Dinuclear Platinum Complexes with Hydrogen-Bonding Functionality: Noncovalent Assembly of Nanoscale Cyclic Arrays

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Abstract: The preparation and solution behavior of a series of novel, dinuclear organoplatinum(II) complexes of nicotinic acid **3** and **4**, isonicotinic acid **5**, and nicotinamide **6** are reported. For **3** and **4**, comprehensive ^{1}H NMR titration studies demonstrate their spontaneous self-association to afford discrete, hydrogen-bonded aggregates in CD_2Cl_2 solution at 298 ± 0.1 K. For **3**, the titration data are consistent with the formation of a nanoscale cyclic entity $(\mathbf{3})_3$ which, despite the presence of bulky PPh_3 ligands, is strongly favored in solution ($K_3 = 1.99 \times 10^4 \pm 7.89 \times 10^2$ mol^{-2} dm^6). Complex **4** aggregates to form a cyclic dimer $(\mathbf{4})_2$ with $K_2 = 98.2 \pm 1.1$ mol^{-1} dm^3, and complexes **5** and **6** appear to afford oligomeric (or polymeric) aggregates. The X-ray crystal structure of **6** shows the dications associate to form corrugated chains connected by hydrogen bonds. This work demonstrates that the noncovalent assembly of multimeric cyclic arrays with nanoscale dimensions from simple diplatinum(II) complexes is feasible in nonaqueous solution.

Introduction

The use of the coordinate-covalent bond in the construction of molecular polygons and polyhedra by self-assembly is now well-established.[1] These studies have paralleled the use of the highly directional hydrogen bond as a means of controlling self-assembly processes in several supramolecular systems.[2,3] Crystal engineering studies utilizing transition metal complexes in hydrogen-bonded networks have been reported by several workers,[4,5] but despite the ubiquitous nature of hydrogen-bonding motifs in supramolecular organic systems,[3] few studies exist of the hydrogen bond-mediated assembly of discrete, cyclic entities in transition metal chemistry.[6,7] In these cases, the findings are usually limited to the solid state, where the formation of cyclic aggregates is confirmed primarily by means of X-ray crystallography. For example, Mingos et al.[6a] reported the preparation of platinum(II) complexes of 5-aminoorotic acid which were found to crystallize in various conformations, including a cyclic tetramer.

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Scheme 1

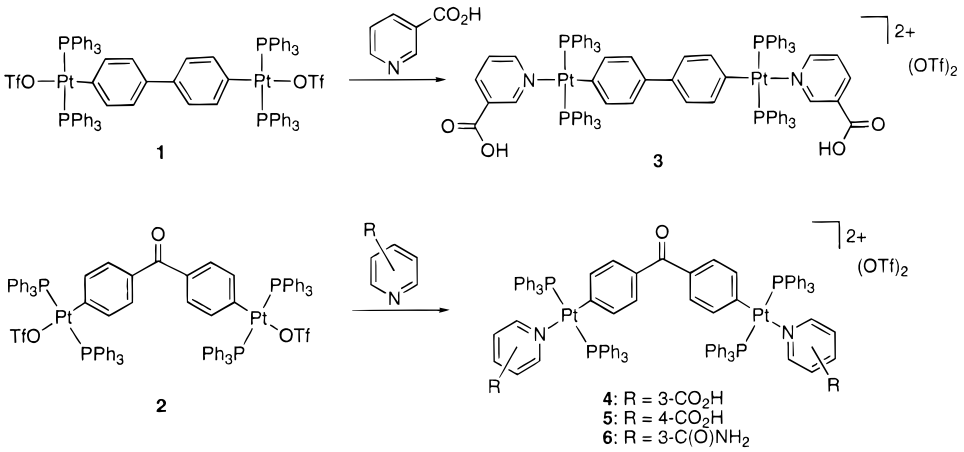

Table 1. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Data for Complexes **3**−**6**[a]

	δ (^{1}H)						δ (^{13}C)				
complex	H^{2}	H^{4}	H^{5}	H^{6}	H$^{o,o'}$	H$^{m,m'}$	C^{2}	C^{6}	R	C=O	δ (^{31}P)[b]
3	8.63 (s)	7.87 (d, $^{3}J_{HH}$ = 7.8)	6.82 (dd, $^{3}J_{HH}$ = 8.1, $^{3}J_{HH}$ = 5.7)	8.18 (d, $^{3}J_{HH}$ = 4.8)	6.78 (d, $^{3}J_{HH}$ = 8.1)	6.42 (d, $^{3}J_{HH}$ = 7.8)	154.0	154.7	164.3	*e*	20.6 (3040)
4	8.65 (s)	7.88 (d, $^{3}J_{HH}$ = 7.5)	6.90 (dd, $^{3}J_{HH}$ = 6.3, $^{3}J_{HH}$ = 7.5)	8.31 (d, $^{3}J_{HH}$ = 5.4)	6.93 (d, $^{3}J_{HH}$ = 7.8)	6.50 (d, $^{3}J_{HH = 7.8)}$	154.1	154.7	164.3	196.8	20.7 (2985)
5	8.24 (d, $^{3}J_{HH}$ = 6.0)	*e*	7.28[c,d]	*f*	6.90 (d, $^{3}J_{HH}$ = 7.8)	6.45 (d, $^{3}J_{HH}$ = 7.8)	153.2	153.2	164.3	196.5	20.6 (2991)
6	8.69 (s)	7.93 (d, $^{3}J_{HH}$ = 7.8)	6.80 (dd, $^{3}J_{HH}$ = 8.1, $^{3}J_{HH}$ = 5.1)	8.09 (d, $^{3}J_{HH}$ = 4.8)	6.93 (d, $^{3}J_{HH}$ = 7.2)	6.37[g]	152.7	153.2	164.3	196.8	20.7 (2993)

[a] Measured in CD_2Cl_2; coupling constants in hertz. Quoted multiplicities do not include ^{195}Pt satellites. [b] $^{1}J_{PtP}$ coupling constants (Hz) in parentheses. [c] Equivalent to H^{3}. [d] Resonance masked by other aromatic signals. [e] Not applicable. [f] Equivalent to H^{2}. [g] Resonance partly obscured by NH_2 signal.

Lippert and co-workers[7] have determined both the solution and X-ray crystal structures of mononuclear platinum(II)−ammine complexes of the type *trans*-[Pt(NH$_3$)$_2$(9-EtG-*N*7)(1-MeC-*N*3′)]X (X = 2,4,6-trinitrophenolate (picrate), trifluoromethanesulfonate (triflate), perchlorate, nitrate), which contain the modified nucleobases 1-methylcytosine (1-MeC) and 9-ethylguanine (9-EtG). The solid-state structures of the complex are highly dependent on the nature of the anion X, and when X = picrate, a cyclic base quartet consisting of a hydrogen-bonded dimer of cations was found. Furthermore, the cyclic structure is favored for all complexes in DMSO solution, irrespective of the nature of the anion X. This study demonstrated that the self-assembly of discrete, cyclic entities involving both transition metals and hydrogen bonding is feasible in solution. The work provides a firm basis for the development of metal-containing systems that are capable of self-associating in solution to afford discrete molecular polygons of *nanoscale* dimensions whose structures are driven and preserved by hydrogen-bonding interactions. Hybrid aggregates of this type may greatly expand the utility of molecular polygons that are composed of robust coordinate-covalent bonds in that, for example, the size of the cavity may be "tuned" easily as a result of the self-complementary and noncovalent nature of the bonding that holds the cyclic structure intact. Furthermore, these entities may act as potential self-assembling molecular receptors in the presence of suitable guest molecules.

Herein we describe the preparation and solution behavior of a series of novel, dinuclear organoplatinum(II) complexes with hydrogen-bonding functionality. In some cases, the complexes are shown to aggregate noncovalently into discrete multimeric assemblies including nanoscale cyclic dimers and trimers.

Results and Discussion

Syntheses. The preparation of the labile platinum precursors **1** and **2** followed established methodologies.[8,9] Addition of nicotinic acid to the bis(triflato)-4,4′-biphenyldiplatinum(II) complex **1** in CH_2Cl_2 solution resulted in the rapid formation of the dinuclear species **3** (Scheme 1). Similarly, reaction of the 4,4′-benzophenone complex **2** with nicotinic acid, isonicotinic acid, or nicotinamide led to the formation of **4**, **5**, or **6**, respectively. All the complexes were prepared in high yield (>95%) and purity, and they were fully characterized by multinuclear 1D (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and 2D (COSY and, in most cases, ^{1}H−^{13}C HSQC and HMBC) NMR spectroscopy and, for **6**, by an X-ray structure.

NMR Characterization of Complexes. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data for complexes **3**−**6** are shown in Table 1. The assignment of aromatic proton resonances was facilitated by COSY NMR experiments, whereby distinct cross-peaks were observed for all protons of the pyridyl ring system. For complexes **3**, **4**, and **6**, the assignments were relatively straightforward, with the H^{2} proton appearing as a singlet at δ ∼8.6 owing to its proximity to the pyridyl nitrogen atom. The H^{5} proton appears as a doublet of doublets at δ 6.80, with the expected three-bond couplings to the adjacent H^{4} and H^{6} protons. The characteristic AA′XX′ resonances at δ ∼6.90 and ∼6.50 were unambiguously assigned to the H$^{o,o'}$ and H$^{m,m'}$ protons of the bridging σ-aryl ligand, respectively, with cross-peaks to each other in the COSY spectrum. For complex **5**, its

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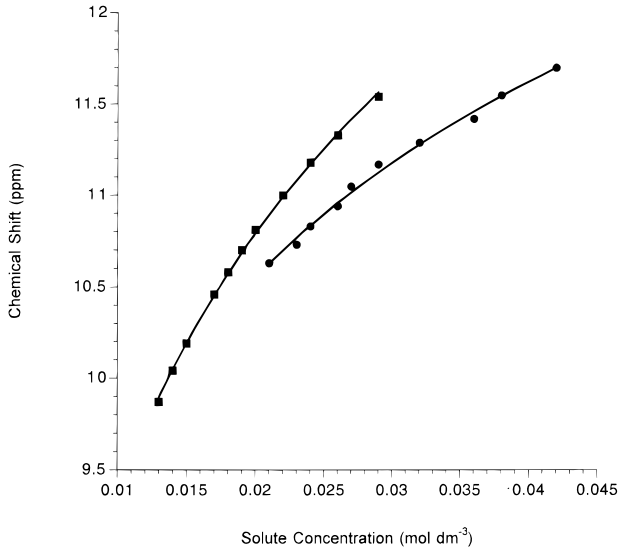
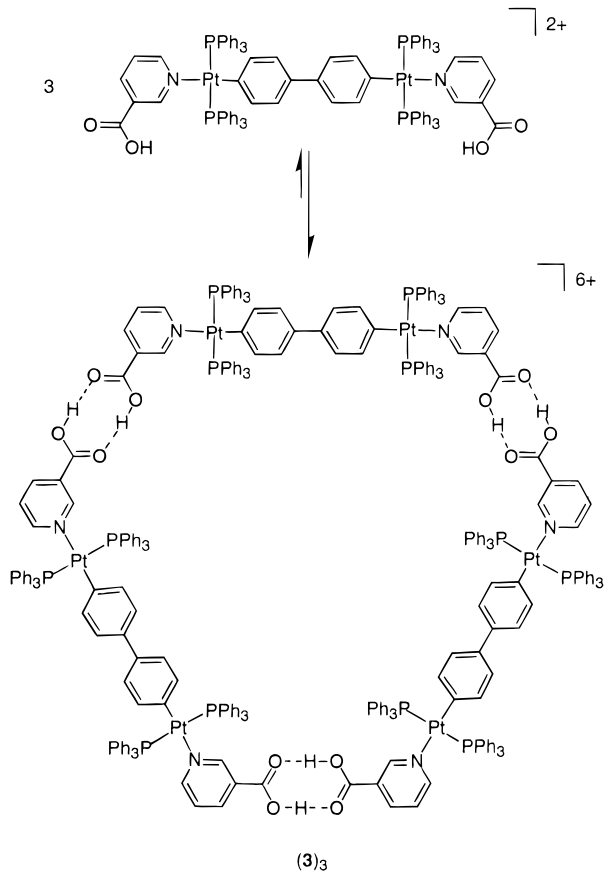


Figure 1. NMR titration plot of the carboxylic acid O−H chemical shift as a function of solute concentration for **3** (●) and **4** (■) in CD_2Cl_2 solution at 298 ± 0.1 K. For **3**, the curve represents the best theoretical fit of the data to the Saunders−Hyne trimer model. From the data, $K_3 = 1.99 \times 10^4 \pm 7.89 \times 10^2$ mol^{-2} dm^6, variance of optimization 2.30×10^{-4} ppm^2, and variance of reproducibility 4×10^{-4} ppm^2. For **4**, the curve represents the best theoretical fit of the data to the Saunders−Hyne dimer model. From the data, $K_2 = 98.2 \pm 1.1$ mol^{-1} dm^3, variance of optimization 7.68×10^{-5} ppm^2, and variance of reproducibility 1×10^{-4} ppm^2.

high symmetry allowed for a straightforward assignment of ring protons, with $H^{2,6}$ and $H^{3,5}$ appearing as characteristic AA′XX′ signals at δ 8.24 and 7.28, respectively. The latter resonance was obscured by the broad PPh_3 multiplet, and it was identified by virtue of a cross-peak to the $H^{2,6}$ signal in the COSY spectrum. In the $^{13}C\{^1H\}$ NMR spectra of complexes **4**−**6**, the downfield signals at δ ∼196 and ∼164 are due to the keto functionality of the bridging 4,4′-benzophenone ligand and the carboxyl (or amide) group, respectively. The pyridyl C^2 and C^6 resonances were assigned by means of $^1H-^{13}C$ HSQC experiments. Indeed, HSQC and HMBC experiments confirmed the assignments for the majority of carbon atoms for which one-bond and two-/three-bond $^{13}C-^1H$ couplings, respectively, were observed as cross-peaks in the 2D-NMR spectra. The $^{31}P\{^1H\}$ NMR spectra of complexes **3**−**6** show the expected singlet resonance that is flanked by ^{195}Pt ($I = {}^1/_2$; abundance, 33.8%) satellite signals. The chemical shift of the resonance (δ ∼21) and the magnitude of $^1J_{PtP}$ (∼3000 Hz) are comparable to those reported for other σ-arylplatinum(II) complexes with mutually trans PPh_3 ligands.[10]

NMR Titration Studies. Despite the limited concentration range over which the complexes remained soluble in CD_2Cl_2 solution,[11] comprehensive ^1H NMR titration experiments with **3** and **4** were conducted under strictly anhydrous conditions at 298 ± 0.1 K.[12] In both cases, the carboxylic acid O−H chemical shift was monitored as a function of solute concentration, and the data were fitted to models for a *n*-merization process according to the method of Saunders and Hyne (Figure 1).[12,13]

Scheme 2



For **3**, the titration data are consistent with the formation of a cyclic, hydrogen-bonded aggregate $(\mathbf{3})_3$ by spontaneous trimerization at low concentrations (<0.045 mol dm^{-3}) (Scheme 2).[14] Despite the considerable steric bulk of the phosphine ligands in **3**, the remarkably large value of the trimerization constant K_3 ($1.99 \times 10^4 \pm 7.89 \times 10^2$ mol^{-2} dm^6) is consistent with the highly cooperative nature of the assembly process that leads to the formation of $(\mathbf{3})_3$.[3c,15] Interestingly, the value of K_3 is identical (within experimental error) to that previously determined for the quinoline derivative pyrido[4,3-*g*]quinolinedione, which was shown to form a cyclic trimeric species by self-association in 10% DMSO-d_6/$CDCl_3$ solution ($K_3 = 2 \times 10^4$ mol^{-2} dm^6).[3c] The trimer $(\mathbf{3})_3$ is quite robust in CD_2Cl_2 solution, and even the addition of small amounts of DMF (<10%) to the solution does not appear to inhibit the aggregation process. From space-filling models, the cavity of $(\mathbf{3})_3$ has a diameter of ∼1.3 nm.

At low concentrations (<0.03 mol dm^{-3}), complex **4** self-associates in solution to form a hydrogen-bonded dimer $(\mathbf{4})_2$ with $K_2 = 98.2 \pm 1.1$ mol^{-1} dm^3 (Scheme 3), as determined from the best-fit dimer model derived from the Saunders−Hyne analysis (Figure 1).[12,13] The value of the dimerization constant is comparable to that of simple organic acids in the same solvent, e.g., acetic acid ($K_2 = 126 \pm 20$ mol^{-1} dm^3 at 298 K).[16] The titration data can only be fitted to a dimer model in which all four of the O−H groups are involved in hydrogen bonding, i.e.,

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(11) We were unable to model these systems at higher concentrations owing to their limited solubility in CD_2Cl_2, but we are addressing this problem with the significantly more soluble $PMePh_2$ and PCy_3 analogues.

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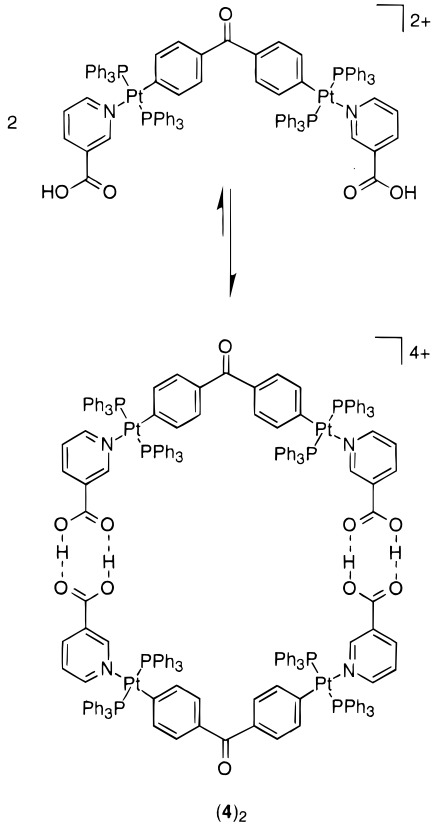
(13) Kudryavtsev, A. B.; Linert, W. *Physico-chemical Applications of NMR: A Practical Guide;* World Scientific: Singapore, 1996.

(14) The experimental data do not fit other models (e.g., dimer or tetramer).

(15) In the Saunders−Hyne analysis, it is assumed that K_3 corresponds to the equilibrium constant for the spontaneous formation of a trimer from three *monomers*. It makes no allowance for the addition of a monomer to a preexisting dimer.

Scheme 3



a cyclic species. Our results are not consistent with an open-chain dimer structure for $(\mathbf{4})_2$ containing two free and two hydrogen-bonded O−H groups. Indeed, a cyclic species would be favored on enthalpic grounds owing to the greater number of hydrogen bonds formed per dinuclear complex.[2c] From space-filling models, it is estimated that the cavity of $(\mathbf{4})_2$ has a diameter of ~1 nm.

The aggregation behavior of **4** was controlled by simply modifying either the position of the carboxylic acid group on the pyridyl ring or the nature of the functional group, as found in **5** or **6**, respectively. In direct contrast to **4**, the addition of **5** to CD_2Cl_2 resulted in the rapid formation of a dark yellow, colloidal dispersion which, upon standing for several hours, afforded a two-phase system. As a result, we were unable to model the system adequately by the Saunders−Hyne analysis.[12,13] It appears that high molecular weight oligomeric (or polymeric) aggregates are likely to account for the solution properties described above. Alternatively, a cyclic hexameric species $(\mathbf{5})_6$ is also feasible. Indeed, hydrogen-bonded, cyclic hexamers of isophthalic acid derivatives have been reported elsewhere,[3b,g] but we have no evidence to support the presence of a related aggregate with **5**.

The nature of the functional group in the complexes also has a major influence on their aggregation behavior. With **6**, the concentration and temperature dependence of the chemical shifts of the amide resonances in its ^{1}H NMR spectrum are consistent with intermolecular hydrogen bonding in CD_2Cl_2 solution. In contrast to **4**, the aggregation stoichiometry of **6** in this solvent is unknown owing to the complicated nature of its ^{1}H NMR spectrum, possibly due to the existence of several types of hydrogen-bonded motifs involving the primary amide group (e.g., cyclic dimers and chains, or perhaps a combination of the two motifs).[17] Hence, a comprehensive ^{1}H NMR titration study of **6** was not possible.

Table 2. Crystallographic Data for **6**

formula	$C_{99}H_{80}F_6N_4O_9P_4Pt_2S_2\cdot 0.5\ C_6H_4Cl_2\cdot 5\ H_2O$
fw (g mol^{-1})	2325.5
crystal system	monoclinic
space group	*C*2/c
crystal color	colorless
a (Å)	23.7736(5)
b (Å)	33.0990(4)
c (Å)	28.1790(6)
β (deg)	108.096(1)
V (Å^3)	21076.8(6)
Z	8
T (K)	173(1)
observed reflections[a]	6625
$R(F)^b$	0.084
$R_w(F)^c$	0.110

[a] Observation criterion $I \geq 3.0\sigma(I)$ ($1° < \theta < 30°$). [b] $R(F) = \sum||F_O| - |F_C||/\sum|F_O|$. [c] $R_w(F) = [\sum w(F_O - F_C)^2/\sum w(F_O)^2]^{1/2}$.

ESI-MS Studies. The successful detection of hydrogen-bonded supramolecular aggregates by means of the ESI-MS technique has been reported for certain organic systems.[18] In our hands, positive-ion ESI-MS of complexes **3**−**6** did not provide any evidence for the hydrogen-bonded aggregates, even in low-polarity solvents such as 1,2-dichloroethane. In some cases, the $[M - 2OTf]^{2+}$ peak attributed to the monomeric complex was observed. For example, it was detected at *m*/*z* 933 for **4**, with half mass unit intervals confirming the 2+ charge state of the species. In addition, the pyridyl ligands in this complex were sequentially lost and peaks at *m*/*z* 871 and 809, corresponding to the species $[M - 2OTf - C_5H_4N(CO_2H)]^{2+}$ and $[M - 2OTf - 2C_5H_4N(CO_2H)]^{2+}$, respectively, were also detected. When the complexes were dissolved in CH_3CN solution, peaks attributed to $[M - 2OTf - 2C_5H_4NX]^{2+}$ (X = CO_2H for **3**−**5** or $C(O)NH_2$ for **6**) were observed. It is apparent from these results that the strong trans effect of the bridging σ-aryl group leads to the facile loss of the pyridyl ligands, particularly in the presence of coordinating solvents such as CH_3CN.

X-ray Analysis of 6. The molecular structure of the cation in **6** is illustrated in Figure 2, and a view of a strand of the cations in **6** is presented in Figure 3. Crystal data and data collection parameters are presented in Table 2. The X-ray analysis of **6** shows that it does not form discrete aggregates in the solid state, but instead, the dication associates to form corrugated chains that are connected by hydrogen bonds. The crystallographic asymmetric unit of **6** comprises a dication, triflate anions, 1,2-dichlorobenzene molecules, and water molecules of solvation in the ratio 1:2:0.5:5. The dication features two platinum centers linked via a σ-bonded 4,4′-benzophenone ligand (Figure 2). The three remaining sites in the square-planar geometry about each platinum atom are occupied by two PPh_3 ligands, each disposed cis to the benzophenone moiety, and a pyridine N-atom of the nicotinamide molecule. The overall cation adopts a curved shape as a result of the angle subtended at the carbonyl carbon atom (118(2)°). In addition, a twist within

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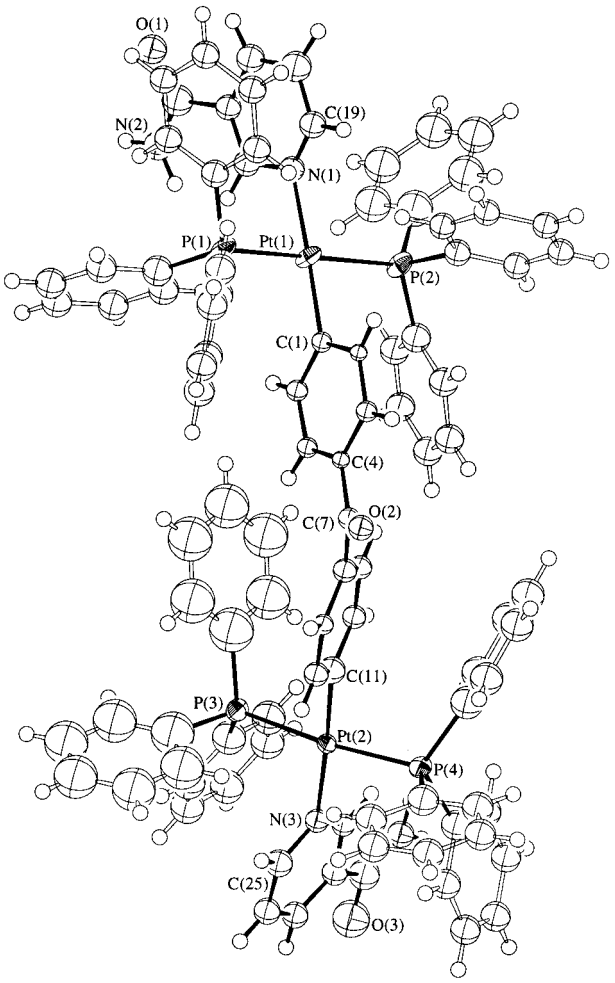

Figure 2. ORTEP (35% probability ellipsoids) plot of the cation in **6**. Selected bond distances: Pt(1)−P(1) 2.332(5) Å, Pt(1)−P(2) 2.305(5) Å, Pt(1)−N(1) 2.16(2) Å, Pt(1)−C(1) 2.04(2) Å, Pt(2)−P(3) 2.328(7) Å, Pt(2)−P(4) 2.307(6) Å, Pt(2)−N(3) 2.12(1) Å, and Pt(2)−C(11) 2.06(2) Å. Selected bond angles: P(1)−Pt(1)−P(2) 172.4(2)°, N(1)−Pt(1)−C(1) 177.3(6)°, P(3)−Pt(2)−P(4) 173.3(2)°, and N(3)−Pt(2)−C(11) 176.3(6)°.

the cation is evident owing to the nonplanarity of the benzophenone molecule. Further, contributing to this twist is the approximate orthogonal relationship between each square-planar geometry and the respective phenyl group of the benzophenone moiety (presumably so as to minimize intramolecular interactions between the phenyl groups) so that the dihedral angle between the two square planes is 66.9°. As would be expected, there are a number of significant intramolecular interactions in the lattice involving the cation, anions, and solvent molecules. In the context of the present study, the most significant are those involving the carbonyl O(1) atom at one end of the molecule and the amino-H(4n2) atom at the other end. Thus, symmetry-related molecules associate such that O(1)···H(4n2)^i is 1.99 Å, O(1)−N(4)^i is 2.95(2) Å, and O(1)···H(4n2)^i −N(4)^i is 164° (symmetry operation i: $0.5 - x, -0.5 + y, -0.5 - z$). This mode of association leads to the formation of planar corrugated chains that are isolated from neighboring chains owing to "solvation" by anions and solvent molecules. It is possible that crystal-packing effects determine the aggregation state of **6** in the solid state. Indeed, other types of noncovalent aggregates involving the cation may be present in solution (vide supra).

Conclusions. The ^{1}H NMR solution studies with complexes **3**−**6** clearly demonstrate that the supramolecular assembly process is sensitive to both the nature and position of the hydrogen-bonding functional group. In our systems, discrete cyclic aggregates are only observed when nicotinic acid is used as a ligand. In effect, each pyridyl group acts as a 120° bridging ligand upon intermolecular hydrogen bonding and it thus facilitates the formation of cyclic trimeric and dimeric aggregates $(\mathbf{3})_3$ and $(\mathbf{4})_2$, respectively. When the hydrogen-bonded pyridyl system acts as a 180° bridging ligand between two platinum centers, as found in the isonicotinic acid derivative **5**, long-chain polymers (or perhaps cyclic, hexameric arrays) are favored instead. For **6**, the bifunctional primary amide group allows for several hydrogen-bonded motifs such as cyclic dimers and chains which, in solution, appear to favor the formation of several types of supramolecular species, but in the solid state a polymeric corrugated chainlike structure is found.

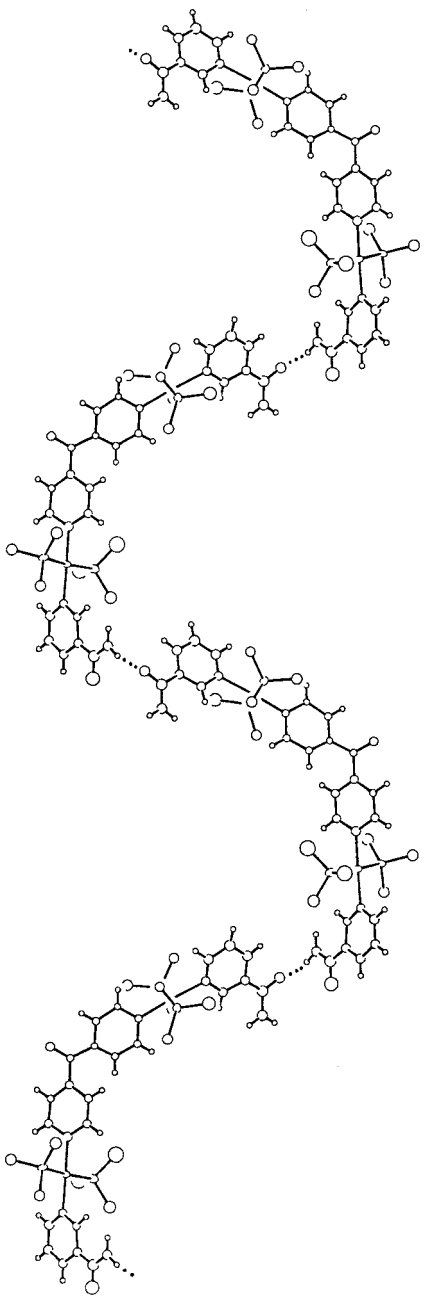

Figure 3. View of a strand of the cations in **6** (viewed down the crystallographic *a*-axis) highlighting their mode of association. The solvent molecules, triflate ions, PPh_3 phenyl groups (except *ipso*-C atoms), and hydrogen atoms have been omitted for clarity.

In summary, we have demonstrated that the noncovalent assembly of nanoscale cyclic aggregates from simple diplati-

num(II) complexes is feasible in nonaqueous solution. The facile preparation of the discrete entities $(\mathbf{3})_3$ and $(\mathbf{4})_2$ allows one to study their potential to act as self-assembling molecular receptors, and we are currently determining whether anionic guest molecules can be incorporated into their cavities. We are also interested in determining whether certain guests can spontaneously induce (or nucleate) the aggregation processes in polar solvents. The results of these studies will be reported in due course.

Experimental Section

General Synthetic and Analytical Methods. All synthetic work was performed under an inert atmosphere of dry dinitrogen, utilizing standard Schlenk line techniques. CH_2Cl_2 was dried using CaH_2. Nicotinic acid, isonicotinic acid, and nicotinamide were stored in a desiccator over P_2O_5. CD_2Cl_2 and $CDCl_3$ were stored over 4-Å molecular sieves under a dinitrogen atmosphere. *trans*-4,4′-Biphenylbis-[(triflato)bis(triphenylphosphine)]diplatinum(II) (**1**) and *trans*-4,4′-benzophenonebis[(triflato)bis(triphenylphosphine)]diplatinum(II) (**2**) were prepared according to the literature procedures.[8,9]

All 1D and 2D NMR spectra were recorded at 298 K by means of a Varian Gemini 300-MHz NMR spectrometer. Heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC) experiments were performed on a Varian Unity Inova 600-MHz NMR instrument.

^{1}H and ^{13}C{^{1}H} chemical shifts are reported in ppm relative to tetramethylsilane (TMS). ^{31}P{^{1}H} NMR spectra were referenced to a sealed external standard of 85% phosphoric acid. Coupling constants (*J*) are given in hertz.

Electrospray ionization (ESI) mass spectra were recorded by means of a Finnegan LCQ mass spectrometer. Complexes were dissolved in HPLC grade 1,2-dichloroethane or CH_3CN. Analyses were conducted in the positive-ion mode.

Elemental analyses were performed by the Department of Chemistry, The University of Otago, Dunedin, New Zealand.

Preparation of Complexes. *trans*-4,4′-Biphenylbis[(nicotinic acid)-bis(triphenylphosphine)]diplatinum(II) Bis(triflate) (3). To a Schlenk flask containing freshly prepared *trans*-4,4′biphenylbis[(triflate)bis-(triphenylphosphine)]diplatinum(II) (0.348 g, 0.167 mmol) was added nicotinic acid (0.041 g, 0.334 mmol) and anhydrous CH_2Cl_2 (15 mL). The solution was stirred at room temperature for 6 h, and the solvent was removed in vacuo to afford a white microcrystalline solid. Yield: 0.35 g (98%). ESI-MS (CH_3CN): *m*/*z* 795 $[M - 2OTf - 2C_5H_4N(CO_2H)]^{2+}$. Anal. Calcd for $C_{98}H_{78}F_6N_2O_{10}P_4Pt_2S_2{\cdot}CH_2Cl_2$: C, 53.54; H, 3.63; N, 1.26. Found: C, 53.02; H, 3.56; N, 1.35.

***trans*-4,4′-Benzophenonebis[(nicotinic acid)bis(triphenylphosphine)]-diplatinum(II) Bis(triflate) (4).** To a Schlenk flask containing freshly prepared *trans*-4,4′benzophenonebis[(triflate)bis(triphenylphosphine)]-diplatinum(II) (0.503 g, 0.263 mmol) was added nicotinic acid (0.065 g, 0.526 mmol) and anhydrous CH_2Cl_2 (20 mL). The solution was stirred at room temperature for 9 h, and the solvent was removed in vacuo to afford a white microcrystalline solid. Yield: 0.56 g (99%). ESI-MS ($C_2H_4Cl_2$): *m*/*z* 932 $[M - 2OTf]^{2+}$, 871 $[M - 2OTf - C_5H_4N(CO_2H)]^{2+}$, 809 $[M - 2OTf - 2C_5H_4N(CO_2H)]^{2+}$. ESI-MS ($CH_3CN$): *m*/*z* 809 $[M - 2OTf - 2C_5H_4N(CO_2H)]^{2+}$. Anal. Calcd for $C_{99}H_{78}F_6N_2O_{11}P_4Pt_2S_2$: C, 54.95; H, 3.63; N, 1.29. Found: C, 54.58; H, 3.60; N, 1.43.

***trans*-4,4′-Benzophenonebis[(isonicotinic acid)bis(triphenylphosphine)]diplatinum(II) Bis(triflate) (5).** To a Schlenk flask containing freshly prepared *trans*-4,4′benzophenonebis[(triflate)bis(triphenylphosphine)]diplatinum(II) (0.203 g, 0.097 mmol) was added isonicotinic acid (0.024 g, 0.195 mmol) and anhydrous CH_2Cl_2 (15 mL). The solution was stirred at room temperature for 6 h, and the solvent was removed in vacuo to afford a white microcrystalline solid. Yield: 0.21 g (99%). ESI-MS (CH_3CN): *m*/*z* 809 $[M - 2OTf - 2C_5H_4N(CO_2H)]^{2+}$. Anal. Calcd for $C_{99}H_{78}F_6N_2O_{11}P_4Pt_2S_2$: C, 54.95; H, 3.63; N, 1.29. Found: C, 54.49; H, 3.56; N, 1.30.

***trans*-4,4′-Benzophenonebis[(nicotinamide)bis(triphenylphosphine)]-diplatinum(II) Bis(triflate) (6).** To a Schlenk flask containing freshly prepared *trans*-4,4′benzophenonebis[(triflate)bis(triphenylphosphine)]-diplatinum(II) (0.129 g, 0.062 mmol) was added nicotinamide (0.015 g, 0.124 mmol) and anhydrous CH_2Cl_2 (13 mL). The solution was stirred at room temperature for 6 h, and the solvent was removed in vacuo to afford a white microcrystalline solid. Yield: 0.13 g (95%). ESI-MS (CH_3CN): *m*/*z* 809 $[M - 2OTf - 2C_5H_4N(CONH_2)]^{2+}$. Anal. Calcd for $C_{99}H_{80}F_6N_4O_9P_4Pt_2S_2{\cdot}CH_2Cl_2$: C, 53.46; H, 3.68; N, 2.49. Found: C, 53.56; H, 3.86; N, 2.39.

^{1}H NMR Titration Experiments. All NMR titration experiments were performed on a Varian Gemini 300-MHz spectrometer. In all cases, the experiments were conducted at 298 ± 0.1 K. All titrations were performed under *strictly* anhydrous conditions in a high-purity dinitrogen atmosphere. Dilutions were performed by adding 50-μL aliquots of anhydrous CD_2Cl_2 to a NMR tube containing a known concentration of the complex in the same solvent. The equilibration time between successive dilutions was ∼15 min. For each compound, the chemical shift data were obtained in triplicate.

For a detailed discussion of the computer programs (OPTIMI.FOR and SELFAS.FOR) and the data manipulation used in the modeling of all NMR titration data, see ref 13.

X-ray Structure Determination of 6. Colorless crystals of **6** were grown from a mixture of 1,2-dichlorobenzene and $CHCl_3$. X-ray data were collected on a Nonius Kappa CCD and corrected empirically for absorption using SORTAV. The structure was solved using DIRDIF and refined using teXsan. The asymmetric unit comprises a dication (P-bound phenyl groups were constrained as C_6H_5 rigid groups, Pt and P atoms were refined anisotropically, remaining non-H atoms were refined isotropically, and H atoms were included in their calculated positions), two triflate anions (the positional parameters for the CF_3 atoms of the second anion were fixed), 0.5 of a 1,2-$C_6H_4Cl_2$ molecule (located about a crystallographic 2-fold axis, Cl refined anisotropically, C isotropically, and H in calculated positions) and five water molecules of crystallization (isotropic refinement, H-atoms not included, and O(12) and O(13) with 50% site occupancy).

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Supporting Information Available: X-ray crystallographic data file, in CIF format, for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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