# Self-Assembly of Supramolecular Structures from Palladium Chloride and Guanidinium Salts of Pyridinecarboxylic Acids − A Dramatic Change on Passing from the *para*- to the *meta*-Substituted Acid

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*Dedicated to the late Prof. Salvatore Castellano*

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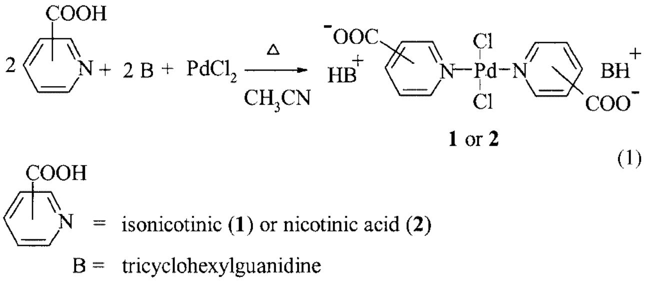
Supramolecular structures **1** and **2** were obtained in the solid state from the reaction between palladium chloride and guanidinium salts of *p*- and *m*-pyridinecarboxylic acid, respectively. The pyridinecarboxylate anions were *trans*-coordinated to palladium dichloride through nitrogen, and the carboxylate groups formed hydrogen bonds with guanidinium cations. The present paper describes a remarkable change in the stoichiometry and structural organization of the solid **3** derived from the *meta*-substituted acid **2**, triggered by the elimination of one guanidine molecule as hydrochloride per molecule of palladium chloride, during crystallization from methanol. The corresponding isonicotinate **1** structure appears to be stable under the same conditions. As shown by the analysis of the crystal structures, the guanidinium nicotinate organic salt **4** turns out to be preorganized to host palladium chloride both in **2** and **3**.

Interest in the solid-state structures of hybrid materials organised by cooperative interactions of different strength, directionality and range of action (coordinative, electrostatic, lipophilic, hydrogen bonds) is rapidly increasing in the field of crystal engineering.[1] In the framework of a programme aimed at the incorporation of metal salts into supramolecular organic structures, we studied the reaction of palladium chloride with tricyclohexylguanidinium ($BH^+$) salts of *p*-pyridinecarboxylic acid (isonicotinic acid) or *m*-pyridinecarboxylic acid (nicotinic acid). The formation of supramolecular assemblies self-organized in the solid state according to different stoichiometries showed a hydrogen bond distribution involving both the carboxylic group and the nitrogen base.

Equation (1) indicates the stoichiometry of the reaction of $PdCl_2$ with isonicotinic or nicotinic acids and tricyclohexylguanidine in refluxing acetonitrile, which resulted in the precipitation of yellow solids in both cases. Recrystallisation from a methanol/acetonitrile mixture (1:1) at room temperature led to crystals of the respective palladium complexes (**1** and **2**) of analogous stoichiometry.



(1)

Surprisingly, recrystallisation of **2** from pure methanol gave a crystalline compound (**3**) with one less guanidine molecule per molecule of $PdCl_2$. This behaviour was not observed with complex **1**, which was recovered unchanged from methanol after crystallisation. The proposed course of the reaction leading from **2** to **3** (Scheme 1) is based on the products isolated (see Exp. Sect.). A reasonable interpretation is that during crystallisation one molecule of the $Pd^{II}$ complex is reduced to $Pd^0$ by methanol (which is oxidized to formaldehyde dimethyl acetal, as confirmed experimentally) with concomitant expulsion of guanidine hydrochloride and nicotinic acid. A second molecule of complex **2** then loses one molecule of guanidine as its nicotinic acid salt, forming complex **3**. It is worth noting that mixing one

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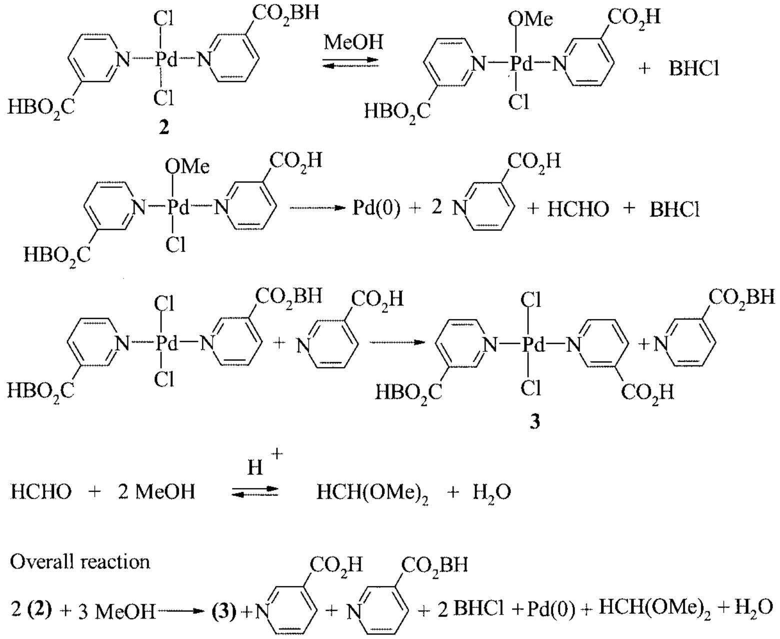


Scheme 1. Proposed course of formation of **3** from **2**

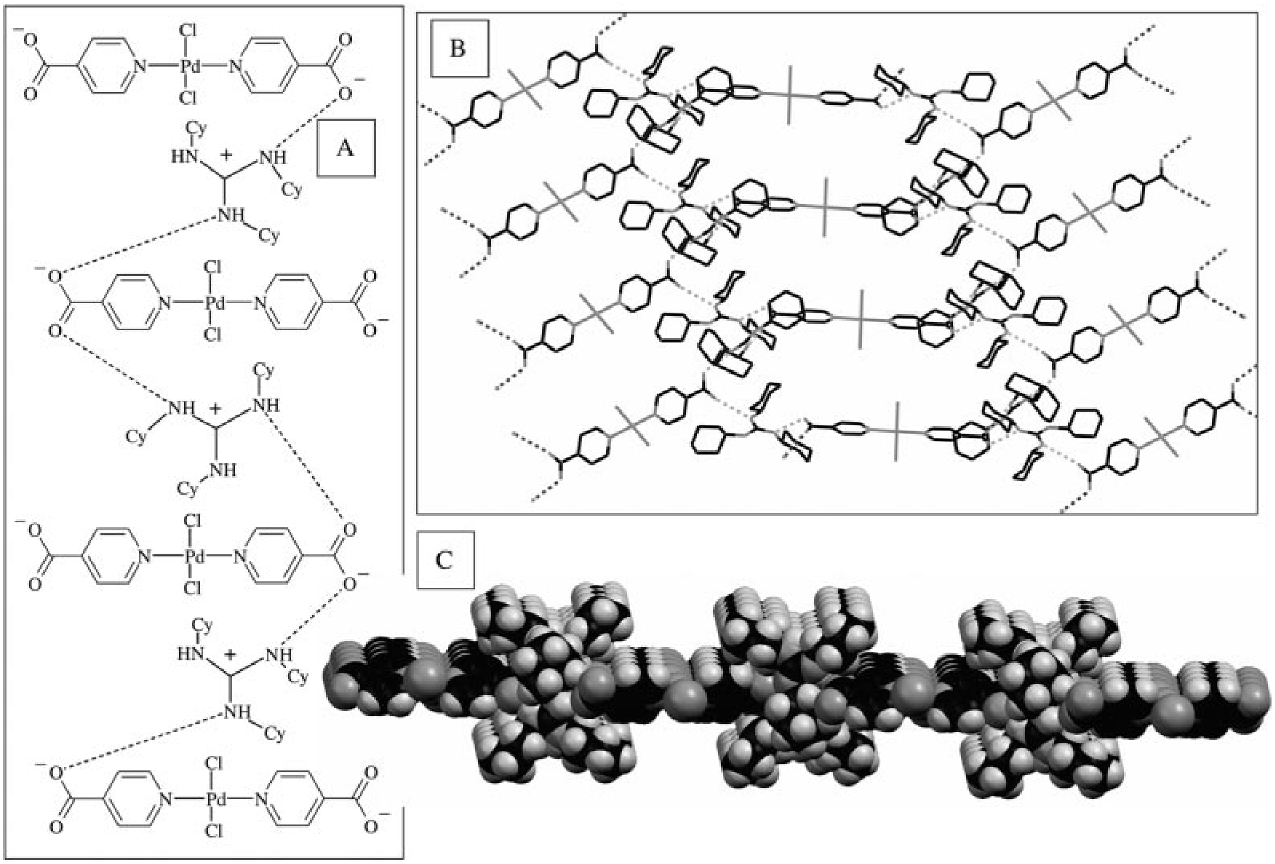


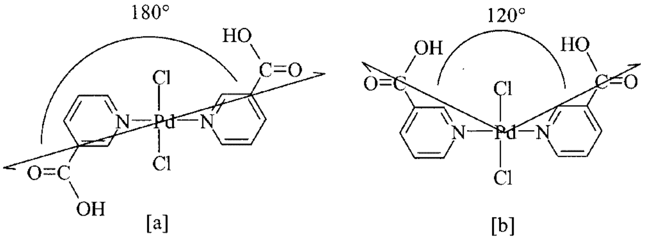
Figure 1. Solid-state arrangement of compound **1**: (A) chains built by NH···O hydrogen bonds between cations and anions, one NH is not involved in the chain formation, Cy = cyclohexyl; (B) the chains are assembled in sheets by coordination of $PdCl_2$ to the dangling pyridinic nitrogen atoms; (C) space-filling view of the section of the sheets; the ridges are formed by the protruding cations; the free NH groups point out of the ridges, to fit in the chlorine array of the adjacent sheets, with consequent staggering of the layers

molecule of guanidine with two molecules of nicotinic acid and one of $PdCl_2$ led to a solid precipitate with stoichiometry corresponding to compound **3**, which was not analysed by X-ray diffraction since its crystallinity was not satisfactory. The direct addition of dry $CF_3COOH$ to **2** also failed to afford suitable crystals, although the stoichiometry of the solid obtained was in agreement with that of complex **3**.

In order to elucidate the structural reasons for the diverse behaviour of the two chemically similar systems **1** and **2**, the crystal structures of **1**, **2** and **3** were determined. In **1** cations and anions are assembled in chains built by $-NH^{+}\cdots{}^{-}O_2C-$ hydrogen bonds involving two guanidinic NH donors and both the carboxylate oxygen acceptors [$N\cdots O = 2.791(7), 2.935(9)$ Å] (Figure 1a). The chains are covalently linked in sheets by the inorganic $PdCl_2$ spacers through the pyridinic nitrogens, thus defining a ladder motif in which the rung width, 14 Å, depends on the length of the [*trans*-$PdCl_2$(*i*nic-COO)$_2$]$^{2-}$ spacer. The resulting bidimensional network is formed by meshes with a section of $9 \times 20$ Å$^2$ (dimensions are expressed as atom-atom distances) rimmed by four anions and four cations (Figure 1b). The sheets are assembled so that the -NH ridges of one sheet match the hollows of the adjacent sheets, corresponding to the $PdCl_2$ sites, thus blocking the development of channels or three-dimensional pores perpendicular to the sheets (Figure 1c).

The local structural perturbation introduced by changing the position of the N donor on the pyridinecarboxylate ring greatly affects the self-assembly of the multicomponent system, showing how the crystal organization depends critically on the shape of the *trans*-$PdCl_2L_2$ unit. With L = nicotinic acid this unit could give rise to a *syn* and an *anti* arrangement (Scheme 2).

Only the latter, however, is present in **2**, where the structural organization of **1** is retained, the only difference being that all the NH groups are involved in intra-chain hydrogen bonds [$NH^{+}\cdots O^{-} = 2.764(6), 2.901(6), 2.990(6)$ Å] (Figure 2a). The skew $PdCl_2L_2$ units (length = 13 Å) link paral-



Scheme 2. Geometry and shape of the $PdCl_2L_2$ spacers in: (a) compound **2**, *anti* isomer, linear; and (b) compound **3**, *syn* isomer, bent

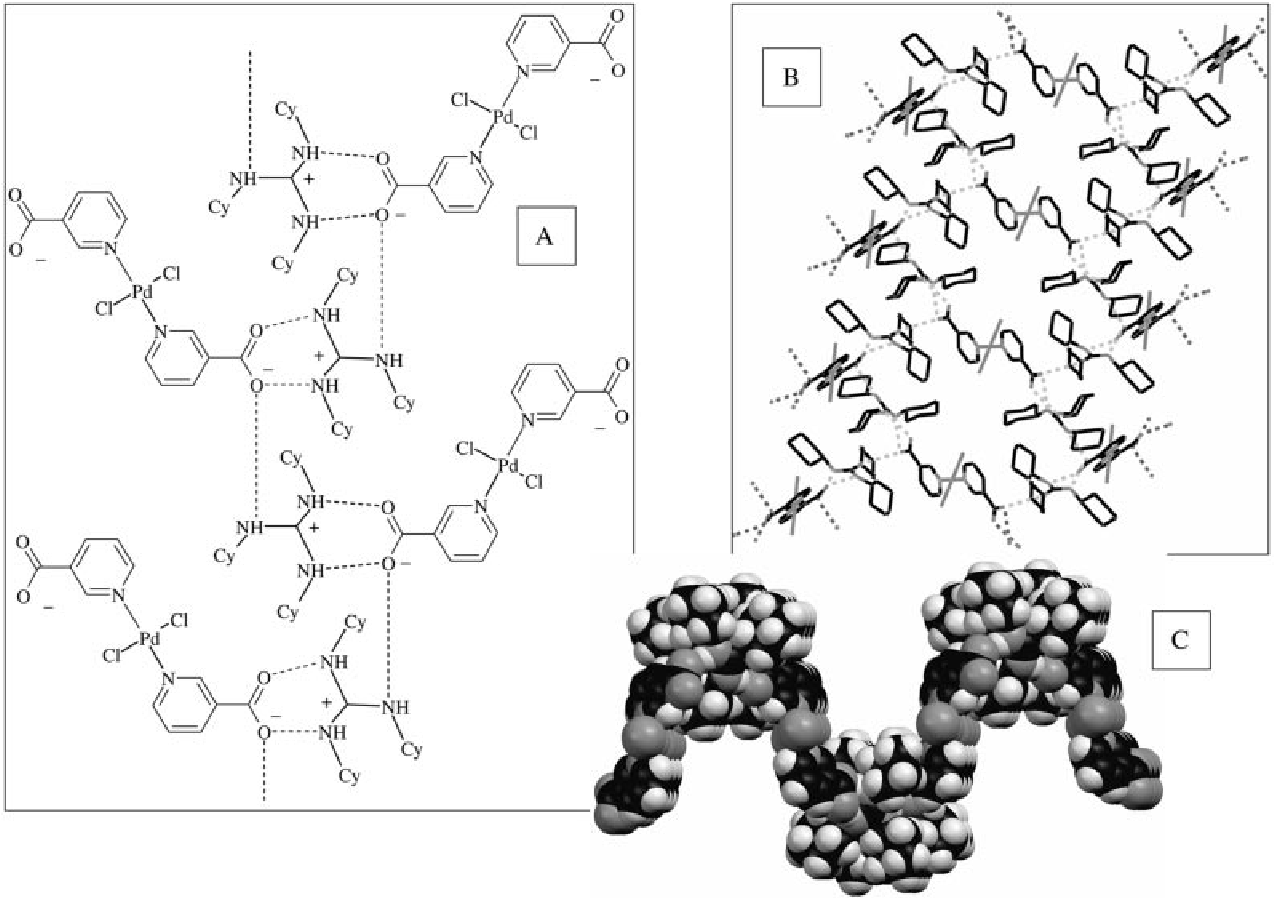


Figure 2. Solid-state arrangement of compound **2**: (A) chains built by NH···O hydrogen bonds as in **1**, all NH groups are involved in the chain formation, Cy = cyclohexyl; (B) sheets organization as in **1**; (C) space-filling view of the section of the sheets; the sheets are corrugated due to the shape of the inorganic spacer

lel chains, forming 10 × 17 $Å^2$ meshes defined by four anions and four cations (Figure 2b). Due to the shape of the *anti* complex, the sheets are corrugated and assemble in three dimensions in a bump-hollow arrangement (Figure 2c). In both **1** and **2** the bidimensional structural assembly is controlled by coordination bonds and hydrogen bonds resulting in a robust network with wide meshes, promising for the building up of nanometre-sized pores in the third dimension. However, the stacking of the porous sheets is controlled by the close packing principle, and the voids are filled by means of multiple weak dispersive interactions. The largest cavities in structures **1** and **2** are 10 and 33 $Å^3$, respectively.

A bent *syn*-$PdCl_2L_2$ unit is present in **3**, and this is accompanied by a dramatic change in the stoichiometry and structure of the supramolecular complex, as shown by the X-ray crystal structure. The cations and anions are arranged in hydrogen-bonded chains [N···O = 2.97(1), 2.82(2) Å] generated by translation and the complex is aligned with the direction of the chain (Figure 3a). Only one oxygen on each carboxylate interacts with a nitrogen of the cation, while the other is employed in $O-H\cdots O^-$ strong interactions [O···O = 2.43(2) Å] between chains related by a $2_1$ operation (Figure 3b), generating a double-strand motif (Figure 3c). This requires that each complex is monodeprotonated, and causes the observed change in the stoichiometry. The polymeric motif consisting of -$CO_2H\cdots{}^-OOC$-hydrogen-bonded chains is quite common in the structure of monodeprotonated dicarboxylic acids, and has a stabilising nature.[2] Examples of crystalline salts of monodeprotonated dicarboxylic acids with protonated nitrogen bases where the structure is built through a network of $O-H\cdots O^-$ and $N^+-H\cdots O^-$ interactions have recently been reported.[3] In our case the special arrangement of complex **3** is reached through an unusual series of events: protonation of one carboxylate group of **2** (Scheme 1) triggers the supramolecular polymerisation of $[PdCl_2(nic\text{-}COO)(nic\text{-}COOH)]^-$, and induces the precipitation of the *syn*-isomer of the monoanionic complex, which can form chains appropriately arranged in double strands.

The fact that guanidine expulsion occurs with the nicotinic rather than isonicotinic complex points to a favourable arrangement of the former. As a matter of fact the comparison with the structure of guanidinium nicotinate **4** shows that the latter is pre-organised for hosting palladium chloride. The crystal packing of **4** is based on catemers of hydrogen bonds linking cations and anions with the same topology as in **1** and **2** (Figure 4a). The pyridinic N is used to connect adjacent chains through NH···N interactions with the third guanidinium NH. In the crystal, the hydro-

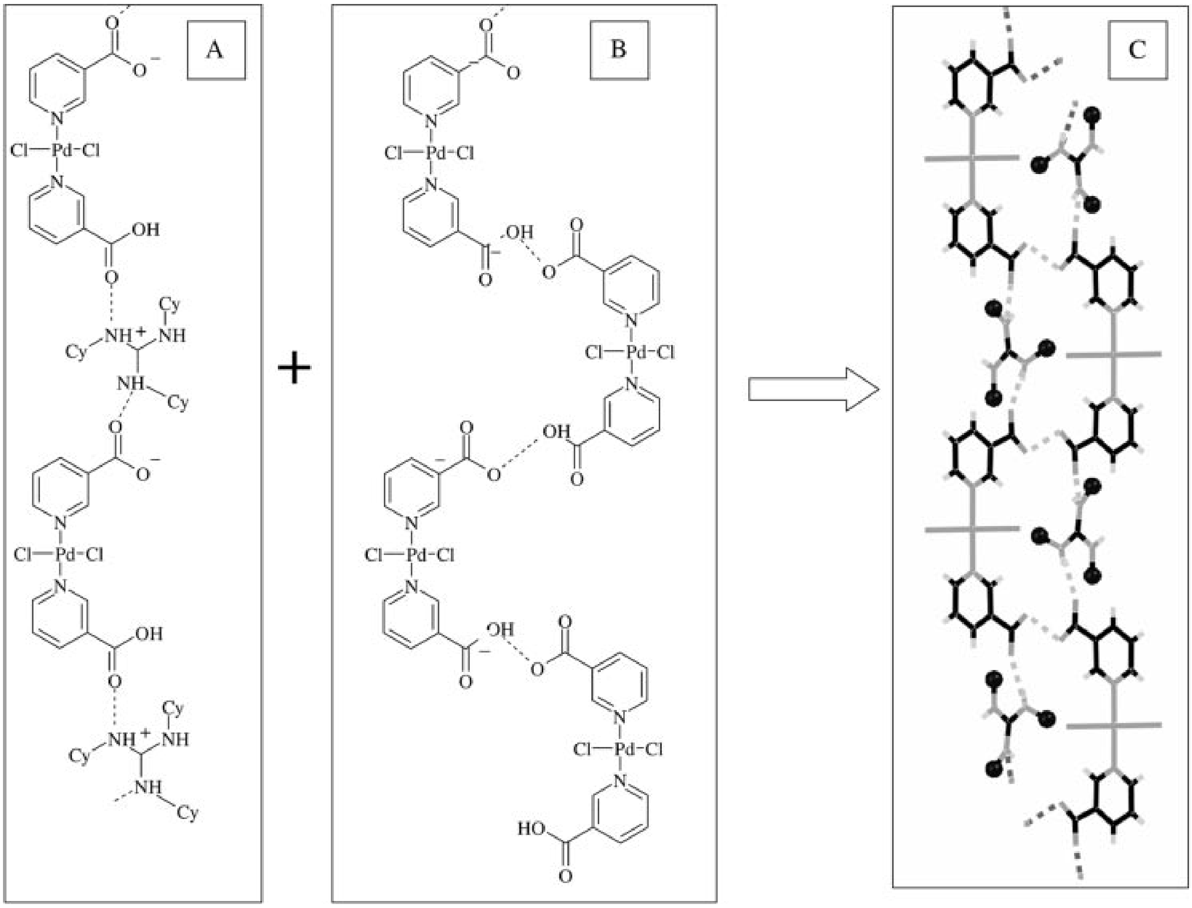


Figure 3. Crystal organization of **3**: (A) chain motif generated by hydrogen bonding between cations and monoanionic complexes, Cy = cyclohexyl; (B) association between pairs of chains via OH···O hydrogen bonds; (C) double strand obtained by assembling a pair of catemers by O−H···O hydrogen bonds; cyclohexyls are represented as solid balls

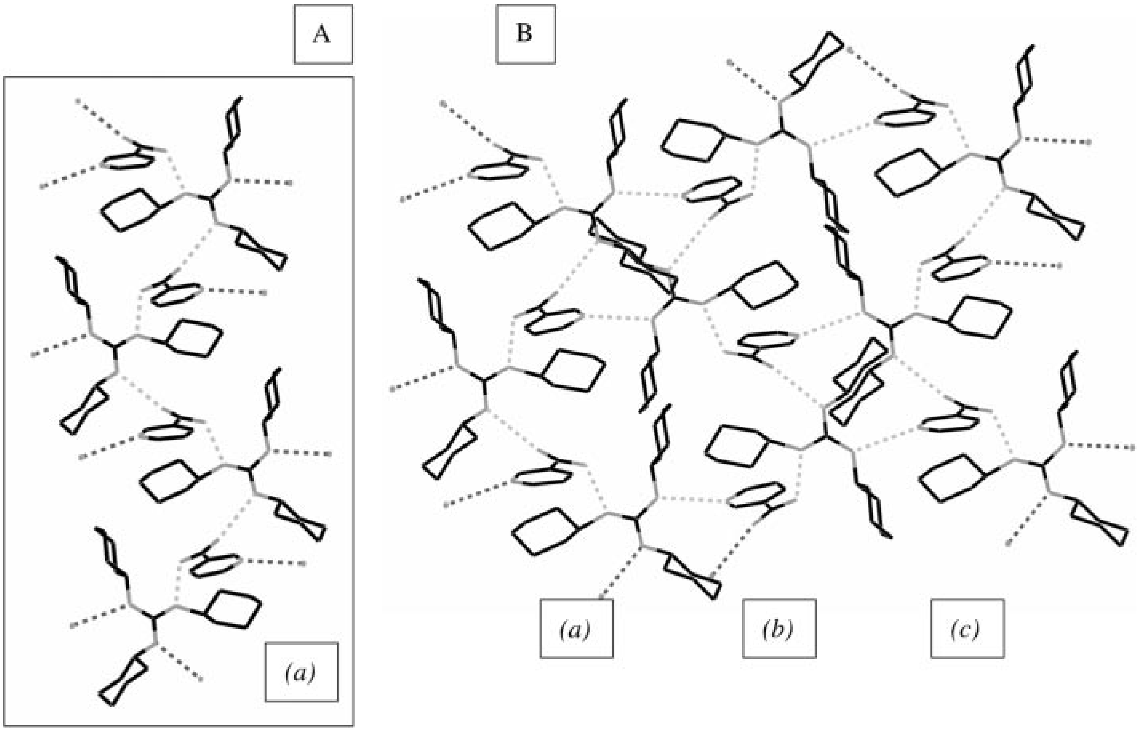


Figure 4. (A) Chain motif in **4**, generated by hydrogen bonds between alternating cations and anions as in **1** and **2**; (B) the chains (*a, b, c*) are arranged in sheets by hydrogen bonding between pyridinic nitrogens and one NH group of the cations

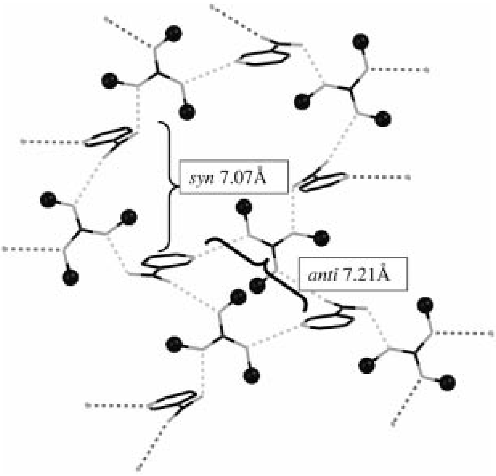


Figure 5. Spatial preorganization of **4** showing how a slight rotation of pyridinic rings can accommodate the $PdCl_2$ unit, giving the structural motif observed either in **2** (*anti* isomer), by sliding of the chains, or in **3** (*syn* isomer) by release of a neutral guanidine; cyclohexyls are represented as solid balls

gen bond of **4** plays the same function as the N−Pd−N covalent link in **1** and **2** in forming bidimensional sheets (Figure 4b). In **2** and **3** the coordination of the incoming Pd requires a concerted rotation of the aromatic rings, to bring the pyridine N atoms into a favourable arrangement. Depending on the mutual position of the pair of pyridinic N atoms, the inorganic spacer orients itself either perpendicular to the organic chains (**2**, *anti* spacer) or parallel to them (**3**, *syn* spacer; Figure 5), in this case causing the release of the guanidine bridging the pair of anions involved in complexation. Guanidine expulsion leaves free -$O^-$ acceptors and -OH donors regularly spaced on the newly formed metal-containing chain, favouring the association of two chains in the observed double strands. The versatile preorganization of the organic salt **4** justifies the remarkable differences in the solid-state organization of the *anti*- and *syn*-spacers and explains how the release of guanidine can occur with a modest expense in terms of structural rearrangement to **3**. Nevertheless guanidine is not expelled spontaneously and liberation of HCl as shown in Scheme 1, is needed.

In conclusion we have reported novel supramolecular arrays held together both by nitrogen coordination to palladium and hydrogen bonds. The structure derived from a guanidine salt of nicotinic acid readily responds to dissolution in methanol by guanidine expulsion and formation of a new structure where the original $NH^+\cdots OOC^-$ bonds are replaced by $NH^+\cdots$OOC-COOH bonds. This type of response can be expected to offer a new tool for working out supramolecular architectures sensitive to chemical stimulation. Work in progress has already shown that similar structures can be obtained with other bi- and tetrasubstituted guanidines.

## Experimental Section

Tricyclohexylguanidinium isonicotinate and nicotinate were both prepared in almost quantitative yield by dissolving the pyridinecarboxylic acid (0.73 g, 6 mmol) and tricyclohexylguanidine (1.83 g, 6 mmol) in 20 mL of acetonitrile and refluxing the solution for 6 hours under argon. The corresponding $PdCl_2$ complexes **1** and **2** were prepared in 88% and 86% yield, respectively, by dissolving the guanidinium salt (0.43 g, 1 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 11 mL of acetonitrile. The solutions were refluxed at 70 °C for 6 hours. After cooling and filtering, the precipitates were recrystallised from a 1:1 mixture of methanol and acetonitrile at room temperature to obtain crystals suitable for X-ray analysis. Analogous results were obtained by allowing $PdCl_2$, nicotinic or isonicotinic acid and tricyclohexylguanidine (1:2:2 molar ratio) to react in refluxing $CH_3CN$ for 6 hours. Satisfactory elemental analysis were obtained (available as supporting information).

In order to investigate the process leading from **2** to **3**, complex **2** (0.103 mg 0.1 mmol) dissolved in the smallest quantity of MeOH was left to crystallise. Yellow crystals of complex **3** (24 mg 0.035 mmol) were selected for X-ray analysis. The residue, consisting of crystals of guanidine hydrochloride, nicotinic acid, guanidine nicotinate and palladium(0), was treated with $Et_2O$ to remove formaldehyde dimethylacetal.

The above-described procedure was used for the direct synthesis of complex **3**. Thus $PdCl_2$ (0.044 g, 0.25 mmol), nicotinic acid (0.062 g, 0.50 mmol) and tricyclohexylguanidine (0.076 g 0.25 mmol) were refluxed under argon in dry $CH_3CN$ (4.0 mL) for 6 hours. The mixture was filtered and the yellow precipitate was recrystallised from $CH_3OH/CH_3CN$ (1:1). The solid precipitate gave a satisfactory elemental analysis but was not suitable for single crystal X-ray diffraction.

**Treatment of Complex 2 with $CF_3COOH$:** $CF_3COOH$ (0.023 mL, 0.3 mmol) was added to crystals of complex **2** (0.31 g, 0.3 mmol) suspended in dry $CH_3CN$ (6 mL) at 0 °C. After stirring for 2 hours the mixture was filtered and a yellow solid was dried and recrystallised from $CH_3CN/CH_3OH$ (1:1). The solid precipitate gave a satisfactory elemental analysis in agreement with the composition of complex **3**, but was not suitable for single crystal X-ray analysis.

**Crystallographic Analysis:** Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 293$ K for **1**, **3** (Siemens AED diffractometer) and **2** (SMART AXS 1000 CCD diffractometer), and Cu-$K_\alpha$ ($\lambda = 1.54178$ Å), $T = 173$ K for **4** (Enraf−Nonius CAD4 diffractometer). Lorentz and polarisation corrections were applied. The structures were solved by direct methods using SIR97[4] and refined by full-matrix least-squares on all $F^2$ using SHELXL-97.[5] Hydrogen atoms were introduced in calculated positions, and refined riding on their carrier atoms. Anisotropic displacement parameters refined for all non-hydrogen atoms.

**1:** 0.4 × 0.2 × 0.1 mm, monoclinic, space group $P2_1/c$, $a = 12.743(5)$, $b = 9.725(5)$, $c = 22.345(7)$ Å, $\beta = 105.76(5)°$, $V = 2665(2)$ Å$^3$, $\rho = 1.289$ Mg·m$^{-3}$, 5232 unique reflections, 1459 observed [$I > 2\sigma(I)$], 307 parameters, $R = 0.0592$, $R_w = 0.1401$. The palladium is on a crystallographic inversion centre.

**2:** 0.3 × 0.2 × 0.1 mm, monoclinic, space group $P2_1/a$, $a = 10.565(2)$, $b = 22.739(3)$, $c = 11.509(2)$ Å, $\beta = 94.785(2)°$, $V = 2755.3(1)$ Å$^3$, $\rho = 1.247$ Mg·m$^{-3}$, 2288 unique reflections, 1636 observed [$I > 2\sigma(I)$], 307 parameters, $R = 0.0332$, $R_w = 0.0823$. The palladium is on a crystallographic inversion centre.

**3:** 0.1 × 0.2 × 0.2 mm, monoclinic, space group $C2/m$, $a = 22.786(5)$, $b = 17.730(5)$, $c = 10.405(5)$ Å, $\beta = 108.31(5)°$, $V = 3991(2)$ Å$^3$, $\rho = 1.213$ Mg·m$^{-3}$, 4093 unique reflections, 1077 observed [$I > 2\sigma(I)$], 274 parameters, $R = 0.0698$, $R_w = 0.1825$. The metal and the chlorine atoms are on a crystallographic symmetry plane, as well as the carbocationic C atom of guanidinium. The cation is disordered over two equivalent orientations, which do not alter the hydrogen bonding scheme.

**4:** 0.2 × 0.2 × 0.4 mm, triclinic, space group $P\bar{1}$, $a = 16.843(5)$, $b = 14.612(5)$, $c = 11.156(5)$ Å, $\alpha = 66.54(5)$, $\beta = 103.29(5)$, $\gamma = 104.70(5)°$, $V = 2410(1)$ Å$^3$, $\rho = 1.181$ Mg·m$^{-3}$, 9138 unique reflections, 4436 observed [$I > 2\sigma(I)$], 583 parameters, $R = 0.1108$, $R_w = 0.2668$. Two independent molecules are present in the asymmetric unit.

CCDC-189488−189491 (**1−4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting information available (see footnote on the first page of this article): elemental analysis, ORTEP drawings, crystal data and structure refinement tables for **1−4**.

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