Supramolecular assembly of anion-channel and anion-layer structures of $[PtL_4]X_2$ (L = nicotinamide; X = Cl or PF_6): surprisingly robust arene ring ‘herringbone’ motifs and adaptable amide–amide hydrogen bonding

Letter

Juan C. Mareque Rivas and Lee Brammer*

Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121-4499, USA; E-mail: lee.brammer@umsl.edu

Square-planar platinum cations PtL_4^{2+} (L = nicotinamide) form layer structures dominated by interdigitation of the ligands *via* ‘herringbone’ packing motifs; intercation amide–amide hydrogen bonding adapts to accommodate anion-channel or anion-layer structures.

Specific and directional intermolecular interactions such as hydrogen bonds have been used to assemble organic molecular building blocks into well-defined crystalline networks.[1] Metals of well-defined coordination geometry have been interconnected *via* (typically rigid) “spacer” ligands to yield coordination polymer grids of a variety of topologies.[2] However, these two branches of the field of crystal engineering[1–3] have to a large extent developed separately. In this Letter we combine the major features of these two approaches. Thus, rigid ligands are coordinated to metals in well-defined geometries, as in the strategy for designing inorganic coordination polymers. However, the chosen ligands do not have a second site suitable for coordination to another metal center, but rather carry hydrogen bonding substituents suitable for linking molecules together.

This study also provides an extension of earlier work, which has examined the various roles of metals in hydrogen-bonding interactions[4] taking place in the metal and ligand domains, to adopt the terminology of Dance.[5] Here hydrogen bonding taking place in the periphery domain is considered. The electronic influence of the metal on the peripheral hydrogen bond donor/acceptor groups can be anticipated to be small. However, metals with well-defined coordination geometries might be expected to play a spatial role in directing hydrogen bonding in this domain.

It is important for the advancement of crystal engineering using molecular building blocks to develop an understanding of the relative importance of different possible intermolecular interactions, and of the “robustness” of particular intermolecular arrangements, termed supramolecular synthons.[6] These aspects are explored here by use of a hydrogen-bonding ligand (L) with limited conformational flexibility and by examining the role of changing the anion (X) in the crystal structures presented.

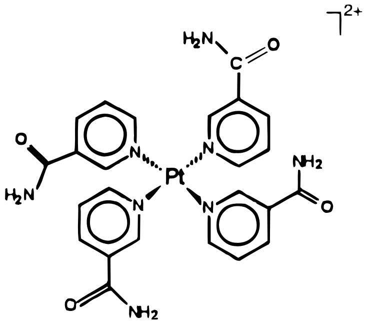
Complexes of the form $[PtL_4]X_2$ were selected as good candidates to meet the previously outlined criteria for this combined coordination compound/hydrogen bonding approach to crystal engineering. Platinum(II) forms four-coordinate complexes of square-planar geometry, with few exceptions. The nicotinamide ligand (L) was used since much is known about amide–amide hydrogen-bonding patterns in supramolecular organic systems.[7] An analogous approach has recently been reported for silver(I) complexes which have the added advantage or disadvantage of a variable coordination number at the metal.[8] The nicotinamide ligand(s) can in principal exhibit two degrees of freedom in positioning the amide functional group, namely (restricted) rotation about the M—N bond and about the amide-ring C—C bond, permitting the possibility of amide–amide hydrogen bonds being perpendicular or even parallel to the PtN_4 plane.

The chloride salt, $[Pt(NC_5H_4CONH_2)_4]Cl_2$ (**1**) was prepared quantitatively by adapting a literature procedure[9] and crystallized from water or water–acetone mixtures. Stoichiometric anion exchange using NH_4PF_6 in aqueous solution then yielded $[Pt(NC_5H_4CONH_2)_4][PF_6]_2$ (**2**), which was crystallized from aqueous solution and isolated as its monohydrate. Single-crystal X-ray structures of **1** and $\mathbf{2}\cdot H_2O$ show¶ that both structures comprise cation sheets with the metal coordination plane inclined approximately parallel (**1**, 9.0, **2**, 13.9°) to the sheet. However, unexpectedly it is arene ring interdigitation (herringbone packing and π–π stacking) within the cation sheets and not the pattern of hydrogen bonding that is the persistent feature of the two structures. This suggests that the amide–amide hydrogen-bonding interactions, which differ in the two structures, then accommodate this preferred arrangement as well as the presence of the anions (and solvent in **2**).

In both **1** and **2** the coordinated arene rings lie approximately perpendicular to the PtN_4 square plane. The metals sit at inversion centers, and this defines the orientation of the amide groups (“two-up, two-down”) relative to the metal coordination plane (Scheme 1). Fig. 1 shows that in the crystal structure of **1** the cations form layers in the *bc* plane (interlayer spacing *ca.* 7.690 Å), with each cation being linked to another in the plane above and below by a pair of the familiar $R_2^2(8)$ hydrogen-bonded ring motifs.[1b] The remaining N—H group forms a short N—H···Cl hydrogen bond to an anion and locks the orientation of the amide groups. Indeed each anion sits in a binding pocket approximately axial to one metal center (Pt···Cl 3.713 Å) surrounded by two N—H and

---

¶ *Crystal data:* **1**, $M = 754.50$, triclinic, $P\bar{1}$, $a = 8.1500(1)$, $b = 8.7935(1)$, $c = 10.0075(1)$ Å, $\alpha = 85.985(1)$, $\beta = 89.699(1)$, $\gamma = 70.680(1)°$, $U = 675.06(1)$ Å^3, $Z = 1$, $D_c = 1.856$ Mg m^{-3}, $\mu = 5.442$ mm^{-1}, $T = 213(5)$ K, $R_1(F) = 0.039$, $wR_2(F^2) = 0.080$, $S(F^2) = 0.97$ for 33 422 $F^2 > 2\sigma(F^2)$. **2**, $M = 1009.57$, triclinic, $P\bar{1}$, $a = 9.678(3)$, $b = 10.099(2)$, $c = 10.321(2)$ Å, $\alpha = 69.03(2)$, $\beta = 65.40(2)$, $\gamma = 70.32(2)°$, $U = 835.3(4)$ Å^3, $Z = 1$, $D_c = 2.007$ Mg m^{-3}, $\mu = 4.416$ mm^{-1}, $T = 213(5)$ K, $R_1(F) = 0.063$, $wR_2(F^2) = 0.104$, $S(F^2) = 0.99$ for 4236 $F^2 > 2\sigma(F^2)$. Distances and angles involving hydrogen atoms are calculated assuming N—H and C—H bond lengths normalized to standard neutron values of 1.01 and 1.08 Å, respectively. CCDC reference number 440/066.



Scheme 1

four C—H hydrogen-bond donor groups and may exert a templating effect upon the cation self-assembly. Furthermore, collectively the chloride ions sit 4.1 Å apart along a channel that runs along the *b* axis. Both anion-templating and ion-channels are topics attracting considerable current interest.[10]

Fig. 2 shows one cation layer of **1** viewed perpendicular to the layer (*i.e.* orthogonal to the view in Fig. 1). The nicotinamide ligands are interdigitated in a closely packed arrangement within the layer. Along the *b* axis propagation occurs *via* a true herringbone arrangement (between cations shown in the same shade of grey in Fig. 2), with a pair of short C—H···π hydrogen bonds [H···π(ring centroid) 2.55 Å; C—H···π 160.3°]. A similar, but slipped, herringbone interaction occurs between cations along the *c* axis except that the *para* C—H of one ring points not at the ring centroid of the other but towards the ring carbon bearing the amide group (H···C 2.80 Å; C—H···C 175.4°). This less compact arrangement is consistent with the *c* axis [10.0075(1) Å] being longer than *b* axis [8.7935(1) Å].

Complex **2** exhibits similar cation layers to those seen in **1**, again in the *bc* plane. However, in this case the anions and water molecules fully occupy the interlayer region leaving no direct links between cation layers. Cations interact through hydrogen bonds with the PF_6^- anions and water, both of which are well-ordered (Fig. 3). Accommodation of the larger anions leads to an increased interlayer spacing (8.582 Å) and the water molecules occupy a similar site to the chloride ions in **1**.

Turning to the intralayer arrangement of cations, it is clear that the persistent feature of the two structures is the interdigitation of nicotinamide ligands along *b* in **2** analogous to the arrangement along *c* in **1** (between molecules of different shade in Figs. 4 and 2, respectively). This is further evidenced by comparison of the corresponding axial lengths: $c = 10.0075(1)$ Å in **1** and $b = 10.099(2)$ Å **2**. The short C—H···π hydrogen bonds found in **1** are absent in **2** due to a slippage of the rows of the cations within the layer. Thus, the cations in **2** are now linked along the *c* axis, by amide–amide N—H···O hydrogen bonds and by C—H···O hydrogen bonds [$R_1^2(7)$ graph set[1b]], in a less compact cation arrangement than along *b* in **1**. This leads to an increased cell dimension [$c = 10.321(2)$ Å in **2** *vs.* $b = 8.7935(1)$ Å in **1**] and, of course a substantial change in cell angle [$\Delta\alpha = 16.95(2)°$].

The present study demonstrates the importance in crystal engineering and its development toward the design of new materials of carefully considering all intermolecular interactions when planning crystal synthesis. While it is important to develop a ranking of the significance of possible interactions it is not always the few strongest (hydrogen bonds) that ultimately dominate the final arrangement of molecules. Attention has been drawn to this point recently by Desiraju and collaborators in rationalizing the structures of the three isomers of aminophenol where the persistent feature of the structures is again herringbone packing of the arene rings, and the pattern of strong hydrogen N—H···O and O—H···N bonds adapts in each case to accommodate this arrangement.[11] Ongoing work seeks to extend the present study by varying the ligand substitution pattern (*e.g.* nicotinamide *vs.*

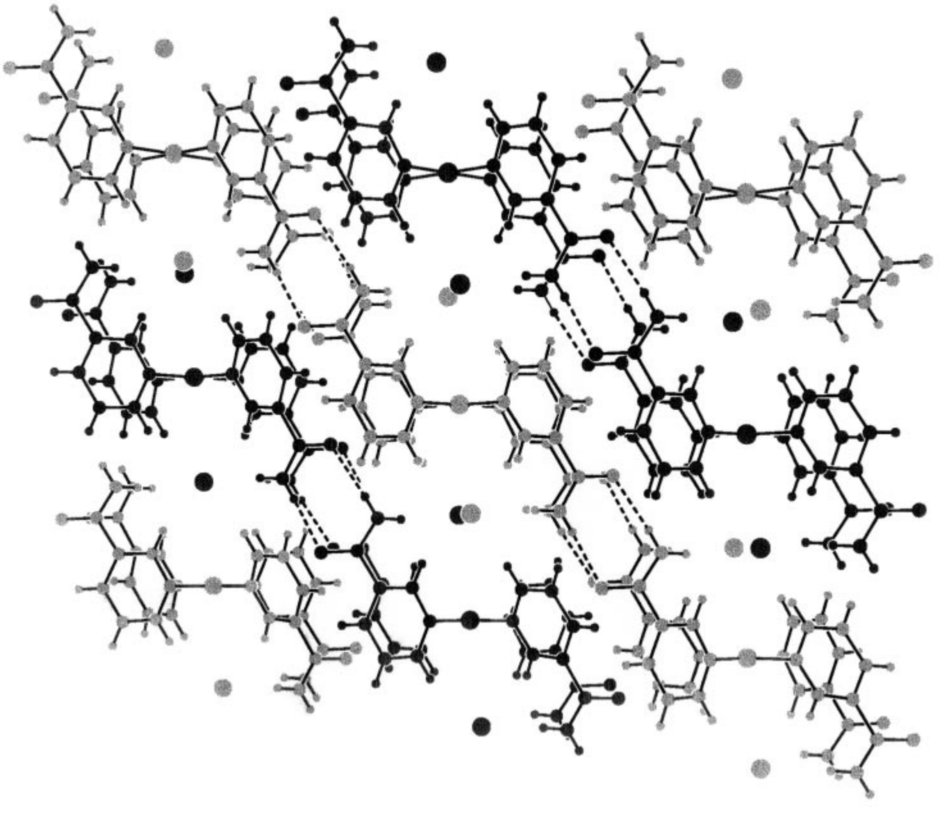


Fig. 1 View of **1** parallel to cation layers shown extending horizontally along the *c* axis (cations shown in alternating shades). $R_2^2(8)$ amide–amide hydrogen bonding occurs between cations shown with the same shade but in different layers and chloride channels run along the *b* axis (perpendicular to page)

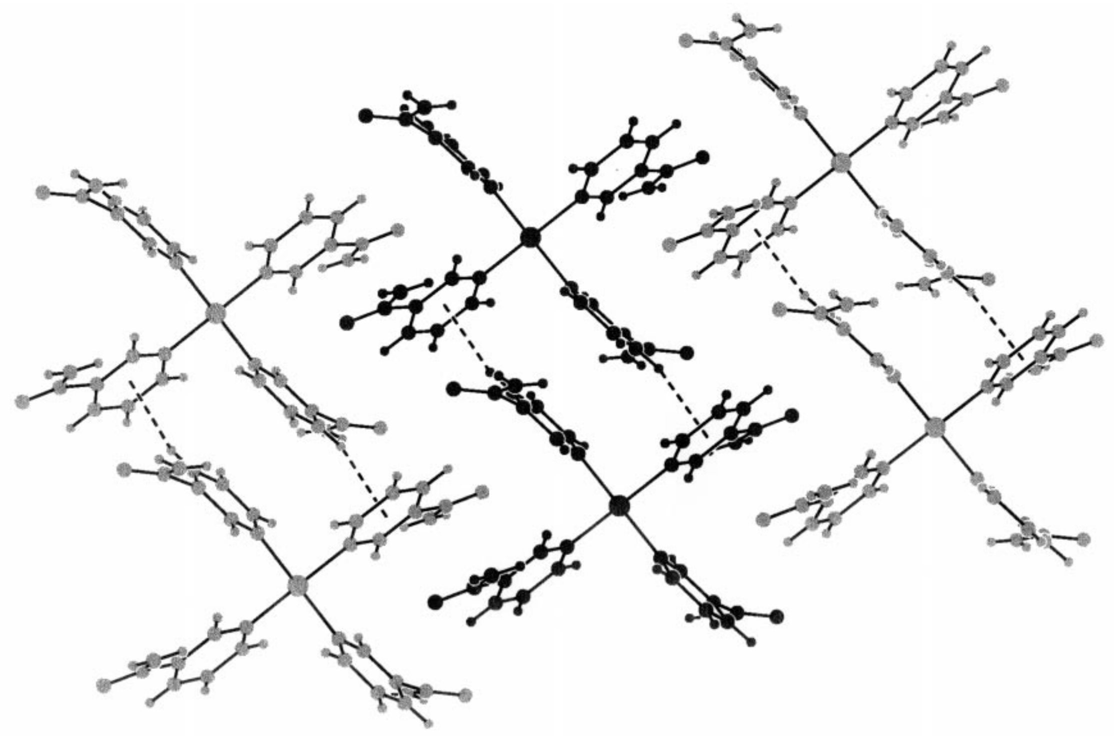


Fig. 2 Single layer of cations of **1** viewed perpendicular to the layer shown in Fig. 1 and illustrating the two types of interdigitation between cations (represented in the same shade of grey) along the *b* axis and between cations (shown in different shades of grey) along the *c* axis

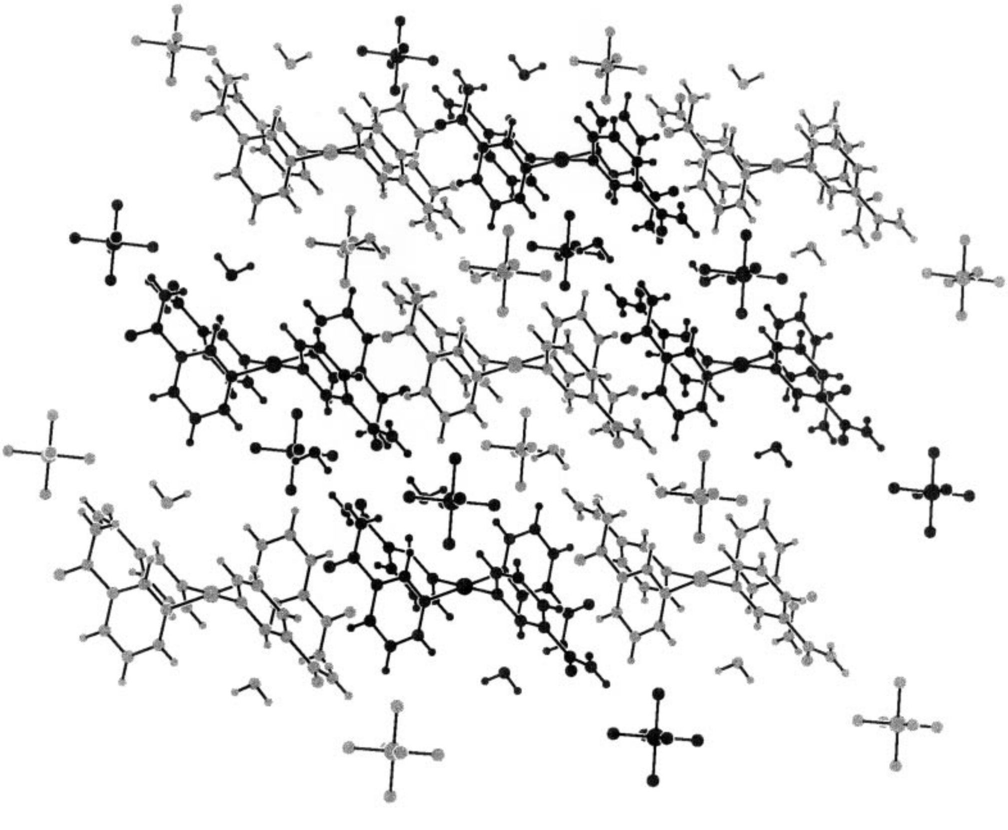


Fig. 3 View of **2** parallel to cation layers extending horizontally along the *b* axis (neighboring cations are shown in different shades). Anion/solvate layers alternate with the cation layers along the *a* axis

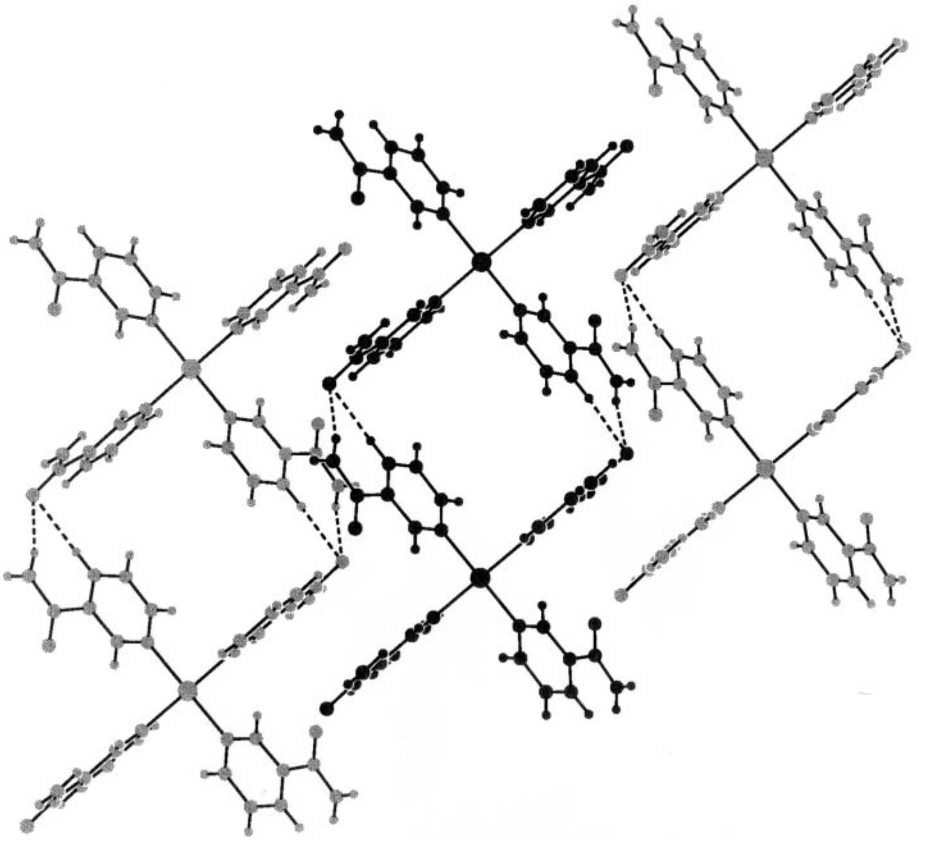


Fig. 4 Single layer of cations of **2** viewed perpendicular to the layer shown in Fig. 3, showing interdigitation between cations (represented in different shades) along the *b* axis and amide–amide hydrogen bonding between cations (represented in the same shade) along the *c* axis

isonicotinamide) and selective variation of the ligand set as well as exploring templating by the anion and by guest molecules.

References

1 (*a*) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989; (*b*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (*c*) S. Subramanian and M. J. Zawarotko, *Coord. Chem. Rev.*, 1994, **137**, 357; (*d*) V. A. Russel, M. C. Etter and M. D. Ward, *J. Am. Chem. Soc.*, 1994, **116**, 1941; C. B. Aakeröy and M. Nieuwenhuyzen, *J. Am. Chem. Soc.*, 1994, **116**, 10983; S. V. Kolotuchin, E. E. Fenlon, S. R. Wilson, C. J. Loweth and S. C. Zimmerman, *Angew Chem., Int. Ed. Engl.*, 1995, **34**, 2654; (*e*) A few studies have also extended this approach to include coordination compounds[1f] or organic–organometallic co-crystals.[1g] (*f*) For example, see A. D. Burrows, C.-W. Chan, M. M. Chowdry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329; (*g*) D. Braga, F. Grepioni, J. J. Byrne and A. Wolf, *J. Chem. Soc., Chem Commun.*, 1995, 1023.

2 (*a*) *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davis, D. D. MacNicol and F. Voegtle, Pergamon, Oxford, 1996, Vol. 11; (*b*) M. J. Zawarotko, *Chem. Soc. Rev.*, 1994, **23**, 283; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562; (*d*) S. W. Keller, *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 247.

3 (*a*) *Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, Wiley, Chichester, 1996; (*b*) C. B. Aakeröy, *Acta Crystallogr., Sect. B.*, 1997, **53**, 569; (*c*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.

4 (*a*) L. Brammer, D. Zhao, F. T. Ladipo and J. Braddock-Wilking, *Acta Crystallogr., Sect. B*, 1995, **51**, 632; (*b*) J. C. Mareque Rivas and L. Brammer, *Coord. Chem. Rev.*, 1998, in press; (*c*) D. Braga, F. Grepioni and G. R. Desiraju, *J. Organomet. Chem.*, 1997, **548**, 33; (*d*) G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653; (*e*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.

5 (*a*) Metal domain = metal atoms; ligand domain = atoms bound directly to the metals and framework that connects them; periphery domain = periphery of the metal complex. (*b*) I. G. Dance, in ref. 3(*a*).

6 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

7 (*a*) L. Leiserowitz and M. Tuval, *Acta Crystallogr., Sect. B*, 1978, **34**, 1230; (*b*) Biradha *et al.* have noted[7c] similar patterns of amide–amide hydrogen bonding in organic and organometallic complexes based upon a search of the Cambridge Structural Database; (*c*) K. Biradha, D. Braga, F. Grepioni and G. R. Desiraju, *Organometallics*, 1996, **15**, 1284.

8 (*a*) C. B. Aakeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067; (*b*) C. B. Aakeröy, A. M. Beatty and B. A. Helfrich, *J. Chem. Soc., Dalton Trans.*, 1998, 1943.

9 (*a*) *Gmelin Handbuch der Anorganische Chemie*, Verlag Chemie, Weinheim, 1957, vol. 68D; (*b*) A full description of the synthesis is provided in the supplementary material (available from the authors upon request) together with ^{1}H, ^{13}C and ^{31}P NMR data.

10 For example see, R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1258; J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffrey, J. A. McCleverty and M. D. Ward, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1279; J. L. Atwood, T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401; M. Mascal; *J. Chem. Soc., Perkin Trans. 2*, 1997, 1999; B. Hille, *Ionic Channels of Excitable Membranes*, Sinawer Associates, Sunderland, MA, 1992.

11 F. H. Allen, V. J. Hoy, J. A. K. Howard, V. R. Thalladi, G. R. Desiraju, C. C. Wilson and G. J. McIntyre, *J. Am. Chem. Soc.*, 1997, **119**, 3477.

Received 29*th June*, 1998; *Letter* 8/07485B