

## Crosslinking a palladium(II) polymer gives a laminated sheet structure

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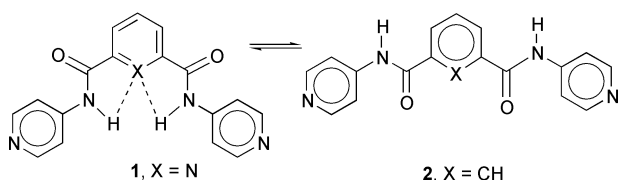
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Chains of a zigzag coordination polymer containing bis(pyridyl) bridging groups between palladium(II) centres can be arranged to give a laminated sheet structure by a biomimetic approach in which hydrogen bonding involving amide groups is the key feature.

There is great interest in supramolecular transition metal chemistry since self-assembly through coordinate bond formation is a powerful tool for constructing rings, polymers and networks of interest as molecular materials.<sup>1–3</sup> The combination of bis(pyridine) ligands with square planar palladium(II) and platinum(II) centers has yielded an impressive range of polygons, cages and catenanes.<sup>2</sup> For example, if the metal is constrained to have *cis* stereochemistry, molecular dimers, triangles, squares or polymers may be formed.<sup>2</sup> In nature, secondary and tertiary structure is often determined through hydrogen bonding effects between amide groups, and this article shows how the biomimetic approach can enhance self-assembly using coordination chemistry by controlling tertiary structure.<sup>4</sup> The effect is achieved in this case by modifying bridging bis(pyridyl) ligands with amide substituents that can provide structural control through hydrogen bonding.

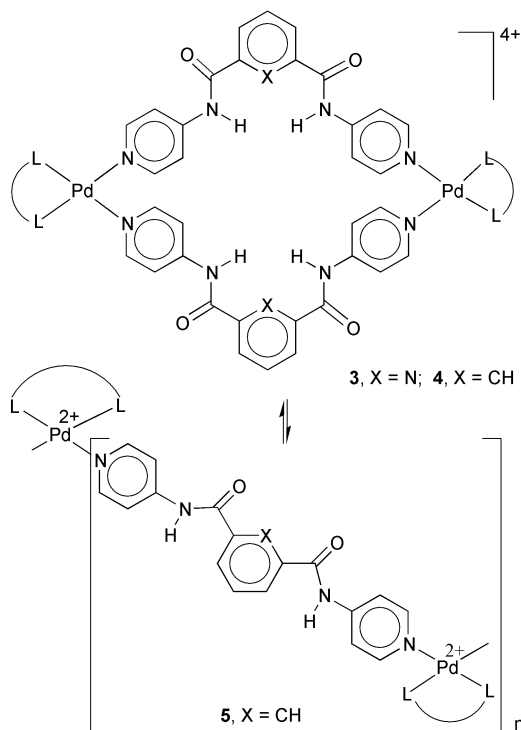
The bis(pyridyl) ligand **1** is expected to adopt the conformation shown, as a consequence of intramolecular hydrogen bonding, whereas the similar ligand **2** is less constrained.<sup>5</sup>



Ligand **1** reacted with the complexes  $[\text{Pd}(\text{LL})(\text{O}_3\text{SCF}_3)_2]$  to give the corresponding, easily soluble, macrocyclic complexes  $[\{\text{Pd}(\text{LL})(\mu\text{-1})\}_2](\text{CF}_3\text{SO}_3)_4$ , **3a**, LL =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ , dppm; **3b**, LL =  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ , dppp; **3c**, L =  $\text{PPh}_3$ ; **3d**, LL = 4,4'-di-*tert*-butyl-2,2'-bipyridine,  $\text{bu}_2\text{bipy}$ . Based on their NMR spectra, the complexes **3** have effectively planar structures.<sup>†</sup> Thus the  $^{31}\text{P}$  NMR spectrum of **3b** contained a single resonance and there was only a single resonance in the  $^1\text{H}$  NMR spectrum for each of the  $\alpha$ - and  $\beta$ - $\text{CH}_2$  groups.

The structure of complex **3a** is shown in Fig. 1 and features a roughly square 32-membered ring,  $\text{Pd}_2(\mu\text{-1})_2^{4+}$ , containing two palladium atoms, each of which carries a chelating dppm ligand. The ligands **1** are significantly bowed so that a single oxygen atom of a triflate anion hydrogen bonds weakly to both NH groups. Fluxionality is needed to give the effectively flat structures indicated by the NMR data.<sup>†</sup>

The ligand **2** reacted with  $[\text{Pd}(\text{LL})(\text{O}_3\text{SCF}_3)_2]$  to give the corresponding complexes, whose NMR spectra were fully consistent with the expected macrocyclic structures  $[\{\text{Pd}(\text{LL})(\mu\text{-2})\}_2](\text{CF}_3\text{SO}_3)_4$ , **4a**, LL = dppm; **4b**, LL = dppp; **4c**, L =  $\text{PPh}_3$ ; **4d**, LL =  $\text{bu}_2\text{bipy}$ .<sup>†</sup> However, while **4c** and **4d** were easily soluble in common organic solvents, complexes **4a** and **4b** were very sparingly soluble except in DMF or DMSO, suggesting a polymeric structure  $[\{\text{Pd}(\text{LL})(\mu\text{-2})\}_x](\text{CF}_3\text{SO}_3)_{2x}$ .



**5a**, LL = dppm; **5b**, LL = dppp, in the solid state; this was confirmed for **5b** by an X-ray structure determination.

The structure of **5b** is shown in Fig. 2. The cation exists in the form of a one-dimensional zigzag coordination polymer in which all carbonyl groups are oriented on one side and all NH groups on the other. The bridging ligand **2** adopts an unusual conformation in which the amide groups are displaced to opposite sides of the central  $\text{C}_6\text{H}_4$  group to give a stretched

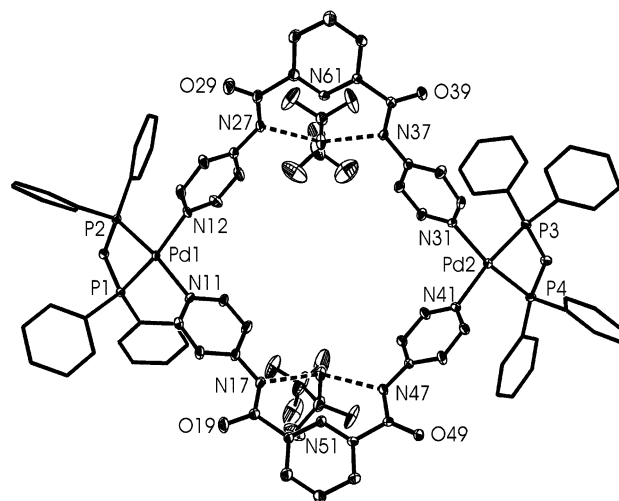


Fig. 1 A view of the structure of complex **3a**.

conformation. This can be compared to the more bowed conformation of the similar ligand **1** in complex **3a** (Fig. 1), in which the amide groups are displaced to the same side of the central C<sub>6</sub>H<sub>3</sub>N group. The separation between neighbouring palladium atoms is therefore longer in **5b** at 19.1 Å than in **3a** at 12.6 Å. There is short-range helicity induced by the bridging ligands **2** and, though all palladium atoms are crystallographically equivalent, neighbouring centres have opposite chirality so that the polymer has the unusual syndiotactic structure.<sup>6</sup>

The crystal packing in **5b** is particularly interesting. Adjacent polymer chains are arranged with all NH groups directed inwards and CO groups directed outward, such that direct C=O...HN hydrogen bonding between adjacent chains is not possible. Instead one triflate anion bridges between two NH groups from neighbouring chains with O(57)...N(27) 2.91 and O(56)...N(17A) 2.95 Å. The second triflate anion is not involved in hydrogen bonding. By symmetry, two chains cross each bridging ligand **2**, and the overall result is a laminated sheet structure with the triflate ions sandwiched in the centre. The outside face of the sheet is lined with the carbonyl groups directed outward and an array of phenyl groups. The intersheet interactions appear to be relatively weak, though there is weak C=O...HC hydrogen bonding and  $\pi$ -stacking between phenyl groups, and the solvate acetone and methanol molecules are located in the intersheet region.

The differences in behaviour of the ligands **1** and **2** are remarkable. Ligand **1**, with approximately right-angled coordi-

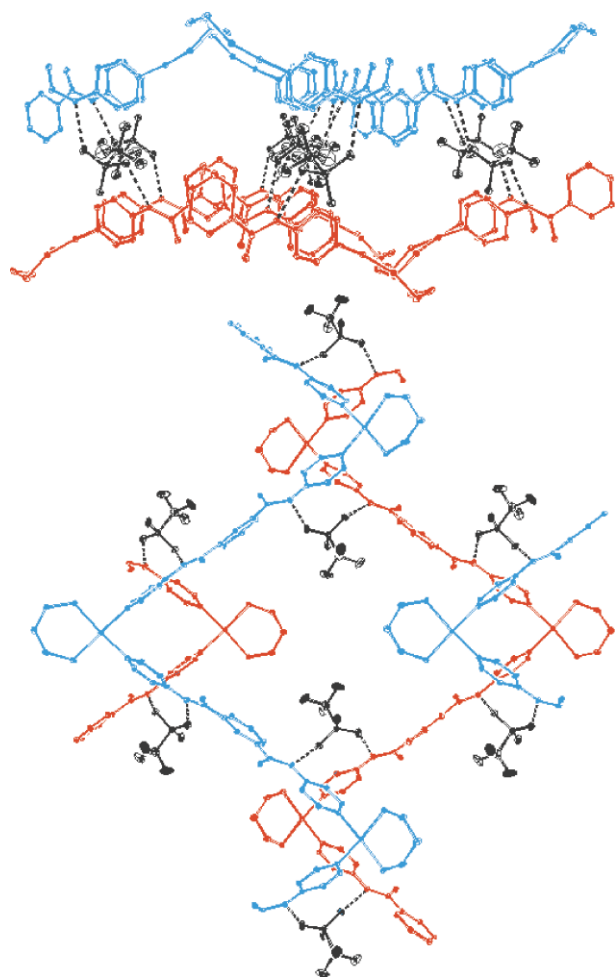
nation geometry determined by intramolecular hydrogen bonding, forms only the cyclic dimers **3** by self-assembly, with additional hydrogen bonding in **3a** occurring between the amide groups and the anions (Fig. 1). The ligand **2** is more flexible and can form similar cyclic dimers **4**, as favoured in all cases studied in the solution phase, or zigzag polymers **5**, as favoured with the diphosphine co-ligands in the solid phase. It is likely that the ring-opening polymerization to give **5** only occurs during the crystallization process. Complex **5b** is remarkable both in forming syndiotactic polymer chains and in the secondary association through hydrogen bonding that leads to the observed laminated sheet structure. The hydrogen bonding is of the type NH...OSO...HN, with a single triflate anion mediating the bridging between NH groups, and is different from the conventional C=O...HN hydrogen bonding that is important in all protein structures.<sup>7</sup> Nevertheless, the potential for orienting and arranging coordination polymers to form sheet structures using the biomimetic approach is clearly demonstrated by this research.

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## Notes and references

† Complex **3a** was prepared from [Pd(dppm)(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] and ligand **1** in CH<sub>2</sub>Cl<sub>2</sub> and isolated in 90% yield. NMR (acetone):  $\delta_{\text{H}}$  11.16 [s, 2H, CONH]; 8.93 [d, <sup>3</sup>J(HH) 4 Hz, 4H, H<sup>2,6</sup> py]; 8.39 [d, <sup>3</sup>J(HH) 8 Hz, 2H, H<sup>3,5</sup> Ar]; 8.33 [t, <sup>3</sup>J(HH) 8 Hz, 1H, H<sup>4</sup> Ar]; 7.61–8.04 [m, 24H]; 5.29 [t, <sup>2</sup>J<sub>PH</sub> 12 Hz, 2H, PCH<sub>2</sub>];  $\delta_{\text{P}}$  -39.92 [s];  $\delta_{\text{F}}$  -79.21 [s]. *Crystal data for 3a*: 4.25Me<sub>2</sub>CO; C<sub>100.75</sub>H<sub>95.50</sub>F<sub>12</sub>N<sub>10</sub>O<sub>20.25</sub>PaPd<sub>2</sub>S<sub>4</sub>; *M* = 2463.29, *T* = 200(2) K,  $\lambda$  = 0.71073 Å, monoclinic, space group *P2<sub>1</sub>/n*, *a* = 20.0823(2), *b* = 18.8209(2), *c* = 29.9815(5) Å,  $\beta$  = 91.181(1)°, *V* = 11329.6(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.444 g cm<sup>-3</sup>, *R*<sub>1</sub> = 0.1382; *wR*<sub>2</sub> = 0.3370. Complex **5b** was prepared from [Pd(dppp)(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] and ligand **2** in CH<sub>2</sub>Cl<sub>2</sub> and isolated in 99% yield. NMR (acetone):  $\delta_{\text{H}}$  10.05 [s, 2H, CONH]; 8.64 [d, <sup>3</sup>J(HH) 5 Hz, 4H, H<sup>2,6</sup> py]; 7.52 [d, <sup>3</sup>J(HH) 7 Hz, 4H, H<sup>3,5</sup> py]; 8.17 [s, 1H, H<sup>2</sup> Ar]; 8.01 [d, <sup>3</sup>J(HH) 8 Hz, 2H, H<sup>4,6</sup> Ar]; 7.66 [t, <sup>3</sup>J(HH) 8 Hz, 1H, H<sup>5</sup> Ar]; 7.55–7.87 [m, 20H, Ph]; 3.37 [br, 4H, PCH<sub>2</sub>]; 2.32 [br, 2H, PCH<sub>2</sub>CH<sub>2</sub>];  $\delta_{\text{P}}$  9.38 [s];  $\delta_{\text{F}}$  -79.40 [s]. *Crystal data for 5b*: Me<sub>2</sub>CO·MeOH; C<sub>51</sub>H<sub>50</sub>F<sub>6</sub>N<sub>4</sub>O<sub>10</sub>P<sub>2</sub>PdS<sub>2</sub>; *M* = 882.75, *T* = 200(2) K,  $\lambda$  = 0.71073 Å, triclinic, space group *P1*, *a* = 11.6074(7), *b* = 13.9377(8), *c* = 24.696(1) Å,  $\alpha$  = 89.994(3),  $\beta$  = 88.272(3),  $\gamma$  = 90.002(3)°, *V* = 3993.5(4) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.468 g cm<sup>-3</sup>, *R*<sub>1</sub> = 0.0814, *wR*<sub>2</sub> = 0.2071. CCDC reference numbers 174281 and 174282. See <http://www.rsc.org/suppdata/cc/b1/b110307e/> for crystallographic data in CIF or other electronic format.

- (a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, New York, 1995; (b) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, VCH, New York, 2000.
- (a) M. Fujita, K. Umamoto, M. Yoshizawa, N. Fujita, T. Kusukawa and T. Biradha, *Chem. Commun.*, 2001, 509; (b) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (c) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.
- (a) R. D. Archer, *Inorganic and Organometallic Polymers*, VCH, New York, 2001; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (c) C.-T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.
- (a) K.-S. Jeong, Y. L. Choi, S.-U. Chang and H.-Y. Chang, *Angew. Chem., Int. Ed.*, 2000, **39**, 1692; (b) L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671; (c) M. Kondo, T. Okubo, A. Asami, S.-I. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Mazsuzaka and K. Seki, *Angew. Chem., Int. Ed.*, 1999, **38**, 140; (d) C. L. Schauer, E. Matwey, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1997, **119**, 10245; (e) S.-S. Sun and A. J. Lees, *Chem. Commun.*, 2000, 1687; (f) P. D. Beer, F. Szemes, V. Balzani, C. M. Sala, M. G. B. Drew, S. W. Dent and M. Maestri, *J. Am. Chem. Soc.*, 1997, **119**, 11864.
- (a) C. A. Hunter and L. D. Sarson, *Angew. Chem., Int. Ed.*, 1994, **33**, 2313; (b) J. M. Rowland, M. L. Thornton, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 2001, **40**, 1069.
- (a) Y. Shii, Y. Motoda, T. Matsuo, F. Kai, T. Nakashima, J.-P. Tuchagues and N. Matsumoto, *Inorg. Chem.*, 1999, **38**, 3513; (b) W. W. Ellis, M. Schmitz, A. A. Arif and P. J. Stang, *Inorg. Chem.*, 2000, **39**, 2547.
- (a) J. Kyte, *Structure in Protein Chemistry*, Garland Inc, New York, 1995; (b) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Systems*, Springer Verlag, Berlin, 1999.



**Fig. 2** Two views of the laminated sheet structure of **5b**. Above, a side view showing triflate anions sandwiched and bridging between sheets. Below, a top view showing the zigzag polymer chains. Phenyl substituents of the dppp ligands and triflate anions that are not involved in H-bonding are omitted for clarity.