

Single- and Double-Stranded Chains Assembled via Concomitant Metal Coordination and Hydrogen Bonding

Christopher J. Kuehl,* Frank M. Tabellion, Atta M. Arif, and Peter J. Stang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received February 12, 2001

The synthesis and X-ray crystal structures of two novel cationic metal complexes bearing ligands capable of multiple hydrogen-bonding interactions (isonicotinamide) are reported. *cis*-(Et₃P)₂Pt(NC₅H₄CONH₂)₂(NO₃)₂ (**2**) crystallizes as its monohydrate via the amide functionality, resulting in infinite, parallel zigzag chains. (C₅Me₅)Rh(NC₅H₄CONH₂)₃(OTf)₂ (**3**), along with one molecule of acetone, crystallizes via the amide functionality, resulting in infinite, doubly stranded, interwoven chains. The preparation and X-ray crystal structure of *cis*-(Et₃P)₂Pt(NO₃)₂ (**1**) is also reported.

Introduction

Both coordination-driven self-assembly and hydrogen bonding have proven to be powerful tools for the formation of a wide variety of discrete supramolecular species.^{1,2} Likewise, many highly ordered coordination polymers³ and hydrogen-bonded networks^{2,4} have been prepared through the propagation of these relatively weak interactions. Far less common, however, have been studies directed toward the simultaneous use of these two distinct bonding motifs.^{5–11} In fact, very few structures of discrete, cyclic metal-containing hydrogen-

bonded systems have been characterized whether in the solid state^{7,8} or in solution.⁸ Recently, by means of NMR titration techniques, Rendina and co-workers demonstrated that the formation of *nanoscale* metallacyclic arrays held together via hydrogen bonds was feasible in nonaqueous solution.⁹

Also of fundamental interest are network solids assembled with combined structural themes. Here the attractiveness of such a design principle lies not only in the synthesis of materials with new and potentially useful properties (e.g., magnetic, optical, mechanical, etc.) but also in furthering our understanding of the significance of particular intermolecular interactions and arrangements.¹⁰ Specifically, a hybrid motif benefits from the generally predictable three-dimensional ar-

(1) For recent reviews see: (a) Leininger, S.; Olenyuk, B.; Stang, P. *J. Chem. Rev.* **2000**, *100*, 853. (b) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, *8*, 1185. (c) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 2(11), 975. (d) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Transition Metals as Assembling and Templating Species*. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair E., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Executive Eds.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 2, p 43. (e) Baxter, P. N. W. *Metal Ion Directed Assembly of Complex Molecular Architectures and Nanostructures*. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair E., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Executive Eds.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 5, p 165. (f) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417. (g) Uller, E.; Demleitner, I.; Bernert, I.; Saalfrank, R. W. *Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry*. In *Structure and Bonding*; Fujita, M., Ed.; Springer: Berlin, 2000; Vol. 96, p 149. (h) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 102.

(2) For recent reviews see: (a) Conn, M. M.; Rebek, J. *Chem. Rev.* **1997**, *97*, 1647. (b) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393. (c) Chapman, R. G.; Sherman, J. C. *Tetrahedron* **1997**, *53*, 15911. (d) Rebek, J. *Chem. Soc. Rev.* **1996**, *25*, 255. (e) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (f) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (g) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229.

(3) (a) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.; Schroder, M. *Inorg. Chem.* **1999**, *38*, 2259. (b) Robson, R. *Compr. Supramol. Chem.* **1997**, *6*, 733. (c) Chen, C.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

(4) (a) Fan, E.; Yang, J.; Geib, S. J.; Stoner, T. C.; Hopkins, M. D.; Hamilton, A. D. *Chem. Commun.* **1995**, 1251. (b) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119. (c) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341. (d) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941. (e) Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2382. (f) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696. (g) Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119. (h) Perisco, F.; Wuest, J. D. *J. Org. Chem.* **1993**, *58*, 95. (i) Ermer, O.; Lindenbergh, L. *Chem. Ber.* **1990**, *123*, 1111. (j) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747. (k) Ermer, O.; Lindenbergh, L. *Helv. Chem. Acta* **1991**, *74*, 825.

(5) For recent reviews see: (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601. (b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (c) Burrows, A. D.; Chan, C.-W.; Chowdry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, *24*, 329.

(6) (a) James, S. L.; Mingos, D. M. P.; Xu, X.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1335. (b) Ulvenland, S.; Georgopoulou, A. S.; Mingos, D. M. P.; Baxter, I.; Lawrence, S. E.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1869. (c) Burrows, A. D.; Mahon, M. F.; Palmer, M. T. *J. Chem. Soc., Dalton Trans.* **1998**, 1941. (d) Burrows, A. D.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 97. (e) Chowdry, M. M.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 899. (f) Chan, C.-W.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 81. (g) Navarro, J. A. R.; Freisinger, E.; Lippert, B. *Inorg. Chem.* **2000**, *39*, 1059. (h) Schröder, G.; Lippert, B.; Sabat, M.; Lock, C. J. L.; Faggiani, R.; Song, B.; Sigel, H. *J. Chem. Soc., Dalton Trans.* **1995**, 3767. (i) Chen, Z.-N.; Zhang, H.-X.; Yu, K. B.; Zheng, K. C.; Cai, H.; Kang, B.-S. *J. Chem. Soc., Dalton Trans.* **1998**, 1133. (j) Carlucci, L.; Ciani, G.; Prosperio, D. M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1801. (k) Cameron, B. R.; Corrent, S. S.; Loeb, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2689. (l) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Chem. Commun.* **1998**, 1435. (m) Schauer, C. L.; Matwey, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10245. (n) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *Chem. Commun.* **1993**, 1078. (o) Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117. (p) MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundburg, J. L.; Henning, R. W.; Schultz, A. J.; Mason, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 11692. (q) Qin, Z.; Jenkins, H. A.; Coles, S. J.; Muir, K. W.; Puddephatt, R. J. *Can. J. Chem.* **1999**, *77*, 155.

(7) Burrows, A. D.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1996**, 3805.

(8) (a) Sigel, R. K. O.; Freisinger, E.; Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1998**, *120*, 12000. (b) Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 12467.

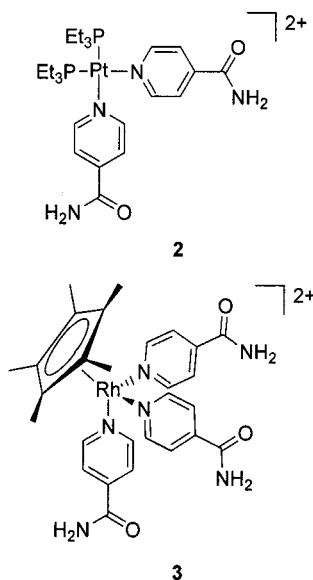
(9) Gianneschi, N. C.; Tiekink, E. R. T.; Rendina, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 8474.

(10) Rivas, J. C. M.; Brammer, L. *New J. Chem.* **1998**, *22*, 1315.

rangement of metal–ligand interactions while offering the versatility of organic functionality as a means to drive and preserve the assembly.

A long-term goal of much of this research is directed toward the development of enclathrating materials that will ultimately be able to function as “tunable” zeolite analogues.^{11a} The promise of metal-containing hydrogen-bonded networks possessing anion channels or layers has been reinforced by the intrinsic flexibility of hydrogen bonds and the surprisingly robust nature of the resultant assemblies. It is envisioned that the flexibility of the hydrogen-bonded moieties will be able to accommodate entering and departing guest molecules, while the recurring metal units provide the necessary geometry and spacing.^{10,11}

The successful and systematic method of using metal ions bearing pyridine derivatives has been reasonably extensively employed, primarily by Aakerøy, in the construction of multidimensional arrays of this type.¹¹ This approach has exclusively made use of naked metal ions coordinated by two, three, or four pyridine ligands, which in turn possess an organic functional group (e.g., amide, oxime, carboxylic acid, etc.) in order to propagate an infinite structure. In all cases, however, the ligands have been situated in a coplanar and highly divergent relationship to one another. This prompted our interest in the type of structures that could be generated by using metal ions bearing ancillary groups which impose a mutually *cis* configuration on the ligand domain. More specifically, our aim was to investigate how a systematic increase in the number of functionalized ligands (dimensionality) in such a stereochemical arrangement would influence network topology. We now report on the homoleptic complexes *cis*-(Et₃P)₂Pt(NC₅H₄CONH₂)₂-(NO₃)₂ (**2**) and (C₅Me₅)Rh(NC₅H₄CONH₂)₃(OTf)₂ (**3**), which have novel two- and three-dimensional solid state architectures, respectively.



(11) (a) Aakerøy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 1815. (b) Aakerøy, C. B.; Beatty, A. M.; Leinen, D. S.; Lorimer, K. R. *Chem. Commun.* **2000**, 935. (c) Aakerøy, C. B.; Beatty, A. M. *Chem. Commun.* **1998**, 1067. (d) Aakerøy, C. B.; Beatty, A. M.; Leinen, D. S. *J. Am. Chem. Soc.* **1998**, *120*, 7383. (e) Aakerøy, C. B.; Beatty, A. M.; Helfrich, B. A. *J. Chem. Soc., Dalton Trans.* **1998**, 1943.

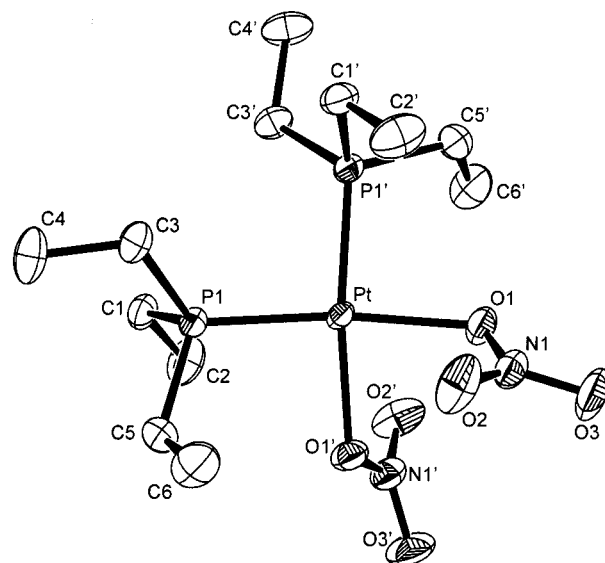


Figure 1. ORTEP diagram of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystallographic Data for **1**

empirical formula	C ₁₂ H ₃₀ N ₂ O ₆ P ₂ Pt
fw	555.41
temperature	200(0.1) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	C2/c
unit cell dimens	$a = 14.2095(4)$ Å $\alpha = 90^\circ$ $b = 8.8381(3)$ Å $\beta = 90.587(2)^\circ$ $c = 15.7748(3)$ Å $\gamma = 90^\circ$
volume	1980.97(10) Å ³
Z	4
density (calcd)	1.862 Mg/m ³
abs coeff	7.271 mm ⁻¹
θ range for data collection	4.61–32.60°
final <i>R</i> indices [$I > 2\sigma(I)$] ^a	R1 = 0.0230, wR2 = 0.0559
<i>R</i> indices (all data)	R1 = 0.0248, wR2 = 0.0569

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

Results and Discussion

Although reaction of isonicotinamide with the previously reported¹² *cis*-(Et₃P)₂Pt(OTf)₂ conveniently afforded the triflate analogue of **2** as assessed by NMR, all attempts at growing single crystals for X-ray analysis gave only fibrous needles. In the course of our search for an alternative crystallization system (i.e., different counteranions), we prepared the hitherto uncharacterized nitrate salt, **1**. The X-ray structure of **1** (Figure 1) shows the platinum complex of distorted square planar geometry in the *cis* configuration as expected. In contrast to several previously reported¹³ triflate salts which revealed one or both triflate counterions displaced by water molecules, in **1** the nitrate anions were found to be directly coordinated to the metal center. Bond lengths and angles are given in Table 2.

Reaction of **1** with 2 equiv of isonicotinamide affords the cationic complex **2** (mp 194–195 °C) in quantitative

(12) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

(13) (a) Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics* **1996**, *15*, 904. (b) Stang, P. J.; Olenyuk, B.; Arif, A. M. *Organometallics* **1995**, *14*, 5281. (c) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Pt–O(1)	2.127(2)
Pt–P(1)	2.2248(7)
O(1)–Pt–O(1')	82.36(13)
P(1)–Pt–P(1')	96.00(4)

Table 3. Crystallographic Data for 2

empirical formula	C ₂₄ H ₄₄ N ₆ O ₉ P ₂ Pt	
fw	817.68	
temperature	200(0.1) K	
wavelength	0.71073 Å	
cryst syst	orthorhombic	
space group	<i>Pbca</i>	
unit cell dimens	<i>a</i> = 16.3582(2) Å	$\alpha = 90^\circ$
	<i>b</i> = 18.4433(3) Å	$\beta = 90^\circ$
	<i>c</i> = 21.7862(4) Å	$\gamma = 90^\circ$
volume	6572.88(18) Å ³	
<i>Z</i>	8	
density (calcd)	1.653 Mg/m ³	
abs coeff	4.422 mm ⁻¹	
θ range for data collection	19.1–32.57°	
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	R1 = 0.0349, wR2 = 0.0800	
<i>R</i> indices (all data)	R1 = 0.0561, wR2 = 0.0921	

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

Table 4. Crystallographic Data for 3

empirical formula	C _{31.50} H ₃₆ F ₆ N ₆	
	O ₁₀ Rh S ₂	
fw	939.69	
temperature	200(0.1) K	
wavelength	0.71073 Å	
cryst syst	monoclinic	
space group	<i>P2₁/c</i>	
unit cell dimens	<i>a</i> = 11.0678(4) Å	$\alpha = 90^\circ$
	<i>b</i> = 19.7310(7) Å	$\beta = 91.8954(18)^\circ$
	<i>c</i> = 18.1870(6) Å	$\gamma = 90^\circ$
volume	39.69.5(2) Å ³	
<i>Z</i>	4	
density (calcd)	1.572 Mg/m ³	
abs coeff	0.624 mm ⁻¹	
θ range for data collection	2.77–30.48°	
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	R1 = 0.0822, wR2 = 0.2057	
<i>R</i> indices (all data)	R1 = 0.1336, wR2 = 0.2365	

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

yield. Single crystals of the complex were obtained as colorless prisms by slow evaporation of a wet nitromethane solution of **2**. As revealed by the crystal structure (space group *Pbca*), the *cis* arrangement of the metal complex was preserved with the isonicotinamide ligands coordinated through the pyridine nitrogen atoms. An angle of approximately 83° separates the two nitrogen-containing ligands, most likely a result of the steric demands of the triethylphosphines (P–Pt–P, 96°). The coordinated arene rings lie approximately perpendicular to the square plane of the metal ligand system. The geometry of **2** is propagated via the amide functionality (Figure 2) through self-complimentary (though not symmetry-related) “head-to-head” [N–H⋯O (1.89 and 2.25 Å)] hydrogen-bonding interactions, resulting in infinite zigzag chains. Hydrogen bonds between the remaining N–H group, nitrate anion, and a water molecule serve to bridge adjacent chains in a parallel fashion. Hence the overall crystal structure has a two-

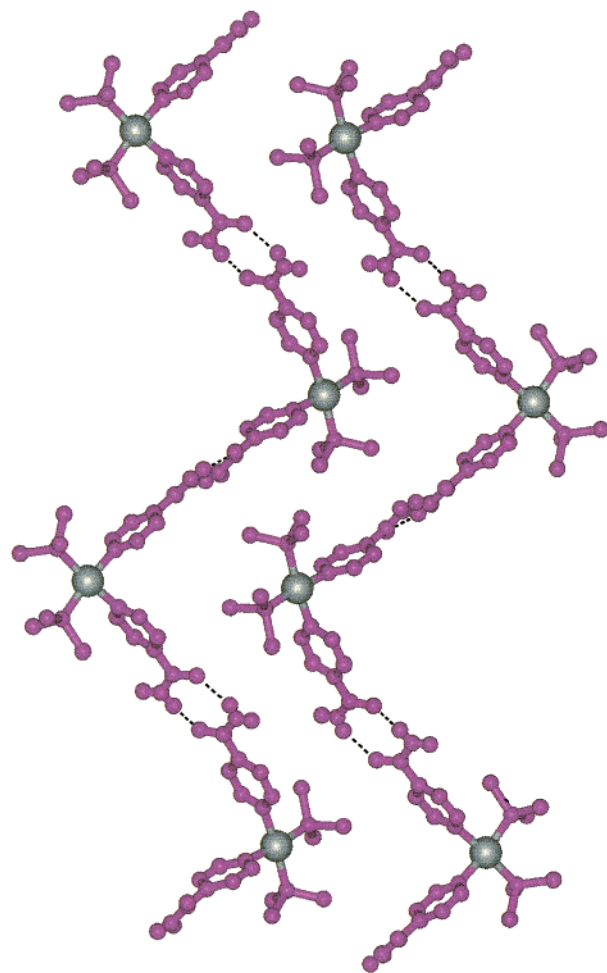


Figure 2. Infinite zigzag chains in **2** formed by head-to-head amide–amide interactions between isonicotinamide ligands. Non-amide hydrogen atoms, counterions, water molecules, and the methyl groups from the triethylphosphines are omitted for clarity.

dimensional architecture, propagated by the water necessary for crystallization.

The reaction of 4 equiv of silver(I) triflate with [(C₅Me₅)RhCl₂]₂¹⁴ in dichloromethane, followed by filtration and the addition of isonicotinamide, affords complex **3** (mp 219–222 °C) as a yellow precipitate. Crystals suitable for X-ray analysis were obtained as yellow prisms after 2 days by allowing an acetone solution of the complex to slowly evaporate.

Like **2**, the crystal structure of **3** (space group *P2₁/c*) showed all isonicotinamide groups bonded to the rhodium metal center through the ring nitrogen atoms with an average Rh–N distance of 2.15 Å. The piano stool-type complex adopts a distorted geometry in the solid state having mutual N–Rh–N bond angles of 85°, 86°, and 98°. Along with two triflate counterions, each asymmetric unit also contains one molecule of acetone.

Analysis of the extended structure of **3** (Figure 3) reveals that the complex ion forms infinite dimeric strands in which all three isonicotinamide groups emanating from each rhodium metal center are set

(14) (a) Cusanelli, A.; Nicula-Dadci, L.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 2211. (b) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (c) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

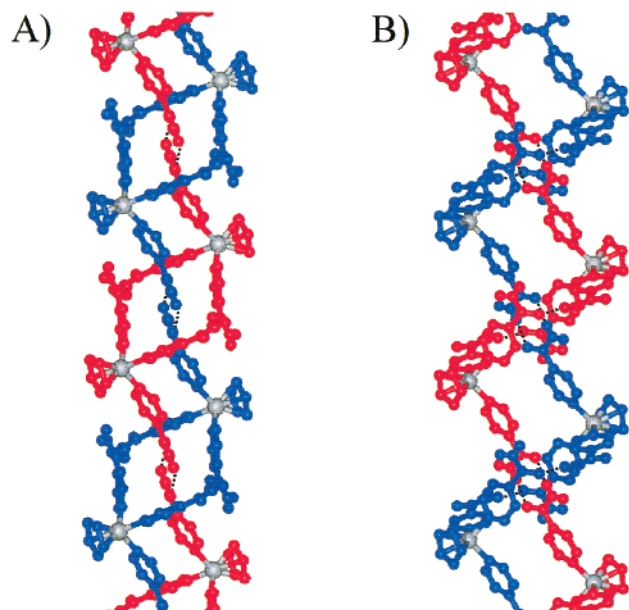


Figure 3. Two different perspectives (A and B) illustrating the inter-woven strands in **3**. Non-amide hydrogen atoms, solvent molecules, counterions, and the methyl groups from the Cp rings have been omitted for clarity.

facing one another along a two-fold screw axis. The rhodium subunits of the dimeric strands have two ligands oriented toward the edges of the strand, while the remaining ligand is directed inward. The ligands oriented toward the edges are linked to the other half through amide–amide hydrogen-bonding interactions [*trans*-N–H \cdots O (2.05 Å)], while the remaining ligand is linked by symmetry-related “head-to-head” [*cis*-(N–H \cdots O) $_2$ (2.19 Å)] hydrogen bonds through the openings created by the former. This self-complimentary arrangement leads to a rather unusual “polycatenane” or “braided” motif. Each strand is offset from the other by approximately 11 Å. Furthermore, individual strands are linked to all four neighboring strands through amide–amide hydrogen bonds [*cis*-N–H \cdots O (1.95 Å)], which propagate the dimeric chains into a three-dimensional structure. The remaining amide N–H groups are hydrogen bonded to oxygen from either a triflate counterion or an acetone molecule.

Conclusion

Metal-containing hydrogen bond donors and acceptors have only recently begun to be explored as a means of assembling multidimensional arrays. The study presented here contributes to ongoing work in the field of crystal synthesis by systematically varying the ligand substitution pattern and number within a class of organic-functionalized coordination compounds. In contrast to purely organic hydrogen-bonded networks based on neutral building blocks, these materials owe their stability to the convolution of hydrogen-bonding interactions in the presence of ionic forces. Incorporation of metal atoms may allow us not only to exploit new topologies but also to endow the target structures with distinctly inorganic properties. Although a high degree of predictability as of yet remains unrealized, these observations confirm that the ligand domain may be manipulated so as to influence the microstructure of

inorganic/organic hybrid materials. Current efforts are directed toward establishing methodologies of controlling ligand interpenetration in the solid state and the characterization of the solution structures of these and related metal complexes.

Experimental Section

NMR spectra were recorded on a Varian XL-300 or a Unity 300 spectrometer. Proton chemical shifts are reported relative to residual protons in the respective deuterated solvent. ^{31}P and ^{19}F chemical shifts are reported relative to an unlocked, external sample of H_3PO_4 (0.0 ppm) and CFCl_3 (0.0 ppm), respectively. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Melting points are uncorrected.

All solvents were reagent grade and were used as received, except for CH_2Cl_2 , which was distilled under a dry nitrogen atmosphere over CaH prior to use.

All reagents were purchased from Aldrich.

Preparation of *cis*-(Et_3P) $_2\text{Pt}(\text{NO}_3)_2$ (1**).** To a stirred solution of $(\text{Et}_3\text{P})_2\text{PtCl}_2$ (61 mg, 0.121 mmol) in 25 mL of acetone was added a suspension of AgNO_3 (45 mg, 0.267 mmol) in 25 mL of acetone. After stirring for 12 h the solvent was removed in vacuo, and the resulting white residue was suspended in 50 mL of CH_2Cl_2 . Filtration and subsequent evaporation of the solvent gives 60 mg of **1** as a white powder (90% yield). ^1H NMR (300 MHz, nitromethane- d_3): δ 1.97 (m, 12H), 1.24 (m, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, nitromethane- d_3): δ 7.14 (s, $^1J_{\text{P-Pt}} = 3761$ Hz). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2\text{-Pt}$: C, 25.95; H, 5.44; N, 5.04. Found: C, 26.30; H, 5.44; N, 5.07.

Preparation of *cis*-(Et_3P) $_2\text{Pt}(\text{NC}_5\text{H}_4\text{CONH}_2)_2(\text{NO}_3)_2$ (2**).** To **1** (30.40 mg, 0.055 mmol) dissolved in 5 mL of H_2O was added a solution of isonicotinamide (13.36 mg, 0.109 mmol) in 5 mL of H_2O , and the reaction mixture was stirred for 12 h. The solvent was removed in vacuo, affording 43.7 mg of **2** as a white powder (99% yield). ^1H NMR (300 MHz, D_2O): δ 9.0 (d, $^3J_{\text{HH}} = 5.1$ Hz, 4H) 7.92 (d, $^3J_{\text{HH}} = 5.9$ Hz, 4H), 1.85 (m, 12H), 1.22 (m, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, D_2O): δ 2.00 (s, $^1J_{\text{P-Pt}} = 3072$ Hz). Anal. Calcd for $\text{C}_{24}\text{H}_{42}\text{N}_6\text{O}_8\text{P}_2\text{Pt}\cdot\text{H}_2\text{O}$: C, 35.25; H, 5.42; N, 10.28. Found: C, 35.29; H, 5.33; N, 10.12.

Preparation of (C_5Me_5) $\text{Rh}(\text{NC}_5\text{H}_4\text{CONH}_2)_3(\text{OTf})_2$ (3**).** To a stirred solution of $[(\text{C}_5\text{Me}_5)\text{RhCl}_2]_2$ (100 mg, 0.162 mmol) in 20 mL of dry CH_2Cl_2 under an argon atmosphere was added, all at once, AgOTf (167 mg, 0.648 mmol). The reaction was allowed to stir at room temperature in the dark for 4 h. During this time a white precipitate formed, which was then cannula filtered off under argon into a Schlenk flask equipped with a magnetic stir bar. To the orange solution was then added solid isonicotinamide (119 mg, 0.971 mmol) in portions with stirring, and the reaction was allowed to stir at ambient temperature for 1 h. Next, the bright yellow product, which had precipitated, was collected on a frit in the open atmosphere and the product dried in vacuo, yielding 244 mg (87% yield) of **3**. ^1H NMR (300 MHz, D_2O): δ 8.79 (d, $^3J_{\text{HH}} = 6.3$ Hz, 6H) 7.98 (d, $^3J_{\text{HH}} = 6.3$ Hz, 6H), 1.55 (s, 15H). ^{19}F NMR (282 MHz, acetone- d_6): δ -78.72 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{F}_6\text{N}_6\text{O}_9\text{S}_2\text{Rh}\cdot\text{H}_2\text{O}$: C, 39.14; H, 3.83; N, 9.13; S, 6.96. Found: C, 39.13; H, 3.54; N, 9.32; S, 6.90.

Acknowledgment. Financial support by the National Science Foundation (CHE-9818472) and the Alexander von Humboldt Foundation via a Feodor Lynen Fellowship for F.M.T. is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, structure refinement details, and SHELXL file for compounds **1**, **2**, and **3** are available free of charge via the Internet at <http://pubs.acs.org>.