommodate cationic, neutral, or anionic guests is a thriving field of research, with increasing emphasis on the use of a combination of dynamic coordination chemistry and hydrogen bonding to allow more efficient synthesis of host molecules through self-assembly.[1−3] The size and shape of the host molecule can be fine-tuned simply by adjusting the ligand structure or the preferred geometry of the metal ion used. For example, cis-protected, square-planar palladium(II) and platinum(II) complexes with mulitdentate pyridine-based ligands have been used to prepare functional macrocycles, cages, and even higher polygons that are soluble in either water or organic solvents.[3]

This article is concerned with the use of bis(amidopyridine) ligands in host−guest chemistry, and although the use of pyridine ligands is well-known, the reasons for combining them with amide groups require some explanation. Organic amides have proved to be useful in self-assembly through hydrogen bonding, and they have obvious relevance to biological systems. For example, oligoamides have been designed that can fold to give single or double helices as well as other supramolecular assemblies.[4] In addition, amide-

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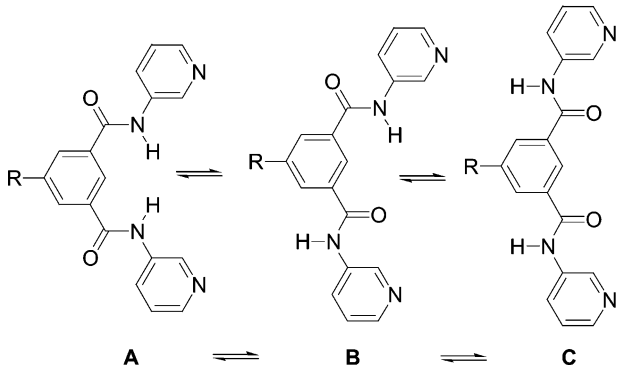
linked catenanes, rotaxanes, and knots have been prepared by template synthesis.[5] Cyclic peptides can self-assemble to give interesting supramolecular structures, most notably giving nanotubes via amide−amide hydrogen bonding.[6] Hence, the known patterns of hydrogen bonding of the amide functionality make this a useful functional group to incorporate into ligands in the design of functional coordination complexes. In previous research, a copper(II) cage complex having four *N*,*N*′-bis(4-aminomethylene-pyridyl)benzene-1,3-dicarboxamide ligands was found to encapsulate an icelike decameric water cluster.[3g] Using similar ligands, square or rectangular macrocycles of osmium(VI) were shown to bind diamide guests selectively or to form pseudorotaxanes, whereas macrocycles of palladium(II) were shown to bind *N*,*N*,*N*′,*N*′′-tetramethylterephthalamide through selective hydrogen bonding.[7] A rhenium(I) complex with *N*,*N*′-bis(4-pyridyl)pyridine-1,3-dicarboxamide, as well as related complexes of ruthenium(II) and osmium(II), shows selective anion recognition.[8] Helical gold(I) complexes have been prepared using *N*,*N*′-bis(3-pyridyl)benzene-1,3-dicarboxamide ligand.[2c] Binuclear, trinuclear, or polynuclear complexes have been prepared using *N*-(4-pyridyl)isonicotinamide complexes of cis-protected palladium(II) and platinum(II).[3a,b]

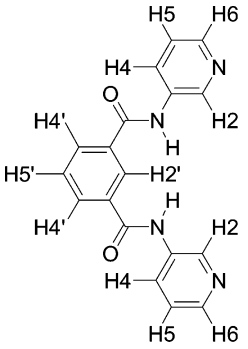
This article reports that functional palladium(II) macrocycles and lantern complexes are formed with the ligands LL = 5-R-C_6H_3-1,3-(CONH-3-C_5H_4N)$_2$, R = H or *t*-Bu (Chart 1), of formula $[Pd_2Cl_4(\mu\text{-LL})_2]$ or $[Pd_2(\mu\text{-LL})_2]^{4+}$, respectively. The lantern complexes have a particularly interesting host−guest chemistry as conformational change of the amide substituents of the ligands (Chart 1) allows different combinations of NH and/or C═O groups of the amide substituents to be directed toward the center of the lantern as required to interact with either nucleophilic or electrophilic guests, respectively. A preliminary account of parts of this research has been communicated.[2d]

Chart 1. [a]



[a] R = H (**1a**) or *t*-Bu (**1b**).

Chart 2



Experimental Section

The reagents 5-(*tert*-butyl)isophthaloyl dichloride[9] and $[PdCl_2(NCPh)_2]$[10] were prepared as described in the literature. ^{1}H and $^{13}C\{^1H\}$ spectra were recorded using a Varian Mercury 400 spectrometer, and chemical shifts are reported relative to $SiMe_4$, with protons labeled according to Chart 2. ESI mass spectra were recorded using a Micromass LCT spectrometer and were calibrated with NaI at a concentration of 2 μg/μL in 50:50 propan-2-ol/water.

***N*,*N*′-Bis(3-pyridyl)benzene-1,3-dicarboxamide (1a).** This compound was prepared as described in the literature.[2a] NMR in $(CD_3)_2SO$: $\delta(^1H)$ = 10.66 (s, 2H, CONH), 8.96 (d, 2H, J_{HH} = 2 Hz, H2), 8.58 (br t, 2H, J_{HH} = 2 Hz, H2′), 8.33 (br dd, 2H, J_{HH} = 5 and 2 Hz, H6), 8.21 (dt, 2H, J_{HH} = 8 and 2 Hz, H4), 8.19 (dd, 2H, J_{HH} = 8 and 2 Hz, H4′), 7.73 (t, 1H, J_{HH} = 8 Hz, H5′), 7.42 (dd, 2H, J_{HH} = 8 and 5 Hz, H5). $\delta(^{13}C)$ = 165.4 (C═O), 144.7, 142.0, 135.7, 134.6, 131.0, 128.8, 127.4, 127.1, 123.6. Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.60. Found: C, 67.57; H, 3.87; N, 17.45%.

***N*,*N*′-Bis(3-pyridyl)-5-*t*-butylbenzene-1,3-dicarboxamide (1b).** This compound was prepared as described in the literature.[2a] NMR in DMF-d_7: $\delta(^1H)$ = 10.77 (s, 2H, CONH), 9.09 (d, 2H, J_{HH} = 2 Hz, H2), 8.55 (t, 1H, H2′), 8.39 (dd, 2H, J_{HH} = 5 and 2 Hz, H4), 8.36 (dm, 2H, H4′), 8.31 (d, 2H, J_{HH} = 2 Hz, H6), 7.46 (dd, 2H J_{HH} = 8 and 5 Hz, H5), 1.41 (s, 9H, *t*-Bu). $\delta(^{13}C)$ = 166.6 (C═O); 152.7, 145.5, 142.9, 137.0, 135.6, 128.6, 127.9, 125.3, 124.2, 31.3 (*t*-Bu). NMR in $(CD_3)_2SO$: $\delta(^1H)$ = 10.66 (s, 2H, CONH), 8.95 (d, 2H, J_{HH} = 2 Hz, H2), 8.42 (br t, 1H, H2′), 8.32 (dd, 2H, J_{HH} = 5 and 1 Hz, H6), 8.20 (br m, 2H, H4), 8.16 (d, 2H, J_{HH} = 1 Hz, H4′), 7.43 (br dd, 2H, J_{HH} = 8 and 5 Hz, H5), 1.38 (s, 9H, *t*-Bu). $\delta(^{13}C)$ = 165.9 (C═O), 151.9, 144.9, 142.3, 135.8, 134.6, 128.1,

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128.0, 123.9, 31.1 (*t*-Bu). Anal. Calcd for $C_{22}H_{22}N_4O_2$: C, 70.57; H, 5.92; N, 14.96%. Found: C, 70.07; H, 5.36; N, 14.68%.

[$Cl_2Pd(\mu$-$NC_5H_4NHCOC_6H_4CONHC_5H_4N)_2PdCl_2$] (2a). To a clear orange solution of [$PdCl_2(NCPh)_2$] (0.050 g, 0.130 mmol) in CH_2Cl_2 (10 mL) was added a solution of **1a** (0.041 g, 0.130 mmol) in DMF (dimethyl formamide, 10 mL). A yellow precipitate was formed upon addition. The solution was stirred for 2 h; then pentane (40 mL) was added, and the yellow solid product was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 0.066 g (51%). NMR in $(CD_3)_2SO$: $\delta(^1H) = 11.03$ (s, 4H, CONH), 9.53 (d, 4H, $J_{HH} = 2$ Hz, H2), 8.97 (m 2H, H2′), 8.51 (d, 4H, $J_{HH} = 6$ Hz, H6), 8.46 (dm, 4H, $J_{HH} = 8$ Hz, H4), 8.34 (d, 4H, $J_{HH} = 8$ Hz, H4′), 7.80 (t, 2H, $J_{HH} = 8$ Hz, H5′), 7.59 (dd, 4H, $J_{HH} = 8$ and 6 Hz, H5). Anal. Calcd for $C_{36}H_{28}Cl_4N_8O_4Pd_2$: C, 43.62; H, 2.85; N, 11.30%. Found: C, 43.76; H, 3.08; N, 11.09%. Single crystals of **2a** as pale yellow, rectangular plates were obtained by slow diffusion of [$PdCl_2(NCPh)_2$] in CH_2Cl_2 into a solution of **1a** in DMF.

[$Cl_2Pd\{\mu$-$NC_5H_4N(H)CO^tBu$-$C_6H_3CON(H)C_5H_4N\}_2PdCl_2$] (2b). This compound was prepared similarly but using ligand **1b** in place of **1a**. Yield: 0.068 g (47%). NMR in $(CD_3)_2SO$: $\delta(^1H) = 10.98$ (s, 4H, CONH), 9.49 (d, 4H, $J_{HH} = 2$ Hz, H2), 8.82 (t, 2H, H2′), 8.51 (dm, 4H, H6), 8.47 (dm, 4H, H4′), 8.32 (d, 4H, H4), 7.60 (dd, 4H, $J_{HH} = 9$ and 6 Hz, H5), 1.42 (s, 18H, *t*-Bu). Anal. Calcd for $C_{44}H_{44}Cl_4N_8O_4Pd_2$: C: 47.89; H, 4.02; N, 10.15%. Found: C, 47.37; H, 4.12; N, 9.85%. Single crystals of **2b** were obtained as colorless blocks by slow diffusion of [$PdCl_2(NCPh)_2$] in PhMe into a solution of *N*,*N*′-bis(3-pyridyl)-5-*tert*-butylbenzene-1,3-dicarboxamide in DMF.

[$Pd\{\mu$-$NC_5H_4N(H)COC_6H_4CON(H)C_5H_4N\}_4Pd](CF_3CO_2)_4$ (3a). To a clear orange solution of [$PdCl_2(NCPh)_2$] (0.050 g, 0.130 mmol) in PhCN (10 mL) was added a solution of silver trifluoroacetate (0.058 g, 0.261 mmol) in PhCN (10 mL). The solution was stirred for 1 h to give a clear yellow solution of [$Pd(O_2CCF_3)_2(NCPh)_2$] and a white precipitate of silver chloride. The solution was filtered and added to a solution of **1a** (0.083 g, 0.261 mmol) in DMF (10 mL). The mixture was stirred for 2 h and then added to an excess of a pentane/diethyl ether mixture (1:1, 50 mL) to precipitate the product. A pale yellow solid was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 0.105 g (41%). NMR in $(CD_3)_2SO$: $\delta(^1H) = 10.21$ (m, 8H, H2), 9.21 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.99 (t, 4H, $J_{HH} = 2$ Hz, H2′), 8.55 (dm, 8H, H4), 8.06 (dd, 8H, $J_{HH} = 8$ and 2 Hz, H4′), 7.70 (dd, 8H, $J_{HH} = 8$ and 6 Hz, H5), 7.49 (t, 4H, $J_{HH} = 8$ Hz, H5′). Anal. Calcd for $C_{81}H_{60}F_{12}N_{16}O_{16}Pd_2$: C, 49.78; H, 3.09; N, 11.47%. Found: C, 49.80; H, 3.08; N, 11.20%. Single crystals of **3a** as colorless blocks were obtained by slow diffusion of a solution of [$Pd(O_2CCF_3)_2(NCPh)_2$] in benzene/acetone into a solution of **1a** in CH_2Cl_2/MeOH.

[$Pd\{\mu$-$NC_5H_4N(H)CO^tBu$-$C_6H_3CON(H)C_5H_4N\}_4Pd](CF_3CO_2)_4$ (3b). This compound was prepared similarly but using ligand **1b** in place of **1a**. Yield: 0.132 g (54%). NMR in DMF-d_7: $\delta(^1H) = 11.57$ (s, 8H, CONH), 10.48 (d, 8H, H2, $J_{HH} = 2$ Hz, H2), 9.59 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.81 (br m, 8H, H4), 8.79 (t, 4H, H2′), 8.46 (d, 8H, $J_{HH} = 2$ Hz, H4′), 8.01 (dd, 8H, $J_{HH} = 8$ and 6 Hz, H5), 1.48 (s, 36H, *t*-Bu). Anal. Calcd for **3b**·$2H_2O$·CH_2Cl_2, $C_{97}H_{94}Cl_2F_{12}N_{16}O_{16}Pd_2$: C, 51.02; H, 4.15; N, 9.81%. Found: C, 50.84; H, 3.81; N, 10.00%.

[$Pd_2(\mu$-$NC_5H_4N(H)CO^tBuC_6H_3CON(H)C_5H_4N)_4]Cl_4(H_2O)_2$ (3c). This compound was prepared from [$PdCl_2(NCPh)_2$] (0.020 g, 0.052 mmol) and **1b** in chloroform solution, in a similar way as described for **2a**. Yield: 0.024 g (50%). The complex was too insoluble to allow characterization by NMR spectroscopy. Anal. Calcd for **3c**·$CHCl_3$·$2H_2O$, $C_{93}H_{93}Cl_7N_{16}O_{10}Pd_2$: C, 54.33; H, 4.56; N, 10.90%. Found: C, 53.86; H, 4.45; N, 11.39%. Single crystals of **3c** as colorless, square prisms were obtained by slow diffusion of [$PdCl_2(NCPh)_2$] in $CHCl_3$ into a solution of **1b** in tetrahydrofuran (THF).

$Na_2[Pd_2(\mu$-$NC_5H_4NHCOC_6H_4CONHC_5H_4N)_4](CF_3CO_2)_6(H_2O)_2$ (4a). To a solution of [$Pd(O_2CCF_3)_2(NCPh)_2$] (0.078 mmol) in PhCN (20 mL), prepared as above, was added a solution of sodium trifluoroacetate (0.021 g, 0.156 mmol) in PhCN (2 mL). The solution was stirred for 15 min, and then a solution of **1a** (0.050 g, 0.156 mmol) in DMF (10 mL) was added. The mixture was stirred overnight and then added to a pentane/diethyl ether mixture (1:1, 50 mL) to precipitate the product as a white solid, which was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 0.068 g (39%). NMR in $C_6D_5NO_2/CD_3OD$: $\delta(^1H) = 10.18$ (br m, 8H, H2), 9.20 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.99 (m, 4H, H2′), 8.55 (dm, 8H, H4), 8.06 (m, 8H, H4′), 7.70 (dd, 8H, $J_{HH} = 6$ and 8 Hz, H5), 7.48 (t, 4H, $J_{HH} = 8$ Hz, H5′). Anal. Calcd for $C_{85}H_{60}F_{18}N_{16}Na_2O_{20}Pd_2$: C, 45.86; H, 2.72; N, 10.07%. Found: C, 45.45; H, 2.65; N, 9.77%. Single crystals of **4a** were obtained as colorless prisms by slow diffusion of [$Pd(O_2CCF_3)_2(NCPh)_2$] in PhCN into a solution of **1a** and NaO_2CCF_3 in DMF/PhCN.

$K_2[Pd_2(\mu$-$NC_5H_4NHCOC_6H_4CONHC_5H_4N)_4](CF_3CO_2)_6(H_2O)_2$ (4b). This compound was prepared similarly but using potassium trifluoroacetate (0.024 g, 0.156 mmol) instead of sodium trifluoroacetate. Yield: 0.078 g (45%). NMR in $C_6D_5NO_2/CD_3OD$: $\delta(^1H) = 10.16$ (d, 8H, $J_{HH} = 2$ Hz, H2), 9.20 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.99 (t br, 4H, $J_{HH} = 2$ Hz, H2′), 8.55 (dm, 8H, H4), 8.06 (dd, 8H, $J_{HH} = 8$ and 2 Hz, H4′), 7.69 (dd, 8H, $J_{HH} = 8$ and 6 Hz, H5), 7.48 (t, 4H, $J_{HH} = 8$ Hz, H5′). Anal. Calcd for $C_{85}H_{60}F_{18}N_{16}K_2O_{20}Pd_2$: C, 45.20; H, 2.68; N, 9.92%. Found: C, 45.09; H, 2.81; N, 9.91%. Single crystals of **4b** were obtained as for **4a**, but using KO_2CCF_3.

$Na_2[Pd_2(\mu$-$NC_5H_4N(H)CO^t$-$BuC_6H_3CON(H)C_5H_4N)_4](CF_3CO_2)_6$ (4c). This compound was prepared similarly to **4a** but using ligand **1b** in place of **1a**. Yield: 0.174 g (55%). NMR in $DCON(CD_3)_2/CD_3OD$: $\delta(^1H) = 9.89$ (d, 8H, $J_{HH} = 2$ Hz, H2), 8.96 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.69 (t, 4H, $J_{HH} = 2$ Hz, H2′), 8.59 (dm, 8H, H4), 8.25 (d, 8H, $J_{HH} = 2$ Hz, H4′), 7.71 (dd, 8H, $J_{HH} = 8$ and 6 Hz, H5), 1.39 (s, 36H, *t*-Bu). Anal. Calcd for **4c**·$3CHCl_3$·$2H_2O$, $C_{103}H_{95}Cl_9F_{18}N_{16}Na_2O_{22}Pd_2$: C, 43.73; H, 3.38; N, 7.92%. Found: C, 43.91; H, 3.26; N, 7.57%.

$K_2[(\mu$-$NC_5H_4N(H)CO^tBuC_6H_3CON(H)C_5H_4N)_4Pd_2](CF_3CO_2)_6$ (4d). This compound was prepared similarly to **4b** but using ligand **1b** in place of **1a**. Yield: 0.167 g (52%). NMR in $DCON(CD_3)_2/CD_3OD$: $\delta(^1H) = 9.89$ (d, 8H, $J_{HH} = 2$ Hz, H2), 8.96 (d, 8H, $J_{HH} = 6$ Hz, H6), 8.68 (t, 4H, $J_{HH} = 2$ Hz, H2′), 8.60 (dm, 8H, H4), 8.25 (d, 8H, $J_{HH} = 2$ Hz, H4′), 7.72 (dd, 8H, $J_{HH} = 8$ and 6 Hz, H5), 1.39 (s, 36H, *t*-Bu). Anal. Calcd for **4d**·$4CHCl_3$·$2H_2O$, $C_{104}H_{96}Cl_{12}F_{18}K_2N_{16}O_{22}Pd_2$: C, 41.91; H, 3.25; N, 7.52%. Found: C, 42.01; H, 3.41; N, 7.23%.

X-ray Data Collection and Reduction. Crystals were mounted on glass fibers, and data were collected using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998). The SHELXTL-NT V6.1 (Sheldrick, G. M., Madison, WI) program package was used to solve and refine the structures by direct methods. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details of the data collection and refinement are given in Tables 1 and 2. Brief comments on unusual features are given below.

Table 1. Crystal Data and Structure Refinement for Compounds **1** and **2**

	1a	**1a**·MeOH	**2a**·2DMF	**2b**·4DMF
formula	$C_{18}H_{14}N_4O_2$	$C_{19}H_{18}N_4O_3$	$C_{42}H_{42}Cl_4N_{10}O_6Pd_2$	$C_{56}H_{72}Cl_4N_{12}O_8Pd_2$
fw	318.33	350.37	1137.46	1395.86
T/K	200(2)	150(2)	200(2)	150(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	*C*2/*c*	$P2_1/n$
cell dimens				
a/Å	10.7731(2)	8.3883(2)	23.6322(4)	9.3407(1)
b/Å	12.9777(3)	8.5081(2)	8.4044(1)	23.6773(4)
c/Å	11.7216(3)	13.3648(4)	22.9866(3)	14.0328(2)
α/deg	90	99.594(1)	90	90
β/deg	103.439(2)	106.214(1)	97.932(1)	95.367(1)
γ/deg	90	104.780(1)	90	90
V/Å^3	1593.92(6)	856.02(4)	4521.8(1)	3089.92(8)
Z	4	2	4	2
d (calc)/Mg/m^3	1.327	1.359	1.671	1.500
μ/mm^{-1}	0.090	0.095	1.091	0.817
R1 [$I > 2\sigma(I)$][a]	0.036	0.047	0.050	0.045
wR2 [$I > 2\sigma(I)$][b]	0.093	0.117	0.120	0.085

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

Table 2. Crystal Data and Structure Refinement for Compounds **3** and **4**

	3a·C_6H_6·2H_2O	**3c**·4$CHCl_3$·8H_2O	**4a**·4PhCN·4H_2O	**4b**·4PhCN·4H_2O
formula	$C_{84}H_{66}F_9N_{16}O_{16}Pd_2$	$C_{92}H_{92}Cl_{16}N_{16}O_{16}Pd_2$	$C_{112}H_{76}F_{18}N_{20}Na_2O_{24}Pd_2$	$C_{112}H_{76}F_{18}N_{20}K_2O_{24}Pd_2$
fw	1939.33	2457.82	2686.71	2718.93
T/K	200(2)	200(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	tetragonal	monoclinic	monoclinic
space group	$P\bar{1}$	*P*4/*n*	$P2_1/n$	$P2_1/n$
cell dimens				
a/Å	12.9654(2)	19.8814(2)	13.3181(1)	13.2979(1)
b/Å	13.1454(2)	19.8814(2)	16.0259(2)	16.0953(2)
c/Å	15.8598(3)	15.8966(2)	26.8179(3)	26.9359(3)
α/deg	81.907(1)	90	90	90
β/deg	88.586(1)	90	90.815(1)	91.374(1)
γ/deg	68.947(1)	90	90	90
V/Å^3	2496.53(7)	6283.4(1)	5723.3(1)	5763.5(1)
Z	1	2	2	2
d (calc)/Mg/m^3	1.290	1.299	1.559	1.567
μ/mm^{-1}	0.442	0.685	0.433	0.495
R1 [$I > 2\sigma(I)$][a]	0.077	0.076	0.048	0.055
wR2 [$I > 2\sigma(I)$][b]	0.216	0.241	0.110	0.150

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

$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N$, **1a.** The molecule has a crystallographic 2-fold symmetry axis through the center of the aryl group. Crystals were grown from methylene chloride/methanol/THF.

$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N$·MeOH, **1a·MeOH.** Crystals were grown from methylene chloride/methanol/toluene.

[$Cl_2Pd(\mu$-$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N)_2PdCl_2$]·2DMF, **2a.** There was 50:50 disorder of the molecule about a center of symmetry at the center of the macrocycle, with the $C_6H_4(CONH)_2$ groups and two DMF solvates affected to the greatest extent. These groups were refined isotropically, while other non-hydrogen atoms were refined with anisotropic thermal parameters.

[$Cl_2Pd(\mu$-$C_{22}H_{22}N_4O_2)_2PdCl_2$]·4DMF, 2b. The molecule has crystallographic inversion symmetry.

[Pd{μ-$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N$}$_4$Pd][$CF_3CO_2$]$_4$·$C_6H_6$·2$H_2O$, **3a.** The molecule is disordered about the center of symmetry, with 50:50 disorder of the $C_6H_4(CO)_2$ groups. Only three trifluoroacetate anions were located, the fourth being disordered. The hydrogen atoms of the water molecules were allowed to refine, with the O−H distance set at 0.84 Å, and an anti-bumping restraint was applied to keep them separated. There were some unrefinable anion/solvent areas (a disordered anion was tentatively located at ($^1/_2$, 1, 1) that were "SQUEEZED" out.

[Pd{μ-$NC_5H_4N(H)C(O)^tBuC_6H_3C(O)N(H)C_5H_4N$}$_4$Pd][Cl]$_4$·4$CHCl_3$·8$H_2O$, **3b.** The *tert*-butyl group was disordered and was modeled as a 50:50 mixture of isotropic atoms. Two of the chloride anions were located in the "lantern", hydrogen bonded to NH groups, and one was outside the lantern associated with a palladium atom. Three distinct molecules of chloroform of solvation were located and refined at partial occupancy, with the SADI command to keep the C−Cl distances consistent. The water molecules were modeled as five distinct and separate anisotropic oxygen atoms; the hydrogen atoms were not located.

Na_2[(μ-$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N)_4Pd_2$][$CF_3CO_2$]$_6$·4PhCN·2$H_2O$, **4a.** There was a center of symmetry at the center of the lantern, with no disorder. The water hydrogens were fixed at 0.84 Å from the oxygen and allowed to refine, with the thermal parameter tied to that of the oxygen.

K_2[Pd{μ-$NC_5H_4N(H)C(O)C_6H_4C(O)N(H)C_5H_4N$}$_4$Pd]-[$CF_3CO_2$]$_6$·4PhCN·4$H_2O$, **4b.** This compound was isomorphous with **4a**. The water molecules were modeled as separate anisotropic oxygen atoms.

Results and Discussion

Ligand Conformations. The conformations of the ligands are important for the host−guest chemistry reported below,

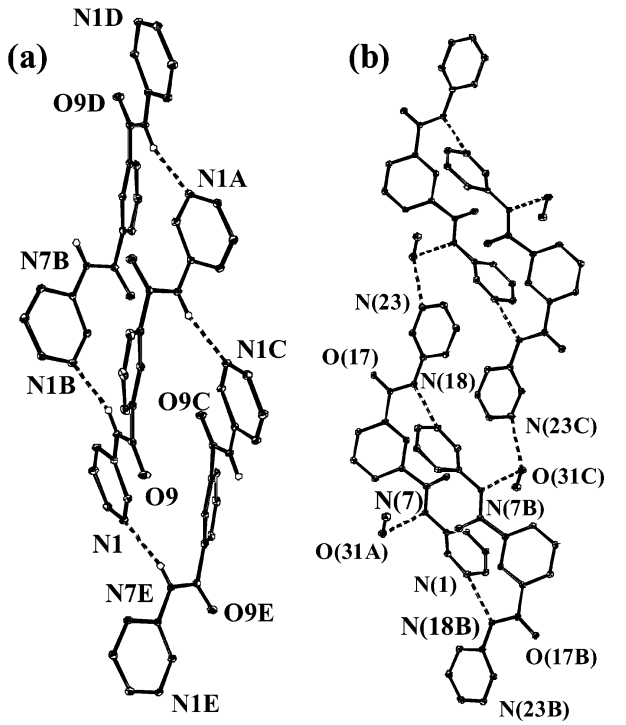


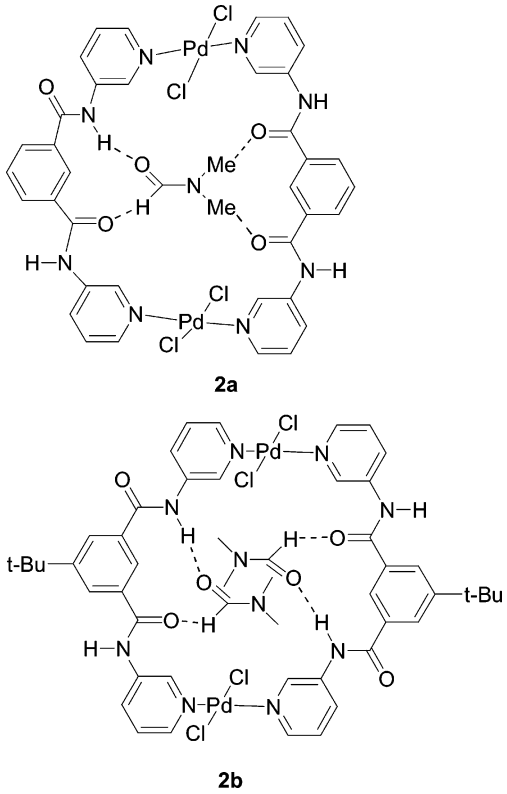
Figure 1. Structures of (a) ligand **1a** in distorted conformer **A** and (b) ligand **1a**·MeOH in conformer **B**. Hydrogen bonds are indicated by dashed lines.

so the structure of the free ligand **1a** was determined for comparison purposes. The structures of the ligand and of its methanol solvate are shown in Figure 1. For the unsolvated ligand (Figure 1a), the carbonyl groups are distorted above and below the central aryl ring so as to allow pairwise N(7)−H···N1(py) intermolecular hydrogen bonds [N(1)···N(7E) = 2.90(1) Å], giving a polymeric ribbon structure. The conformation of the pure ligand (Figure 1a) is closest to **A** [Chart 1, torsion angle C(13)C(10)C(8)O(9) = 144 °], whereas for the methanol solvate (Figure 1b), the conformation of the ligand approximates **B** of Chart 1 [torsion angles C(11)C(10)C(8)O(9) = 23 °, C(11)C(12)C(16)O(17) = 144 °]. Dimers are formed by pairwise NH···N(py) hydrogen bonds [N(1)···N(18B) = 2.93 Å], but these dimers are connected through hydrogen bonding to methanol [N(7)H···O(31)(Me)H···N(23), with N(7)···O(31) = 2.88 Å and N(23)···O(31) = 2.81 Å], giving a polymeric ribbon structure. The ligands **1a** and **1b** are only sparingly soluble in solvents such as dichloromethane and acetone, but they are more soluble in solvents such as DMF and DMSO (dimethyl sulfoxide) that can break down the polymeric hydrogen-bonded structures.

Neutral Dipalladium(II) Macrocycles. Reaction of equimolar amounts of $[PdCl_2(PhCN)_2]$ with either **1a** or **1b** gave the corresponding neutral dipalladium(II) complexes, *trans*,*trans*-$[Pd_2Cl_4(\mu\text{-LL})_2]$, **2a**, LL = **1a**; **2b**, LL = **1b**, as the DMF solvates shown in Chart 3. Complex **2a** crystallizes with one DMF molecule as a guest in the center of the macrocycle, whereas complex **2b** crystallizes with two DMF molecules as guests.

The macrocycles **2** are sparingly soluble in DMF and DMSO but essentially insoluble in dichloromethane or

Chart 3



acetone. The ^{1}H NMR spectrum of macrocycle **2a** in DMSO-d_6 was broader than the corresponding free ligand **1**. No displacement of the ligands was observed in DMSO solution. If $\Delta\delta$ is defined as δ(**2a**) − δ(**1a**) in DMSO-d_6, then significant shifts of $\Delta\delta$ = 0.37 (NH), 0.57 (H2), and 0.41 (H2′) were observed. For complex **2a** in the solid state, two different conformers **B** and **C** of ligand **1a** are present, but only one set of resonances was observed in the ^{1}H NMR spectrum, indicating that easy interconversion between conformers occurs in solution. Similar spectroscopic properties were observed for complex **2b**.

The structure of **2a** hydrogen bonded to the guest DMF molecule is shown in Figure 2. The macrocycle **2a** contains two ligands **1a**, with one present as conformer **B** and one as conformer **C**. This ligand combination causes one NH group and three C═O groups to be oriented inwardly toward the center of the macrocycle. The inwardly oriented NH group forms a hydrogen bond to the carbonyl group of a DMF guest molecule [O(31)···N(18A) = 3.08(1) Å], while one C═O group forms a hydrogen bond to the formyl proton [C(32)···O(9XA) = 2.97(1) Å], and another might form a weak hydrogen bond to a methyl group proton of the guest DMF molecule [C(34)···O(17Y) = 3.37(1) Å]. The second DMF molecule is hydrogen bonded to one of the NH groups that is directed away from the macrocycle cavity [O(41)···N(18Y) = 3.01(1) Å]

The structure of **2b** hydrogen bonded to four DMF molecules is shown in Figure 3. There are significant differences compared to **2a**. Complex **2b** contains both ligands **1b** in conformation **B**, each with one NH and one C═O group directed inward and one NH and one C═O group directed outward. There is some twisting of the ligands

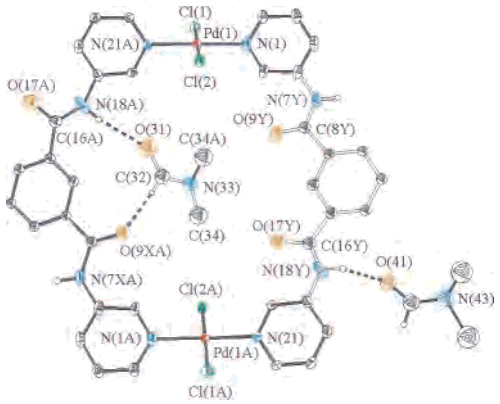


Figure 2. View of the structure of **2a**, with hydrogen bonding to two DMF molecules, showing the presence of one **B** and one **C** ligand conformer. 20% ellipsoids are shown; hydrogen atoms have been omitted for clarity except when involved in H-bonding. Selected distances (Å): Pd(1)−N(21A) 2.015(4), Pd(1)−N(1) 2.024(4), Pd(1)−Cl(1) 2.293(1), Pd(1)−Cl(2) 2.299(1). Hydrogen-bonding distances (Å): O(31)···N(18A) 3.08(1), C(32)···O(9XA) 2.97(1), C(34)···O(17Y) 3.37(1), O(41)···N(18Y) 3.01(1).

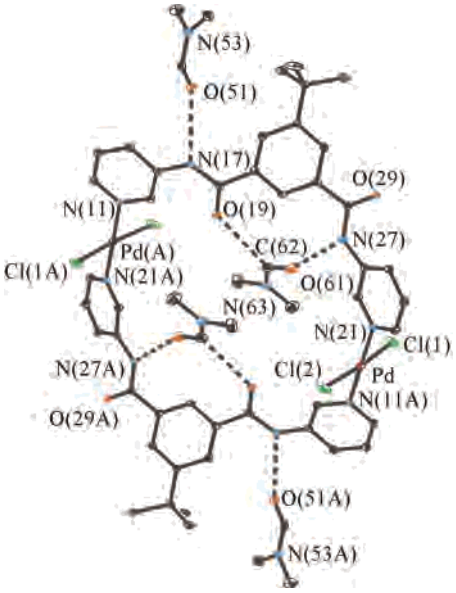
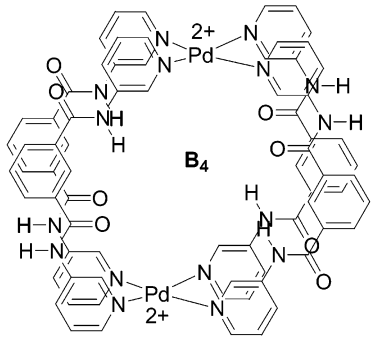


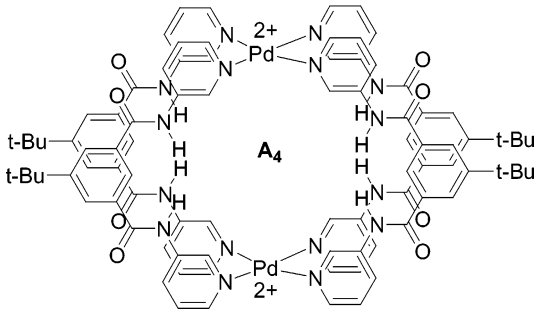
Figure 3. View of the structure of complex **2b**·4DMF, showing the presence of two ligands **1b** in conformation **B**. 20% ellipsoids are shown; hydrogen atoms have been omitted for clarity. Selected distances (Å): Pd−N(21) 2.012(2); Pd−N(11A) 2.012(2); Pd−Cl(1) 2.2983(9); Pd−Cl(2) 2.2917(9).

so that one set of inward-directed NH and C═O groups is directed above and the other set below the center of the macrocycle, and this allows each to hydrogen bond to a DMF guest molecule [N27···O61 = 2.838(3) Å]. Thus, two DMF guest molecules are offset from the center of the macrocycle in **2b** so as to avoid steric effects between them, whereas **2a** has only one guest DMF molecule that is located at the center of the macrocycle. Each outwardly oriented NH group in **2b** is more weakly hydrogen bonded to the carbonyl oxygen of a DMF molecule that is located outside the macrocycle [N(17)···O(51) = 3.028(3) Å]. The transannular Pd···Pd separation in **2b**, with ligand conformations **B**,**B**, is 11.14 Å, which is significantly shorter than the corresponding distance of 11.95 Å in **2a**, with ligand conformations **B**,**C**. This is expected as the natural bite distance is longer for

Chart 4



3a



3c

conformation **C** than for **B** (Chart 1). It is clear that the different conformations observed for **2a** and **2b** are close in energy and can probably interconvert easily in solution. In the solid state, it is likely that the bulky *tert*-butyl groups in **2b** keep the macrocyclic molecules further apart than in **2a**, and this leads to a greater degree of solvent incorporation.

Cationic Dipalladium(II) Lantern Complexes. The reaction of $[PdCl_2(PhCN)_2]$ with 2 equiv of **1a** or **1b**, in the presence of 2 equiv of $[AgO_2CCF_3]$ to abstract chloride, gave the corresponding lantern complexes $[Pd_2(\mu\text{-LL})_4](CF_3CO_2)_4$, **3a**, LL = **1a** or **3b**, LL = **1b**, as shown in Chart 4. In addition, reaction of $[PdCl_2(PhCN)_2]$ with 2 equiv of **1b** gave the chloride salt $[Pd_2(\mu\text{-LL})_4]Cl_4$, **3c**. These were all isolated as solvated compounds that exhibited significant host−guest chemistry. The complexes appeared to be conformationally labile, and compounds were characterized crystallographically in which the four bridging ligands **1** in a given complex **3** had either set of conformations $\mathbf{B}_4$ or $\mathbf{A}_4$. Chart 4 illustrates only the core of complexes $[Pd_2(\mu\text{-LL})_4]^{4+}$, **3**, and the host−guest chemistry is discussed below.

The structure of the lantern complex **3a** is shown in Figure 4. In the lantern complex **3a**, which contains a center of symmetry, each ligand adopts the conformation **B**, and there are two molecules of water as guests within the lantern. It is observed that each of the water molecules hydrogen bonds to two inwardly oriented carbonyl groups of the coordinated ligands [O(99)···O(39A) = 3.08; O(99)···O(49A) = 3.22 Å]. The two encapsulated water molecules lie roughly on the Pd···Pd axis but are well separated [O(99)···O(99A) = 4.40 Å]. Each palladium center has square-planar PdN_4^{2+} coordination, and there are long contacts to one of the encapsulated water molecules [Pd···O(99) = 3.50 Å] and an external trifluoroacetate anion [Pd···O(72) = 3.15 Å].

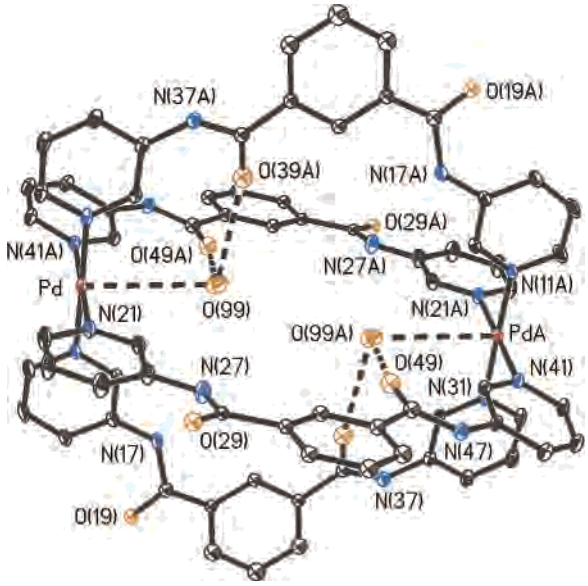


Figure 4. View of the structure of **3a**·2H_2O with four **B** conformers. 30% ellipsoids are shown; hydrogen atoms have been omitted for clarity. Selected distances (Å): Pd−N(11) 2.023(5); Pd−N(21) 2.023(5); Pd−N(31A) 2.030(5); Pd−N(41A) 2.018(5).

The transannular Pd···Pd separation is 11.21 Å, similar to the distance Pd···Pd = 11.14 Å in the macrocycle **2b**, in which the ligands also adopt the conformation **B**. Another trifluoroacetate anion bridges between lantern complexes by being hydrogen bonded to two outward-directed NH groups [N(37)···O(81) = 2.91(1), N(47)···O(82) = 3.06(1) Å] to generate a supramolecular polymer structure, as shown in Figure 5.

In the unsymmetrical conformation **B**, each ligand should have nonequivalent pyridyl groups, but only one set of resonances was observed in the ^{1}H NMR spectrum of **3a** in $C_6D_5NO_2$/CD_3OD solution. This indicates that there is easy conformational change that makes the pyridyl groups equivalent. It would be interesting to study this fluxionality in detail, but the poor solubility of **3a** in solvents suited to low-temperature NMR studies did not allow this. The coordination shift of the ortho pyridyl protons was much greater in the cation **3a** than in the neutral complex **2a**. Thus, $\Delta\delta$(H2) = 1.25 and $\Delta\delta$(H6) = 0.88 for **3a** compared to $\Delta\delta$(H2) = 0.57 and $\Delta\delta$(H6) = 0.18 for **2a**.

The structure of the lantern complex **3c** is shown in Figure 6. All of the ligands **1b** in **3c** adopt the conformation **A**, with all NH groups directed inward and all carbonyls directed outward. There is 4-fold symmetry about the Pd···Pd axis and some disorder of chloride anions and solvent molecules about this axis. Two chloride counterions and four guest water molecules are inside the cavity, while the other two chloride ions are located outside the lantern. Two of the guest water molecules are located on the Pd···Pd axis with short contacts of Pd(1)···O(3) = 3.00 and Pd(2)···O(2) = 3.08 Å. The two encapsulated chloride ions and the other two guest water molecules are disordered over four peripheral positions, with one component illustrated in Figure 6, and are all hydrogen bonded to pairs of NH groups. The presence of the ligands in conformation **A** leads to a short Pd···Pd separation of 9.45 Å.

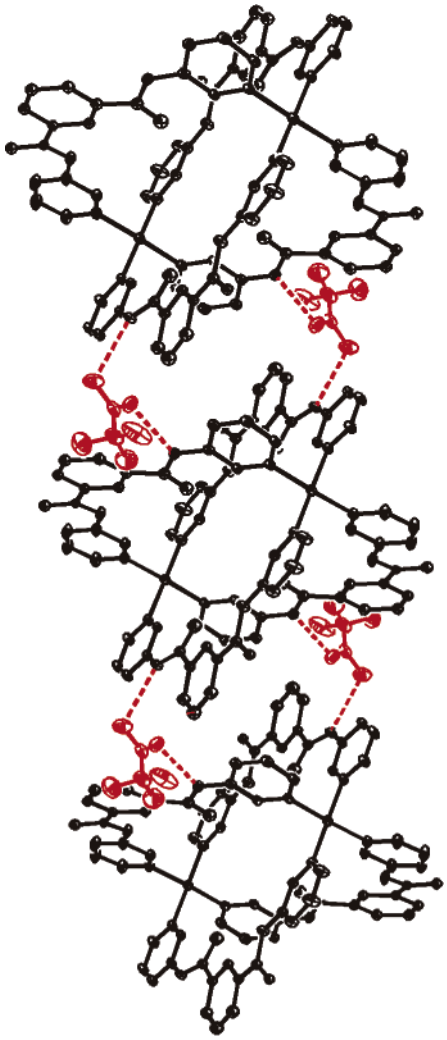


Figure 5. Supramolecular polymer structure observed for complex **3a**, showing individual lantern molecules connected by bridging trifluoroacetate groups. Only the lanterns and bridging trifluoroacetate groups are shown.

Complex **3c** undergoes further self-assembly in the solid state by bridging of external chloride ions between individual lanterns, as shown in Figure 7, to give polymers of lanterns. It is presumably this intermolecular self-assembly that leads to the low solubility of complex **3c**.

Complex **3c** was sparingly soluble even in DMSO, so it could not be characterized by NMR spectroscopy. It was just sufficiently soluble to characterize by ESI-MS in DMSO/methanol and gave major peaks at m/z = 1817 and 1443, corresponding to $[\mathbf{3c} + 3Cl^-]^+$ and $[\mathbf{3c} + 3Cl^- - \mathbf{1b}]^+$, where **3c** is defined as $[Pd_2(\mathbf{1b})_4]^{4+}$. The ESI-MS trace of **3b**, obtained from a dilute solution in DMF/methanol, showed a corresponding major peak at m/z = 2049, corresponding to $[\mathbf{3b} + 3(CF_3CO_2)^-]^+$, where **3b** is defined as $[Pd_2(\mathbf{1b})_4]^{4+}$. Of course, these ESI-MS data do not define the conformations of the ligands, but they do indicate that the lantern structures remain intact in solution and that anions remain closely associated, whereas the encapsulated water molecules are more easily lost. The ^{1}H NMR spectrum of **3b** in DMF-d_7 gave only a single set of pyridyl resonances, with chemical shifts similar to those of **3a**. These data do not define the conformations of the ligands in solution, and

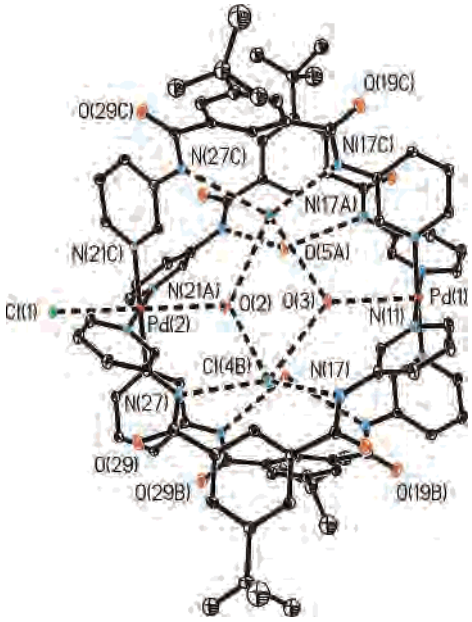


Figure 6. View of the structure of complex **3c**, with four **A** ligand conformers. 20% ellipsoids are shown; hydrogen atoms have been omitted for clarity. Selected distances (Å): Pd(1)N(11) 2.021(4); Pd(2)N(21) 2.037(3).

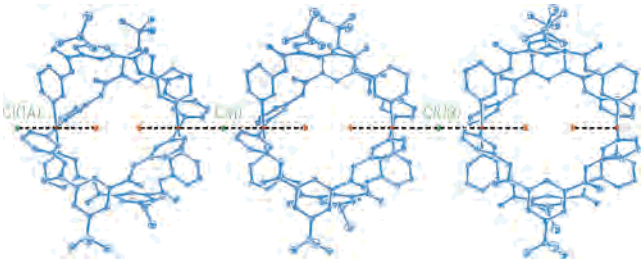


Figure 7. View of the supramolecular polymeric structure of complex **3c**, with chloride anions bridging between lantern molecules. Of the encapsulated groups, only the water molecules along the Pd···Pd axis are shown. Relevant distances are Pd(1)···Cl(1) 3.370(3) Å, Pd(2)···Cl(1) 3.075(3) Å.

so, it is not clear whether the set of conformations of the ligands is $\mathbf{A}_4$ (as in the solid-state structure of **3c**), $\mathbf{B}_4$ (as in the solid-state structure of **3a**), or indeed some other combination.

Encapsulation of Alkali Metal Cations. The lantern complex **3a** can act as a selective host for alkali metal cation guests. Thus, crystallization of **3a** in the presence of either sodium or potassium trifluoroacetate gave the corresponding solvated lantern complexes $M_2[Pd_2(\mu\text{-}\mathbf{1a})_4](CF_3CO_2)_6$, **4a**, M = Na, or **4b**, M = K. The structures of complexes **4a** and **4b** are shown in Figure 8, and bond parameters and hydrogen-bonding interactions are listed in Table 3.

The lantern complexes **4a** and **4b** are isomorphous and essentially isostructural. There is a center of symmetry at the lantern center. In both compounds, the ligands **1a** have the conformation **B**, as found in the precursor complex **3a**, and there are two alkali metal cations encapsulated in the cavity, with each alkali metal cation coordinated to two carbonyl groups of neighboring ligands **1a**, a guest water molecule, two oxygen atoms from a partially enclosed chelating trifluoroacetate anion, and one oxygen atom from a second partially enclosed trifluoroacetate anion. There are

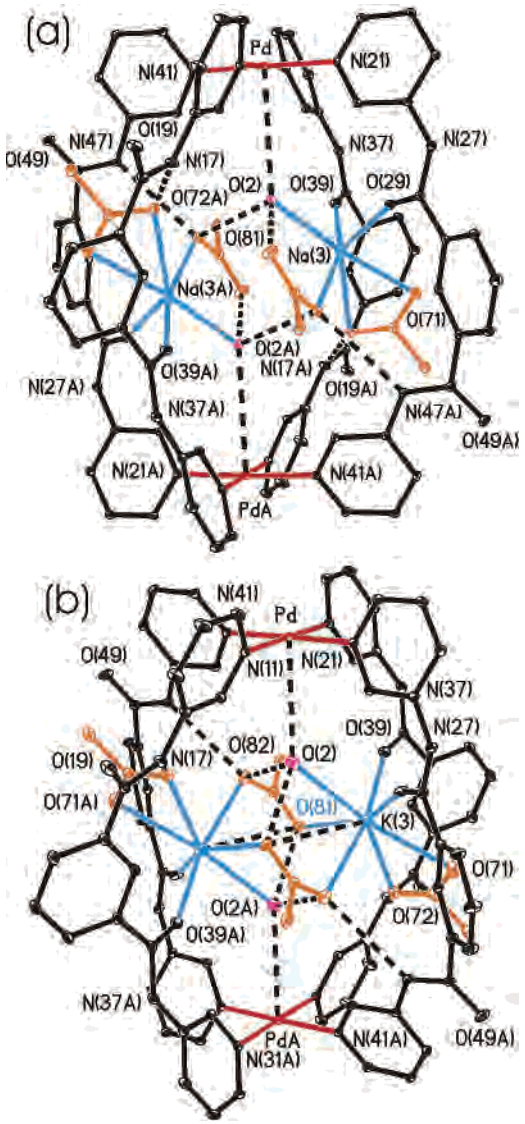


Figure 8. View of the structures of lantern complexes (a) **4a** and (b) **4b** with the encapsulated sodium and potassium ions, respectively. Secondary bonds are indicated by dashed lines. Both have four ligands **1a** in conformation **B**. Hydrogen atoms and fluorine atoms (of the trifluoroacetate anions) have been omitted for clarity.

minor differences that result from the larger size of K^+ compared to Na^+, with the range of distances M−O = 2.388(3)−2.603(3) Å or 2.507(3)−2.717(4) Å when M = Na or K, respectively. The coordination of the larger potassium ion to the carbonyl groups causes the encapsulated K^+ ions to be closer to the lantern center compared to the sodium ions in **4a** [M(3)···M(3A) = 4.908(2) when M = Na, 4.643(2) Å when M = K], and this leads the trifluoroacetate ion that is monodentate in **4a** to be weakly bridging in **4b** [compare M(3)···O(81) = 3.595(3) Å in **4a** vs 3.185(5) Å in **4b**]. The partial encapsulation of trifluoroacetate ions at each lantern window is driven by coordination to the alkali metal cations but is aided by hydrogen bonding to the inward-directed NH groups [N(17)···O(72A) = 2.916(3) Å in **4a** vs 2.850(5) Å in **4b**; N(47)···O(82A) = 3.110(3) Å in **4a** vs 3.087(5) Å in **4b**] and to the encapsulated water molecules [O(2)···O(81) = 2.73(1) Å in **4a** vs 2.73(1) in **4b**; O(2)···O(82A) = 2.91(1) in **4a** vs 2.87(1) in **4b**]. The Pd···Pd

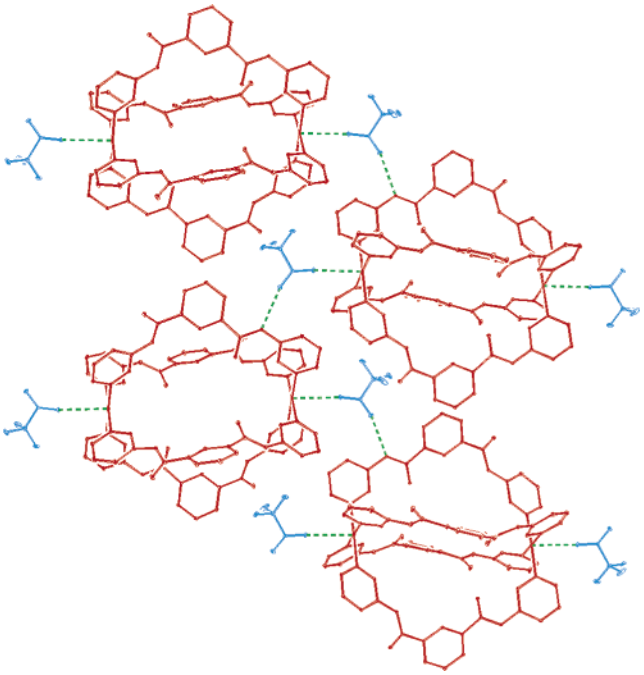


Figure 9. View of the supramolecular sheet structure of complex **4b**. Hydrogen atoms have been omitted, and only the lantern atoms and bridging trifluoroacetate ions are shown, for clarity.

Table 3. Selected Bond Distances (Å) for Lantern Complexes **4a** (M = Na) and **4b** (M = K)

	4a	**4b**
Pd−N(21)	2.016(2)	2.014(3)
Pd−N(41)	2.016(3)	2.020(3)
Pd−N(11)	2.019(2)	2.015(3)
Pd−N(31)	2.020(2)	2.031(3)
M(3)-O(2)	2.417(2)	2.645(4)
M(3)−O(29)	2.372(2)	2.559(3)
M(3)−O(39)	2.390(2)	2.507(3)
M(3)−O(71)	2.452(3)	2.717(4)
M(3)−O(72)	2.584(2)	2.624(3)
M(3)−O(82)	2.582(3)	2.716(4)
	Secondary Bonding	
M(3)−O(81)	3.595(3)	3.185(5)
M(3)−M(3A)	4.908(2)	4.643(2)
N(17)···O(72A)	2.916(3)	2.850(5)
N(27)···O(61)	2.740(4)	2.751(5)
N(37)···O(1A)	2.831(4)	2.828(5)
N(47)···O(82A)	3.110(3)	3.087(5)
Pd···O(62)	2.937(3)	2.974(3)
Pd···O(2)	3.591(3)	3.398(3)

separations are similar at 11.10 Å in **4a** and 11.05 Å in **4b**, and both distances are slightly shorter than in the precursor **3a** (11.21 Å).

There is secondary bonding in complexes **4a** and **4b** that leads to formation of a supramolecular sheet structure, as shown in Figure 9. The square-planar palladium(II) centers have secondary bonding internally to a guest water molecule [Pd···O(2) = 3.59 Å in **4a** and 3.40 Å in **4b**] and to an external trifluoroacetate anion [Pd···O(62) = 2.937(3) Å in **4a** and 2.974(4) Å in **4b**]. In addition, the outward-directed NH groups of each ligand take part in hydrogen bonding, either to a water molecule [N(37)···O(1A) = 2.831(4) Å in **4a** and 2.828(5) Å in **4b**] or to an external trifluoroacetate anion [N(27)···O(61) = 2.740(4) Å in **4a** and 2.751(5) Å in **4b**]. These external trifluoroacetate anions therefore bridge between lantern frameworks through Pd···O−C(R)═O···HN interactions to give the sheet structure illustrated in Figure 9.

There were only minor changes in the ^{1}H NMR spectrum of the lantern complex **3a** upon addition of sodium or potassium trifluoroacetate to form **4a** or **4b**, so the host−guest chemistry could not be studied by NMR titration. However, ESI-MS was found to be useful for studying the cation inclusion chemistry. The ESI mass spectrum of **3a**, obtained from a dilute solution in nitrobenzene/methanol, contained an envelope of peaks centered at m/z = 1825, corresponding to $[Pd_2(\mathbf{1a})_4(CF_3CO_2)_3]^+$, with good agreement with the predicted isotope pattern for this assignment (Figure 10). The base peak at m/z = 319 corresponds to the protonated ligand [**1a** + H$^+$]. There were several peaks with multiple charges z, including major peaks at m/z = 856 (z = 2), corresponding to $[Pd_2(\mathbf{1a})_4(CF_3CO_2)_2]^{2+}$; m/z = 799 (z = 2), corresponding to $[Pd_2(\mathbf{1a})_4(CF_3CO_2) - H^+]^{2+}$; and m/z = 495 (z = 3), corresponding to $[Pd_2(\mathbf{1a})_4 - H^+]^{3+}$, arising from further dissociation of anions. The ESI-MS of **4a** and **4b**, obtained from the same solvent mixture, each showed the same peak centered at m/z = 1825, but there were additional envelopes of peaks centered at m/z = 1961 for **4a** and 1977 for **4b**, assigned to the corresponding cation $[MPd_2(\mathbf{1a})_4(CF_3CO_2)_4]^+$, where M = Na or K, respectively (Figure 11). Note that this corresponds to inclusion of only one alkali metal cation, whereas in the solid state, there are two.

To test the selectivity for inclusion, dilute solutions (~5 mM) of **3a** were treated with increasing amounts of MO_2CCF_3 to give 1:1, 1:2, and 1:5 molar ratios, and the ratio of the intensities of peaks due to $[MPd_2(\mathbf{1a})_4(CF_3CO_2)_4]^+$ and $[Pd_2(\mathbf{1a})_4(CF_3CO_2)_3]^+$ was measured in each case. These ratios were 0.67, 1.45, and 1.45 when M = Na but 0.38, 0.48, and 1.35 when M = K, indicating a significantly higher equilibrium constant for formation of the sodium inclusion complex. A similar addition of LiO_2CCF_3 did not give any peak for a lithium inclusion complex. Further confirmation of the preference for sodium ion inclusion was obtained from the ESI-MS results for a solution of **3a** treated with equimolar amounts of sodium and potassium trifluoroacetate. Only the sodium ion inclusion complex was observed, as shown in Figure 11.

Complex **3b** also formed inclusion complexes with sodium and potassium ions, as indicated by ESI-MS studies, but these complexes could not be crystallized, so the detailed structures are unknown. The ESI mass spectrum of the complex of **3b** with Na$^+$ in dilute solution in DMSO/methanol showed peaks at m/z = 2049 $[\mathbf{3b}(CF_3CO_2)_3]^+$ and 2185 $[Na\cdot\mathbf{3b}(CF_3CO_2)_4]^+$, where **3b** = $[Pd_2(\mathbf{1b})_4]^{4+}$. Similarly, the ESI mass spectrum of the complex of **3b** with K$^+$ in dilute solution in DMSO/methanol showed peaks at m/z = 2049 $[\mathbf{3b}(CF_3CO_2)_3]^+$ and 2201 $[K\cdot\mathbf{3b}(CF_3CO_2)_4]^+$. When a solution of **3b** was treated with 2 equiv each of sodium trifluoroacetate and potassium trifluoroacetate, only peaks at m/z = 2049 and 2185 were observed in the ESI-MS trace, indicating selective inclusion of sodium ions. These results are very similar to those

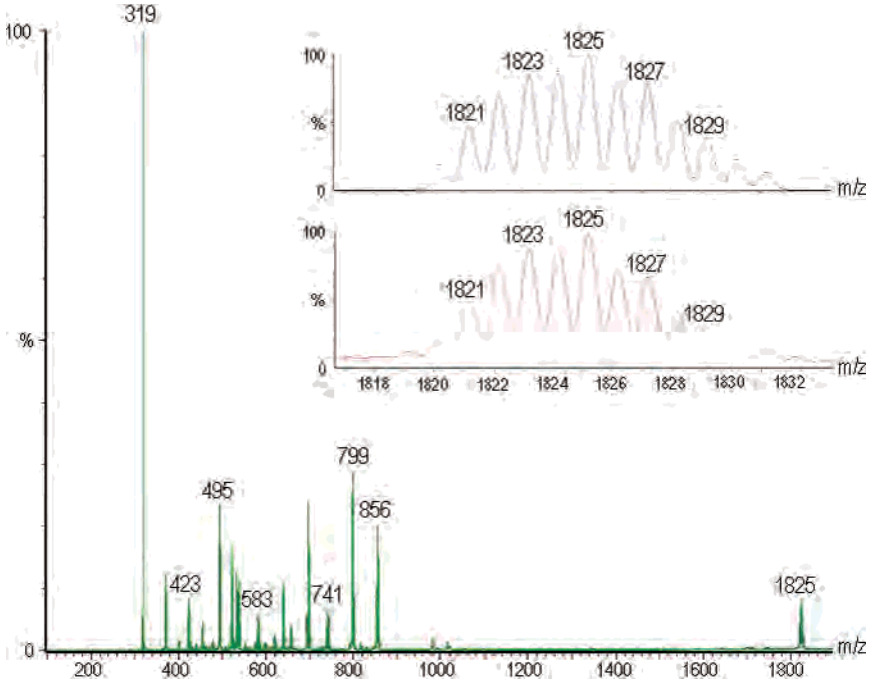


Figure 10. ESI mass spectrum of **3a** obtained from a dilute solution mixture of nitrobenzene and methanol. The insets show the measured isotope pattern (bottom) compared to the calculated (top) for $[Pd_2(\mathbf{1a})_4(CF_3CO_2)_3]^+$.

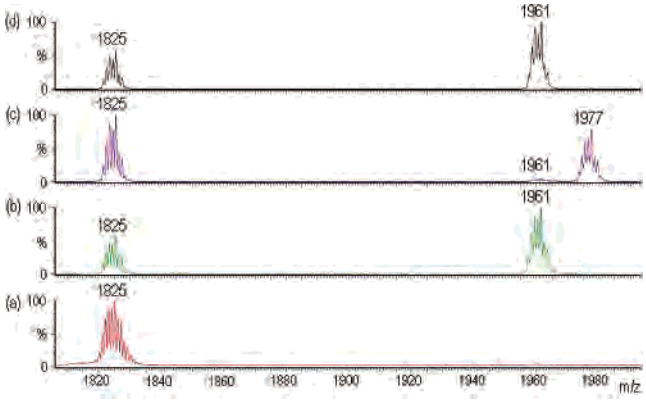


Figure 11. Expanded region of the ESI mass spectra for lantern complexes: (a) complex **3a**, no cation, $m/z = 1825$; (b) complex **4a**, 2 equiv of Na^+, $m/z = 1825$ and 1961; (c) complex **4b**, 2 equiv of K^+, $m/z = 1825$ and 1977; (d) complex **3a** treated with equimolar amounts of NaO_2CCF_3 and KO_2CCF_3 (1 equiv of Na^+ + 1 equiv of K^+), $m/z = 1825$ and 1961 only.

obtained for complex **3a** and indicate analogous inclusion chemistry for **3a** and **3b**.

Conclusions

The bis(amidopyridine) ligands **1** combine easily with palladium(II) to form either the neutral macrocyclic complexes $[Pd_2Cl_4(\mu\text{-}\mathbf{1})_2]$ or the tetracationic lantern complexes $[Pd_2(\mu\text{-}\mathbf{1})_4]^{4+}$. In these bis(pyridine) complexes, the amide groups of the ligands are available to take part in hydrogen bonding or further coordination, and both functions have been observed. The bridging coordination of the bis(amidopyridine) ligands **1** can occur with different ligand conformations **A**, **B**, or **C** (Chart 1), in which both NH groups, one NH and one C═O group, or both C═O groups, respectively, are directed inward. Although several of the complexes contained ligands in the unsymmetrical conformation **B** in the solid state, the ^1H NMR spectra at room temperature indicated higher effective symmetry in solution. This observation is interpreted in terms of easy fluxionality that interconverts the ligand conformations in solution. The ligand conformations can then change easily so as to give the strongest possible interaction with a guest molecule or ion. Because NH groups will tend to bind nucleophilic guests (Nu) by hydrogen bonding of the type NH···Nu and the carbonyl groups will tend to bind electrophilic guests (E) through coordination or hydrogen bonding of the type C═O···E, the preferred conformation will be determined by whether the guest is nucleophilic, electrophilic, or bipolar. This property is unusual, and we have suggested the term "amphitopic receptor" to describe hosts that can adapt to different types of guests and describe it in more detail below.[2d]

The macrocycle **2a** is constructed from one ligand conformer **B** and one ligand conformer **C**, and so has one NH and three C═O groups oriented inward. This conformation is ideal for accommodating a single DMF guest molecule through one strong NH···O═CHNMe$_2$ hydrogen bond, a C═O···HC hydrogen bond involving the formyl proton, and weak C═O···H hydrogen bonding to a methyl-group proton. The analogous macrocycle **2b** is constructed from two ligand conformers **B**, and so has two NH and two C═O groups oriented inward. In this conformation, two DMF molecules can bind internally, but each has only two hydrogen-bonding contacts, namely, a strong NH···O═CHNMe$_2$ hydrogen bond and a C═O···HC hydrogen bond to the formyl proton. It is easy to envision how fast interconversion between the overall conformers seen in **2a** and **2b** will lead to effective equivalence of all the pyridyl groups and also allow easy exchange between free and guest DMF molecules in solution. A neutral DMF guest has both a nucleophilic carbonyl oxygen atom and several weakly electrophilic hydrogen

atoms and so requires at least one ligand to be in conformation **B** in order to optimize hydrogen bonding.

The lantern complex **3a** is constructed from palladium(II) with four ligands **1a** in conformation **B**, with two water guest molecules encapsulated within the cavity, and with the water molecules hydrogen bonded to the inward-directed carbonyl groups as C═O···HOH···O═C. The inward-directed NH groups are not involved in the guest binding in this case. The lantern complexes **4a** and **4b** are also constructed from four ligand conformers **B**, and each has two alkali metal cations ions and two guest molecules of water encapsulated within the cavity. However, in these complexes **4**, the carbonyl groups and water molecules coordinate to the alkali metal cation, as do partially encapsulated trifluoroacetate anions. There is also extensive hydrogen bonding between the inward N−H groups and the O−H groups of the water molecules to oxygen atoms of the trifluoroacetate anions, so that all of the inward-directed C═O and N−H functional groups of the ligands **1a** are involved in binding to guest cations or semi-encapsulated anions.

Finally, the lantern complex **3c** is constructed from two palladium(II) ions and four ligands **1b** in conformation **A**, Chart 1, such that there are eight inward-directed NH groups. There are two chloride ions and two water guest molecules included within the cavity, and even though disorder between the chloride ions and water molecules is a complicating factor, it seems that each guest is chelated by two NH groups NH···Cl···HN or NH···O···HN and that each water molecule also hydrogen bonds to a guest chloride ion Cl···H−O−H···Cl. The conformations of the ligands **1b** thus adapt to bind the anionic chloride guests. Unfortunately, the trifluoroacetate derivative **3b**, as well as its adducts with sodium and potassium trifluoroacetate, failed give good single crystals, so the conformations of the ligands **1b** are not known in these cases. However, from the similarity in the binding of sodium and potassium ions as determined by ESI-MS for **3a** and **3b**, it is likely that conformation **B** is adopted.

The cavity size and shape for the macrocycles **2** and lantern complexes **3** also depends on the ligand conformations, with the Pd···Pd distance varying as conformer **A** < **B** < **C**. However, for the host−guest chemistry studied here, it seems that the conformation adopted by the ligand is controlled primarily by the electronic requirements of the guest molecule or ion, as described above.

Finally, we note that the lantern complexes tend to undergo supramolecular association to give polymer or sheet structures. In the cases of **3a**, **4a**, and **4b**, the supramolecular association involves external trifluoroacetate anions bridging between outward NH groups and palladium or between pairs of NH groups on neighboring lanterns. However, in the case of **3c**, which has no outward NH groups, it involves external chloride ions bridging between pairs of palladium(II) centers. The dual feature of selective anion inclusion using inward-directed functional groups, coupled with the ability to organize the receptors using their outward-directed functional groups, is potentially useful in molecular materials.

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Supporting Information Available: Tables of X-ray data for the complexes in cif format are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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