Pyridinium boronic acid salts in crystal synthesis

Hulya Kara,[ab] Christopher J. Adams,[b] A. Guy Orpen*[b] and Thomas J. Podesta[b]

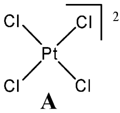
Received (in Durham, UK) 31st March 2006, Accepted 21st June 2006
First published as an Advance Article on the web 26th July 2006
DOI: 10.1039/b604729g

A series of salts of pyridinium boronic acids: $[HNC_5H_4B(OH)_2\text{-}4]_2[M(S_2C_2O_2)_2]\cdot 2H_2O$ (M = Cu **1**, Ni **2**, Pd **3**, Pt **4**), $[HNC_5H_4B(OH)_2\text{-}4]_2[Pt(O_2C_2O_2)_2]$ (**5**); $[HNC_5H_4B(OH)_2\text{-}3]_2\ [M(S_2C_2O_2)_2]$ (M = Cu **6**, Ni **7**, Pd **8**, Pt **9**) and $[HNC_5H_4B(OH)_2\text{-}3]_2[Pt(O_2C_2O_2)_2]$ (**10**) have been prepared and characterized by X-ray diffraction methods. Salts **2**, **3** and **4** are isostructural and isomorphous and contain hydrogen-bonded supermolecules of form $[\text{pyridinium}]_2[M(S_2C_2O_2)_2]$ linked by BOH···OB and B(OH)–water hydrogen bonds into a three-dimensional network. Anhydrous salt **5** has a different structure in which the ions are linked by R(2,2)8 $B(OH)_2\cdots$carboxylate and pyridinium···carboxylate interactions to form a planar hydrogen-bonded ribbon. Salts **6**, **7**, **8** and **10** are all isostructural and isomorphous and contain hydrogen-bonded supermolecules of form $[\text{pyridinium}]_2[M(S_2C_2O_2)_2]$ linked by $B(OH)_2\cdots$carboxylate synthons to form a stepped chain. These chains pack in layers superimposed so as to afford short metal···metal contacts of length 3.6–4 Å between layers. The structure of **5** is isomorphous with that of salts **6–8** and **10** but with a different pattern of NH hydrogen bonding as a result of the different isomer of pyridinium boronic acid present.

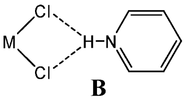
Introduction

Boronic acids have recently become widely used, with applications in the areas of pharmaceuticals, agrochemicals,[1,2] and in medicine as antibiotics,[3] inhibitors of proteases[4] and for the treatment of tumors.[5] Boronic acids also receive a great deal of attention in organic chemistry due to their importance in a wide variety of cross-coupling reactions.[6] Their use in supramolecular chemistry has recently begun to attract attention, largely in respect of hydrogen-bonded derivatives.[7–9] The systematic exploration of a hydrogen-bonding network of boronic acids in the construction of supramolecular assemblies with metal complexes as binary or ternary components is in its infancy.[9e] We were therefore attracted to pyridine boronic acids in order to investigate their utilization for generating different types of supramolecular assemblies, following crystal engineering principles.[10] For this purpose, we have prepared salts of protonated pyridine boronic acids with metal complex anions, where molecular recognition and supramolecular synthesis would take place through hydrogen bonding between the constituent tectons.[11]

We have previously reported a range of charge-assisted hydrogen-bonded salts based on $[PtCl_4]^{2-}$ (**A**) and related anionic tectons (including $[PtCl_6]^{2-}$, $[FeCl_5]^{2-}$ and $[SbCl_5]^{2-}$) as hydrogen-bond acceptors, with a range of organic pyridinium and bipyridinium and related tectons, based on the exploitation of the $MCl_2\cdots HN$ supramolecular synthon (**B**) and related interactions.[12–17] Our studies show that **B** and related synthons allow synthesis of hydrogen-bonded networks with various degrees of complexity based upon the hydrogen-bond donor ability of the cations.

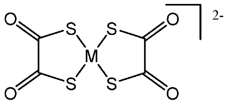


A

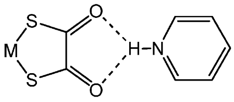


B

Known salts of the anionic tecton $[Ni(\text{dithiooxalate})_2]^{2-}$ (**C**, M = Ni) with pyridinium cations all form an analogous synthon (**D**), and crystals with structures related to those of the $[PtCl_4]^{2-}$ salts may be synthesized.[15,18]



C

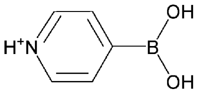


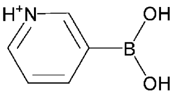
D

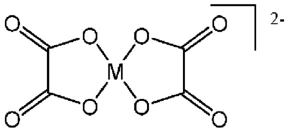
To explore a wider range of organic cations and so generate an enhanced diversity of structure types, here we report the synthesis of structures based on the N-protonated pyridine boronic acid cations **E** and **F** and the square-planar metal bis-dithiooxalate dianions **C** and their oxalate analogues **G**, which might be expected to afford synthon **H**. The use of the isomeric and isosteric, 4- and 3-pyridinium cations **E** and **F** allows us to probe the importance of the geometry of the hydrogen-bond donor groups in the cations—a property that in some circumstances has surprisingly limited effect.[17]

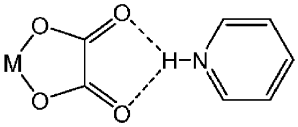
---

[a] *Department of Physics, University of Balikesir, Balikesir, Turkey*
[b] *School of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: Guy.Orpen@bris.ac.uk*


E


F


G


H

In this study we also explore the competition between the various hydrogen-bond acceptor sites available in these salts (the dicarbonyl pocket of synthons **D** and **H** *vs*. the thiocarboxylate or carboxylate functionalities of the anions **C** and **G** *vs*. the boronic acid oxygen atoms) and that between the NH and OH hydrogen-bond donors. The understanding of such competition effects is a necessary requirement for the successful design of supramolecular assemblies such as those reported in this paper.

Results and discussion

The desired salts were prepared by the stoichiometric reaction of the potassium salt of **C** or **G** with the hydrochloride of the relevant pyridine boronic acid (**E** or **F**) in aqueous solution. Compounds $[HNC_5H_4B(OH)_2\text{-}4]_2[M(S_2C_2O_2)_2]\cdot 2H_2O$ (M = Cu **1**, Ni **2**, Pd **3**, Pt **4**), $[HNC_5H_4B(OH)_2\text{-}4]_2[Pt(O_2C_2O_2)_2]$ (**5**), $[HNC_5H_4B(OH)_2\text{-}3]_2[M(S_2C_2O_2)_2]$ (M = Cu **6**, Ni **7**, Pd **8**, Pt **9**) and $[HNC_5H_4B(OH)_2\text{-}3]_2[Pt(O_2C_2O_2)_2]$ (**10**) were isolated. Single-crystal samples of compounds **2–8** and **10** were prepared directly from the reaction mixture using slow diffusion methods. Single-crystal X-ray diffraction analyses of compounds **2–8** and **10** were carried out, but we were not able to obtain suitable single crystals of salts **1** and **9**. In addition, powder X-ray diffraction studies were carried out on compounds **2–8** and **10**, and these confirmed that the bulk phase of these compounds corresponded to that observed in the single-crystal studies. Attempts to prepare crystalline anhydrous salts of $[HNC_5H_4B(OH)_2\text{-}4]^+$ from organic solvents by methods previously used were not successful.[16]

Salts of pyridinium-4-boronic acid

Crystals of $[HNC_5H_4B(OH)_2\text{-}4]_2[M(S_2C_2O_2)_2]\cdot 2H_2O$ (M = Ni **2**, Pd **3**, Pt **4**) are isostructural, with similar unit cell dimensions and the same space group (see Table 1). Intramolecular dimensions are listed in Table 2 and intermolecular interactions given in Tables 3 and 4.

The structures contain the expected planar dianions of type **C** and cations **E** linked by synthon **D** at both ends of the anion, in form **I**. The cations are linked in pairs by hydrogen bonds, one of form BOH···OB and through two water molecules. They thereby form supramolecular dications $\{[HNC_5H_4B(OH)_2\text{-}4]_2\cdot 2H_2O\}^{2+}$ (see **J** below) which in turn makes interactions of type **D** at both ends. As a result, a neutral hydrogen-bonded ribbon is formed with M···M separations of approximately 26 Å within the ribbon (see Fig. 1).

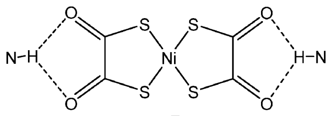
Table 1 Crystal data for **2–8** and **10**

	2	3	4	5	6	7	8	10
Chemical formula	$C_{14}H_{18}B_2N_2O_{10}S_4Ni$	$C_{14}H_{18}B_2N_2O_{10}S_4Pd$	$C_{14}H_{18}B_2N_2O_{10}S_4Pt$	$C_{14}H_{14}B_2N_2O_{12}Pt$	$C_{14}H_{14}B_2N_2O_8S_4Cu$	$C_{14}H_{14}B_2N_2O_8S_4Ni$	$C_{14}H_{14}B_2N_2O_8S_4Pd$	$C_{14}H_{14}B_2N_2O_{12}Pt$
M_r	582.87	630.56	719.25	618.98	551.67	546.84	594.53	618.98
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.2518(8)	7.4820(15)	7.4202(8)	3.6754(6)	3.8956(8)	3.9050(8)	3.9415(8)	3.6590(7)
b/Å	7.4685(9)	7.4948(15)	7.4598(8)	10.5135(17)	10.119(2)	10.220(2)	10.164(2)	10.172(2)
c/Å	20.571(2)	20.573(4)	20.396(2)	12.215(2)	13.447(3)	13.302(3)	13.431(3)	12.576(3)
α/°	94.368(2)	94.45(3)	94.419(2)	102.091(2)	100.74(3)	101.79(3)	100.46(3)	103.24(3)
β/°	94.193(2)	95.44(3)	96.480(2)	96.403(3)	94.97(3)	95.13(3)	94.77(3)	96.89(3)
γ/°	92.638(2)	92.08(3)	92.585(2)	98.557(2)	97.65(3)	98.09(3)	98.41(3)	98.10(3)
V/Å^3	1106.4(2)	1143.9(4)	1116.8(2)	451.38(13)	512.75(18)	510.69(18)	520.1(2)	445.41(2)
T/K	173(2)	298(2)	173(2)	173(2)	298(2)	273(2)	273(2)	173(2)
Z	2	2	2	1	1	1	1	1
μ/mm^{-1}	1.310	1.230	6.712	7.845	1.519	1.406	1.340	7.950
Reflections collected	5025	5232	5057	2041	2241	2334	2365	2042
Independent reflections	4104	4065	4240	2040	1419	1938	2145	2042
Final R_1 [$I > 2\sigma(I)$]	0.0266	0.0413	0.0363	0.0218	0.0590	0.0328	0.0278	0.0151

Table 2 Intramolecular bond distances (Å) in **2–8** and **10**

Bond	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**10**
M–S1	2.184(1)	2.302(1)	2.298(1)		2.297(1)	2.179(1)	2.295(1)	
M–O5				2.021(2)				2.020(1)
M–S2	2.175(1)	2.287(1)	2.285(1)		2.267(1)	2.177(1)	2.301(1)	
M–O6				2.019(2)				2.015(1)
M–S3	2.174(1)	2.288(1)	2.285(1)					
M–S4	2.184(1)	2.301(1)	2.297(1)					
Mean M–S/O	2.179	2.295	2.291	2.020	2.282	2.178	2.298	2.018
C1–S1	1.716(2)	1.718(4)	1.714(6)		1.714(6)	1.710(3)	1.716(3)	
C1–O5				1.293(4)				1.292(3)
C2–S2	1.710(2)	1.709(3)	1.715(5)		1.714(5)	1.706(3)	1.709(3)	
C2–O6				1.288(4)				1.282(3)
C3–S3	1.707(2)	1.702(3)	1.703(6)					
C4–S4	1.717(2)	1.716(4)	1.717(6)					
Mean C–S/O	1.713	1.711	1.712	1.291	1.714	1.708	1.713	1.287
C═O								
C1–O1	1.227(2)	1.224(4)	1.224(7)	1.212(5)	1.235(6)	1.235(3)	1.227(3)	1.228(3)
C2–O2	1.232(2)	1.230(4)	1.230(7)	1.221(4)	1.223(7)	1.230(3)	1.222(3)	1.230(3)
C3–O3	1.229(2)	1.231(4)	1.234(7)					
C4–O4	1.230(2)	1.226(4)	1.225(6)					
Mean C═O	1.230	1.228	1.228	1.217	1.229	1.233	1.225	1.229
B1–O5	1.350(2)	1.346(5)	1.350(7)					
B1–O3				1.338(5)	1.331(9)	1.341(4)	1.327(4)	1.347(3)
B1–O6	1.352(2)	1.338(5)	1.353(7)					
B1–O4				1.357(5)	1.360(7)	1.352(4)	1.364(4)	1.366(3)
B2–O7	1.355(2)	1.343(5)	1.350(7)					
B2–O8	1.351(2)	1.345(5)	1.345(8)					
Mean B–O	1.352	1.343	1.350	1.348	1.346	1.347	1.345	1.357
B1–C7	1.596(2)	1.592(5)	1.587(8)	1.599(5)				
B1–C3					1.582(9)	1.575(4)	1.582(5)	1.584(4)
B2–C12	1.599(2)	1.599(5)	1.596(8)					
Mean B–C	1.598	1.596	1.592	1.599	1.582	1.575	1.582	1.584

These ribbons lie parallel to one another and each ribbon has six nearest neighbours (see Fig. 2), with shortest inter-ribbon M···M distances of *ca.* 7.5 Å.



I

The supramolecular dications **J** contain two different R(3,3)8 motifs formed by the inclusion of the water molecules. There are three exocyclic OH hydrogen-bond donors available in the R(3,3)8 moieties and these form hydrogen bonds with other boronic acid acceptors in neighbouring ribbons which leads to a three-dimensional network of hydrogen bonds. It is notable that the dimer motif **K** seen in a number of boronic acid structures is not present in **2–4**. Thermogravimetric analyses for **2–4** showed weight loss corresponding to the loss of two equivalents of water at temperatures around 110 °C (see Experimental section). All other thermally activated weight loss processes for **1–10** occurred at temperatures above 190 °C.

Table 3 Hydrogen bonds in **2–4**

Atoms Compound	Nature	D–H···A/°			D–H/Å			H···A/Å			D···A/Å		
		2	**3**	**4**	**2**	**3**	**4**	**2**	**3**	**3**	**2**	**3**	**4**
N1–H1A···O1	NH···O═C	149	149	150	0.88	0.86	0.88	2.02	2.06	2.01	2.81	2.83	2.80
N1–H1A···O2	NH···O═C	132	133	131	0.88	0.86	0.88	2.19	2.19	2.19	2.86	2.85	2.85
N2–H2A···O3	NH···O═C	130	131	130	0.88	0.86	0.88	2.23	2.23	2.22	2.88	2.86	2.87
N2–H2A···O4	NH···O═C	152	153	153	0.88	0.86	0.88	2.00	2.04	2.00	2.81	2.83	2.81
O5–H5C···O7	BOH···BOH	178	161	169	0.68	0.55	0.67	2.01	2.20	2.04	2.69	2.72	2.69
O6–H6C···O9	BOH···OH_2	172	174	170	0.84	0.68	0.80	2.02	2.19	2.04	2.85	2.87	2.83
O7–H7C···O9	BOH···OH_2	161	160	170	0.65	0.83	0.60	2.01	1.85	2.04	2.63	2.65	2.63
O8–H2C···O10	BOH···OH_2	169	166	172	0.88	0.75	0.67	1.97	2.12	2.17	2.84	2.86	2.84
O9–H4C···O2	HOH···O═C	164	159	173	0.77	0.79	0.78	2.00	2.02	1.96	2.75	2.77	2.74
O9–H4D···O10	HOH···OH_2	179	165	179	0.69	0.83	0.69	2.06	1.97	2.07	2.75	2.78	2.76
O10–H10C···O3	HOH···O═C	160	158	166	0.75	0.63	0.78	1.99	2.13	1.94	2.71	2.73	2.70
O10–H10D···O5	HOH···HOB	144	146	141	0.72	0.88	0.71	2.15	2.01	2.17	2.76	2.78	2.75

Table 4 Hydrogen bonds in **5–8** and **10**

Atoms	Nature	D–H···A/°					D–H/Å				
		5	6	7	8	10	5	6	7	8	10
N1–H1···O1	NH···O=C		132	129	131	126		0.86	0.86	0.86	0.86
N1–H1···O2	NH···O=C	177	149	152	150	156	0.88	0.86	0.86	0.86	0.86
O3–H3···O1	BOH···O=C	163	148	150	153	160	0.84	0.82	0.82	0.82	0.82
O4–H4···O5	BOH···O–Pt	179				176	0.84				0.82

		H···A/Å					D···A/Å				
		5	6	7	8	10	5	6	7	8	10
N1–H1···O1	NH···O=C		2.25	2.34	2.31	2.39		2.90	2.96	2.95	2.97
N1–H1···O2	NH···O=C	1.86	1.99	1.98	1.97	2.01	2.74	2.77	2.77	2.75	2.82
O3–H3···O1	BOH···O=C	1.86	1.98	1.96	1.94	1.85	2.68	2.71	2.70	2.69	2.63
O4–H4···O5	BOH···O–Pt	2.13				2.38	2.97				3.19

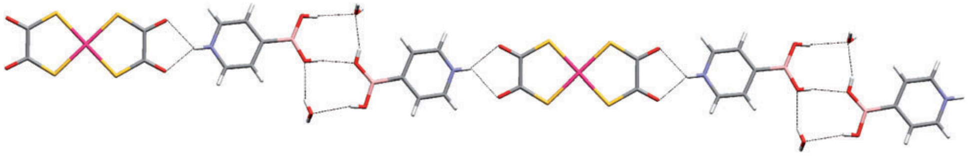
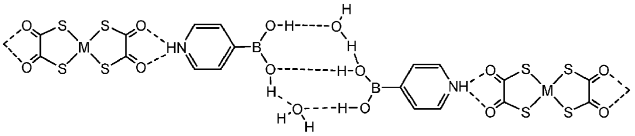
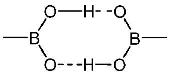


Fig. 1 Structure of the hydrogen-bonded ribbon in crystalline $[HNC_5H_4B(OH)_2\text{-}4]_2[Pd(S_2C_2O_2)_2]\cdot 2H_2O$ (**3**). The NH···O and OH···O hydrogen bonds are indicated.



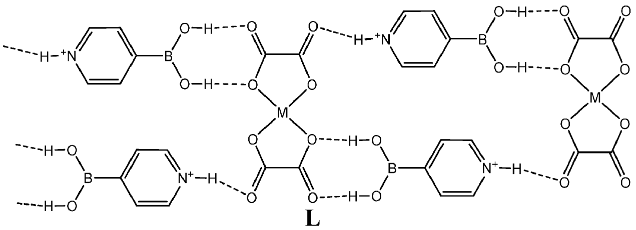
J



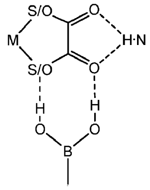
K

Use of a similar synthetic procedure but replacing **D** with **F** led to crystallisation of an anhydrous salt $[HNC_5H_4B(OH)_2\text{-}4]_2[Pt(O_2C_2O_2)_2]$ (**5**). It has a structure differing from those of **2–4** (see Fig. 3 and Tables 1–4) in which the planar ionic tectons form a one-dimensional ribbon of the form **L**. The structure of **5** results from a packing of these planar ribbons in which each has six nearest neighbours with no strong hydrogen bonds between ribbons (see Fig. 4). In contrast to the dozens of pyridinium salts of dithiooxalate complexes we and others have reported, synthon **H** in **5** is not present. Apparently formation of the boronic acid···carboxylate synthon **M** is preferred, or at least is part of an acceptable alternative set of interactions. The pyridinium···carboxylate interaction is highly asymmetric (NH···O distances 1.86 Å, 2.70 Å; *ortho*-CH···O 2.71 Å) and in the plane of the anion.

Compound **1** did not form crystals suitable for single-crystal studies, although analytical results suggest that it has the same formulation as **2–4** (*i.e.* that it contains two molecules of water per formula unit). Powder X-ray diffraction shows that although it appears to consist of a single crystalline phase, it is not isostructural with **2–4**.



L



M

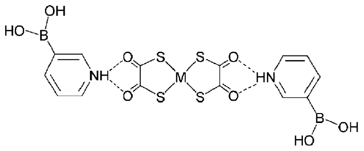
Salts of pyridinium-3-boronic acid

Single-crystal X-ray diffraction revealed that the corresponding salts of the isomeric cation **F**, $[HNC_5H_4B(OH)_2\text{-}3]_2[M(S_2C_2O_2)_2]$ (M = Cu **6**, Ni **7**, Pd **8**) and $[HNC_5H_4B(OH)_2\text{-}3]_2[Pt(O_2C_2O_2)_2]$ **10** are all isostructural (see Fig. 5, Tables 1–4). The structures contain the interaction **D** at both ends of the dianions thereby forming neutral $[HNC_5H_4B(OH)_2\text{-}3]_2[M(S_2C_2O_2)_2]$ supermolecules **N**. The boronic acid groups form R(2,2)8 synthons of type **M** by interaction with the thiocarboxylate (or carboxylate) moieties of neighbouring supermolecules. These interactions therefore link the

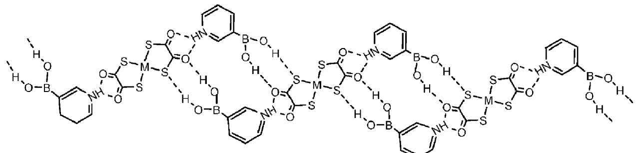
Fig. 2 Packing of the hydrogen-bonded ribbon in crystalline $[HNC_5H_4B(OH)_2\text{-}4]_2[Pd(S_2C_2O_2)_2]\cdot 2H_2O$ (**3**). The inter-ribbon OH···O hydrogen bonds are indicated.

$[HNC_5H_4B(OH)_2\text{-}3]_2[M(S_2C_2O_2)_2]$ moieties edge-to-edge in a stepped chain in which each supermolecule **N** accepts and donates two hydrogen bonds to each of its neighbours in the chain. The metal···metal separations within the chain are of length *ca.* 15 Å. These chains are linked by weaker CH···O interactions into layers (see Fig. 6). The shortest M···M distance between layers is approximately 3.9 Å for **6**, **7** and **8** and 3.7 Å for **10** (Fig. 7). In this system the oxalate salt **10** is isostructural with the dithiooxalate salts **6–8**, with some metric change consequent on the smaller intra- and intermolecular dimensions of **10** due to the replacement of sulfur by oxygen.

Crystals of **9** suitable for diffraction could not be obtained. Elemental analysis suggests a formulation of $[HNC_5H_4B(OH)_2\text{-}3]_2[Pt(S_2C_2O_2)_2]$ (analogous to **6–8**), and powder X-ray studies indicate the presence of a phase isostructural to **6–8**. However, this does not appear to be the only phase present.



N



O

Conclusions

Whilst compounds **2–8** and **10** contain anions with no hydrogen-bond donor ability, their cations show a range of hydrogen-bond donor (NH, OH) and hydrogen-bond acceptor (B–O, H_2O) capabilities. This opens the issue of competition between these various donors and acceptors. In compounds

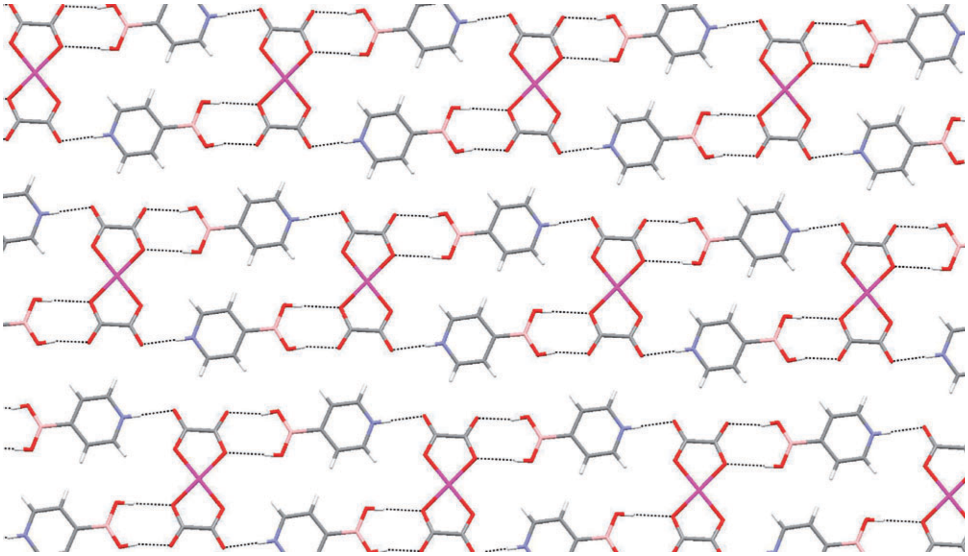


Fig. 3 Packing of the NH···O and OH···O hydrogen-bonded ribbons in layers of crystalline $[HNC_5H_4B(OH)_2\text{-}4]_2[Pt(O_2C_2O_2)_2]$ (**5**).

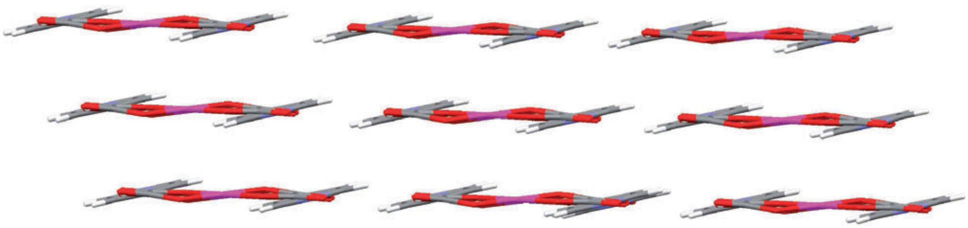


Fig. 4 Packing of layers in crystalline $[HNC_5H_4B(OH)_2\text{-}4]_2[Pt(O_2C_2O_2)_2]$ (**5**).

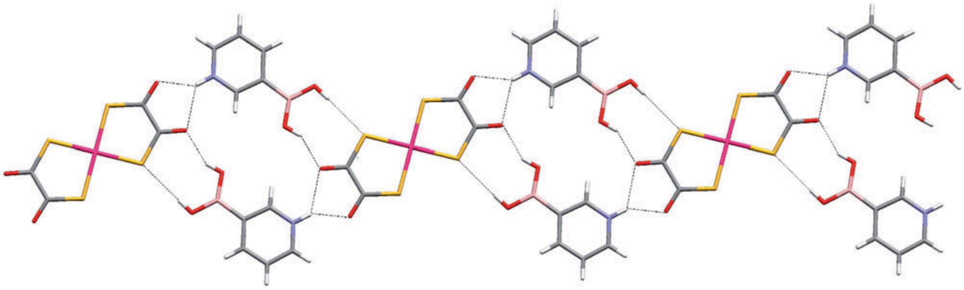


Fig. 5 Structure of the NH···O and OH···O hydrogen-bonded stepped chain in crystalline $[HNC_5H_4B(OH)_2\text{-}3]_2[Pd(S_2C_2O_2)_2]$ (**8**).

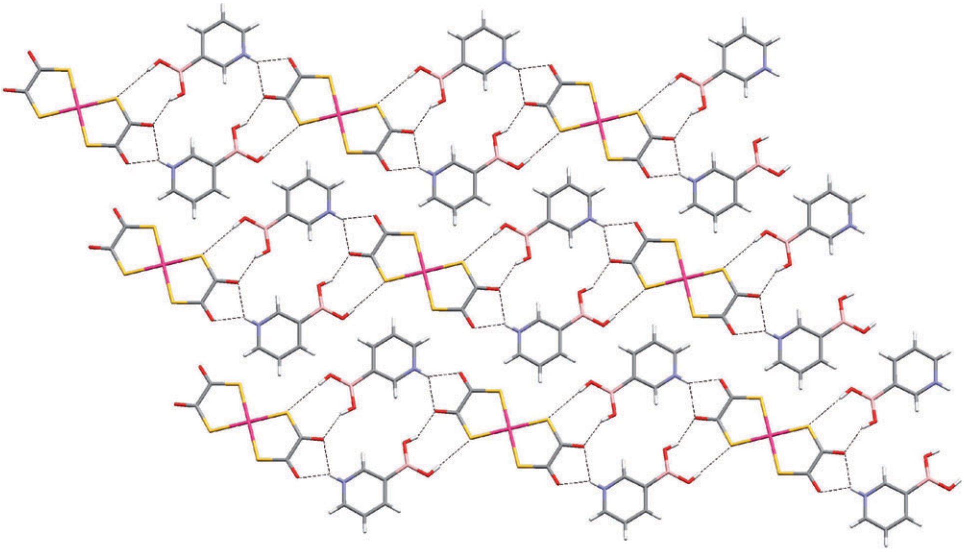


Fig. 6 Layer formed by the NH···O hydrogen-bonded chains in crystalline $[HNC_5H_4B(OH)_2\text{-}3]_2[Pd(S_2C_2O_2)_2]$ (**8**). The NH···O and OH···O hydrogen bonds are indicated.

2–4, **6–8** and **10**, the desired **D**-type synthon is formed, reflecting its good shape matching and charge-assisted hydrogen bonding. After formation of **D** the dithiooxalate ligand retains significant hydrogen-bond acceptor capacity in the plane of the anion, as indicated by the formation of the planar BOH···O=C and BOH···S interactions in **M** in **5–8**. The oxalate anion **G** has similar capability, as implied by the structure of **10**.

As noted in ref. 15, the effectiveness of synthon **D** is such that the crystal structures of pyridinium salts of dianions **C** may be well described as arising by packing of planar supermolecules of stoichiometry [pyridinium]$_2$[**C**] (see Fig. 8). This is true of **2–4**, **6–8** and **10**. The presence of hydrogen-bond donors in these supermolecules beyond those required to form synthon **D** (here, the boronic acid moieties) allows the formation of networks through cross-linking of supermolecules. In **2–4** this is mediated by two water molecules which both allow formation of chains **J** and their further linking into a three-dimensional hydrogen-bond network. In **6–8** and **10** formation of the boronic acid—(thio)carboxylate synthon leads to it adopting one of the two crystal structure noted in ref. 15 for [pyridinium]$_2$[Ni(dtox)$_2$] salts in which stepped ribbons pack side-by-side with (weak) CH···O lateral contacts between them (see Fig. 9). Layer formation is a notable and apparently rather general feature of salts of bis(dithiooxalate) complexes.

In none of the eight structures reported here is the boronic acid dimer **K** formed, implying that this is not a robust tool for the design of supramolecular structures, at least when in the presence of competitors such as carboxylate or thiocarboxylate ligands.

The observation of two series of isostructural and isomorphous salts (**2–4**, **6–8** and **10**) in which the metal varies without changing the form of the crystal structure obtained offers some promise that these materials can be "engineered" so as to modify their properties. That the Cu(II) analogue of **2–4** is apparently not isomorphous with the Ni, Pd and Pt species is an indication that there may be (latent) polymorphism in these systems. Similarly, the replacement of sulfur by oxygen which leads to an isomorphous structure in the case of **10** does not for **5**, indicating that there are limits on the robustness of these structure types. Of the two series, that based on pyridinium-3-boronic acid, is particularly interesting given the present of inter-layer metal–metal contacts of length 3.65–3.95 Å and its greater apparent reliability. Some indication of this reliability is that the structure of **5** is isomorphous with that of **6–8** and **10**! In **5**, of course, the NH donor is in the 4- position and so a

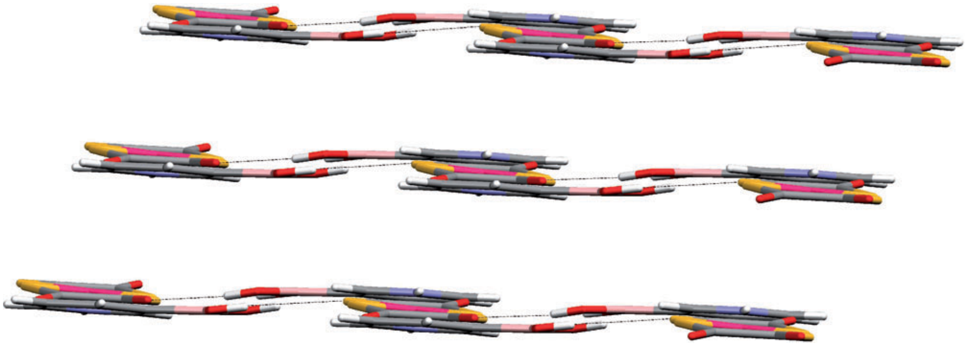


Fig. 7 Packing of layers formed in $[HNC_5H_4B(OH)_2\text{-}3]_2[Pd(S_2C_2O_2)_2]$ (**8**). The NH···O and OH···O hydrogen bonds are indicated.

different pattern of NH···O hydrogen bonds results in which the 3-CH of the cation replaces the NH donors in forming an interaction of type **I** (see Fig. 3), albeit with longer H···O distances (2.56 and 2.57 Å *vs.* 1.97–2.39 Å in **6–8** and **10**, see Table 2).

Finally, in these systems it is clear that the stereochemistry of the hydrogen-bond donor groups in the cations *sometimes* plays an important role in determining their structures—it leads to different behaviour in **2–4** from that of **6–8**, for example. However efficient packing and favourable (partly electrostatic) lattice energies may allow isomeric ions to form isomorphous structures with *different* hydrogen-bond patterns (as reported in detail in ref. 17). It is perhaps surprising that even for relatively small cations, such as the 3- and 4-pyridinium boronic acids, the location of the hydrogen-bond functions may have little effect on the gross features of the structure of their salts, perhaps less so for larger cations (such as bipyridiniums[17] and protonated triazines[19]).

We have demonstrated the use of protonated pyridine boronic acids as new tectons in crystal synthesis. These cations form a robust synthon of form **H** with dithiooxalate C═O acceptor tectons. Introduction of H-bond donors and acceptors through the use of 3-pyridine and 4-pyridine moieties leads to a variety of supramolecular motifs in which the synthon **H** withstands competition from other possible H-bond donors and occurs in a variety of circumstances.

Experimental

X-Ray diffraction

Diffraction measurements were made on three-circle CCD diffractometers using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at −100 °C for **2**, **4**, **5** and **10** and room temperature for **3**, **6**, **7** and **8**, respectively. The intensity data were integrated using the SAINT[20] program. Absorption, Lorentz and polarisation corrections were applied. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXTL.[20] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the U_{equiv} of their attached carbon atoms for methyl hydrogens, and 1.2 times the U_{equiv} of their attached carbon atoms for all others.

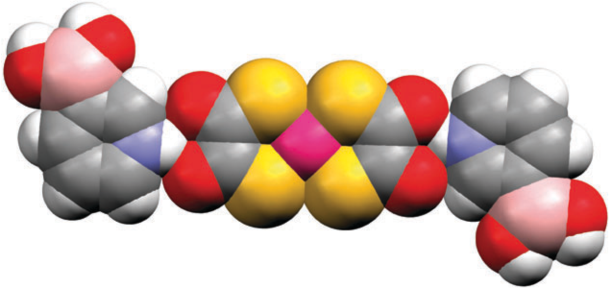


Fig. 8 Space-filling representation of the neutral $[HNC_5H_4B(OH)_2\text{-}3]_2[Ni(S_2C_2O_2)_2]$ supermolecule.

Powder X-ray measurements were performed using Cu-Kα radiation (λ = 1.5418 Å) on a Bruker-AXS D8-Advance diffractometer equipped with a secondary monochromator. The data were collected in the range $5 < 2\theta < 60°$ in θ–θ mode with a step time of n s ($5\text{ s} < n < 10\text{ s}$) and step width of 0.02°. Powder patterns for bulk microcrystalline samples of each of **2–8** and **10** were consistent with the presence of no phase other than that identified in the single-crystal experiment.

CCDC reference numbers 614733–614740.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604729g

Synthesis

The salts $K_2[M(dto)_2]$ (M = Cu, Ni, Pd, Pt and dto = dithiooxalate) were prepared according to the published procedure.[21] Potassium bis(oxalato)platinate(II) dihydrate and

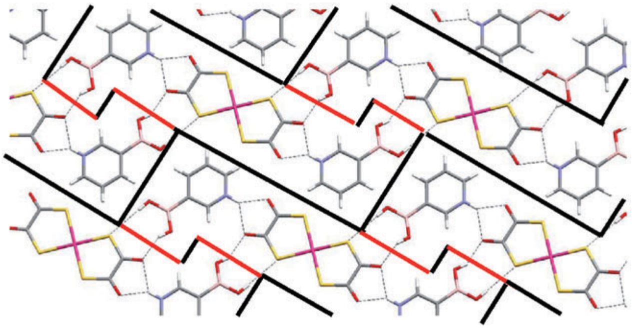


Fig. 9 Schematic representation of the packing of the neutral $[HNC_5H_4B(OH)_2\text{-}3]_2[M(S_2C_2O_2)_2]$ supermolecules in **6–8**.

both pyridine boronic acids were purchased from Aldrich. Both pyridine boronic acids were recrystallised from concentrated hydrochloric acid to form their hydrochloride salts. Elemental analyses were performed by the School of Chemistry Microanalytical Service. TGA measurements were carried out on a STA 409EP instrument in air between 20 and 1000 °C with a temperature ramp of 5 °C min^{-1}.

Single crystals of **2–8** and **10** were prepared by slow diffusion of stoichiometric amounts of the reagents (the pyridine boronic acid hydrochloride and the metal bis{dithiooxalate or oxalate} salt) according to the following methodology, which we term a 'mini H-tube'. Solutions of each of the two reagents were dissolved in water and placed in small vials, and these vials were then placed inside a larger vial. This was then filled with water and capped, care being taken not to disturb the original solutions but to effectively balance the water on top of the reagent solutions. Allowing this to stand for a matter of days (or weeks in some cases) provided crystals for diffraction. Attempts to obtain suitable single crystals of **1** and **9** were unsuccessful.

Preparation of 1. To a solution of $K_2[Cu(dto)_2]$ (0.10 g, 0.262 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-4-boronic acid hydrochloride (83.4 mg, 0.523 mmol) in water (5 ml). The resulting green precipitate of **1** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (132 mg, 0.222 mmol, 84.7%). Microanalytical data (%). Found: C, 28.12; H, 2.55; N, 4.40. Calc.: C, 28.61; H, 3.09; N, 4.77. Powder X-ray diffraction studies indicated that the sample of **1** obtained was crystalline but not isostructural with **2–4**.

Preparation of 2. To a solution of $K_2[Ni(dto)_2]$ (0.10 g, 0.265 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-4-boronic acid hydrochloride (84.5 mg, 0.53 mmol) in water (5 ml). The resulting red precipitate of **2** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (110 mg, 0.189 mmol, 71.3%). Microanalytical data (%). Found: C, 28.82; H, 2.97; N, 4.52. Calc.: C, 28.85; H, 3.11; N, 4.81. TGA showed weight loss in the temperature range 70–175 °C (wt. loss: calc. 6.10%, obsd. 5.78%).

Preparation of 3. To a solution of $K_2[Pd(dto)_2]$ (0.10 g, 0.235 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-4-boronic acid hydrochloride (75.0 mg, 0.470 mmol) in water (5 ml). The resulting orange precipitate of **3** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (90 mg, 0.143 mmol, 60.9%). Microanalytical data (%). Found: C, 26.91; H, 2.80; N, 4.07. Calc.: C, 26.66; H, 2.88; N, 4.44. TGA showed weight loss in the temperature range 70–175 °C (calc. 5.72%, obsd. 4.83%).

Preparation of 4. To a solution of $K_2[Pt(dto)_2]$ (0.10 g, 0.195 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-4-boronic acid hydrochloride (62 mg, 0.389 mmol) in water (5 ml). The resulting red precipitate of **4** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (110 mg, 0.153 mmol, 78.5%). Microanalytical data (%). Found: C, 23.48; H, 2.30; N, 3.24. Calc.: C, 23.38; H, 2.52; N, 3.89. TGA showed weight loss in the temperature range 70–175 °C (calc. 4.07%, obsd. 5.01%).

Preparation of 5. To a solution of potassium bis(oxalate) platinate dihydrate (0.10 g, 0.2 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-4-boronic acid hydrochloride (63.8 mg, 0.4 mmol) in water (5 ml). The resulting yellow precipitate of **5** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (112 mg, 0.181 mmol, 90.5%). Microanalytical data (%). Found: C, 27.12; H, 2.11; N, 4.33. Calc.: C, 27.17; H, 2.28; N, 4.53.

Preparation of 6. To a solution of $K_2[Cu(dto)_2]$ (0.10 g, 0.262 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-3-boronic acid hydrochloride (83.4 mg, 0.523 mmol) in water (5 ml). The resulting green precipitate of **6** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (116 mg, 0.210 mmol, 80.2%). Microanalytical data (%). Found: C, 30.15; H, 2.28; N, 4.84. Calc.: C, 30.48; H, 2.56; N, 5.08.

Preparation of 7. To a solution of $K_2[Ni(dto)_2]$ (0.10 g, 0.265 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-3-boronic acid hydrochloride (84.5 mg, 0.53 mmol) in water (5 ml). The resulting red precipitate of **7** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (121 mg, 0.221 mmol, 83.4%). Microanalytical data (%). Found: C, 30.61; H, 2.47; N, 4.98. Calc.: C, 30.75; H, 2.58; N, 5.12.

Preparation of 8. To a solution of $K_2[Pd(dto)_2]$ (0.10 g, 0.235 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-3-boronic acid hydrochloride (75.0 mg, 0.470 mmol) in water (5 ml). The resulting orange precipitate of **8** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (91 mg, 0.153 mmol, 65.1%). Microanalytical data (%). Found: C, 28.44; H, 2.12; N, 4.21. Calc.: C, 28.28; H, 2.37; N, 4.71.

Preparation of 9. To a solution of $K_2[Pt(dto)_2]$ (0.10 g, 0.195 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-3-boronic acid hydrochloride (62 mg, 0.389 mmol) in water (5 ml). The resulting red precipitate of **9** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (113 mg, 0.165 mmol, 84.6%). Microanalytical data (%). Found: C, 24.67; H, 1.96; N, 3.76. Calc.: C, 24.61; H, 2.07; N, 4.10. Powder X-ray diffraction studies indicated that the sample of **9** obtained was crystalline but apparently not a single phase material.

Preparation of 10. To a solution of potassium bis(oxalate) platinate dihydrate (0.10 g, 0.2 mmol) in water (10 ml) was added dropwise with stirring a solution of pyridine-3-boronic acid hydrochloride (63.8 mg, 0.4 mmol) in water (5 ml). The resulting yellow precipitate of **10** was collected by vacuum filtration, washed with ice-cold water (5 ml), ethanol (5 ml), diethyl ether (5 ml), and dried at the pump (110 mg, 0.178 mmol, 89%). Microanalytical data (%). Found: C, 27.20; H, 2.22; N, 4.46. Calc.: C, 27.17; H, 2.28; N, 4.53.

Acknowledgements

We thank TUBITAK for a NATO-B1 fellowship (for H. K.), the Royal Society, EPSRC and University of Bristol for financial support, and the crystallographic referee for their careful reading of the manuscript.

References

1 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, Germany, 1998, ch. 2.

2 P. R. Parry, C. Wang, A. S. Batsanov, M. R. Bryce and B. Tarbit, *J. Org. Chem.*, 2002, **67**, 7541.

3 (*a*) J. D. Dunitz, D. M. Hawley, D. Miklos, D. N. White, Y. Berlin, R. Marusic and V. Prelog, *Helv. Chim. Acta*, 1971, **54**, 1709; (*b*) H. Nakumura, Y. Iitaka, T. Kitahara, T. Okasaki and Y. Okami, *J. Antibiot.*, 1977, **30**, 714; (*c*) A. M. Irving, C. M. Vogels, L. G. Nikolcheva, J. P. Edwards, X.-F. He, M. G. Hamilton, M. O. Baerlocher, F. J. Baerlocher, A. Decken and S. A. Westcott, *New J. Chem.*, 2003, **27**, 1419.

4 (*a*) A. B. Shenvi, *Biochemistry*, 1986, **25**, 1286; (*b*) C. A. Kettner and A. B. Shenvi, *J. Biol. Chem.*, 1984, **259**, 15106; (*c*) C. N. Pace and R. A. Landers, *Biochim. Biophys. Acta*, 1981, **658**, 410; (*d*) R. S. Reczkowski and D. E. Ash, *Arch. Biochem. Biophys.*, 1994, **312**, 31; (*e*) S. V. Khangulov, P. J. Pessiki, V. V. Barynin, D. E. Ash and G. C. Dismukes, *Biochemistry*, 1995, **34**, 2015.

5 (*a*) A. H. Soloway, W. Tjarks, B. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515; (*b*) M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 950.

6 (*a*) J.-B. Lan, L. Chen, X.-Q. Yu, J.-S. You and R.-G. Xie, *Chem. Commun.*, 2004, 188; (*b*) D. S. Matteson, *Chem. Rev.*, 1989, **89**, 1535.

7 C. B. Aakeröy, J. Desper and B. Levin, *CrystEngComm*, 2005, **15**, 102.

8 (*a*) J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo and E. Galoppini, *J. Am. Chem. Soc.*, 2003, **125**, 1002; (*b*) K. E. Maly, T. Maris and J. D. Wuest, *CrystEngComm*, 2006, **8**, 33.

9 (*a*) P. Rodríguez-Cuamatzi, O. I. Arillo-Flores, M. I. Bernal-Uruchurtu and H. Höpfl, *Cryst. Growth Des.*, 2005, **5**, 167; (*b*) V. R. Pedireddi and N. SeethaLekshmi, *Tetrahedron Lett.*, 2004, **45**, 1903; (*c*) P. Rodriguez-Cuamatzi, G. Vargas-Diaz, T. Maris, J. D. Wuest and H. Hopfl, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, 1316; (*d*) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini and L. Sturba, *Organometallics*, 2003, **22**, 2142; (*e*) N. SeethaLekshmi and V. R. Pedireddi, *Inorg. Chem.*, 2006, **45**, 2400.

10 (*a*) G. R. Desiraju, *Crystal Engineering*, The Design of Organic Solids, Elsevier, Amsterdam, 1989; (*b*) J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*c*) K. K. Arora and V. R. Pedireddi, *J. Org. Chem.*, 2003, **68**, 9177; (*d*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (*e*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.

11 (*a*) V. R. Pedireddi, A. Ranganathan and S. Chatterjee, *Tetrahedron Lett.*, 1998, **39**, 9831; (*b*) V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 997; (*c*) P. Vishweshwar, A. Nangia and V. M. Lynch, *J. Org. Chem.*, 2002, **67**, 556; (*d*) C. V. K Sharma and M. Zaworotko, *Chem. Commun.*, 1996, 2655.

12 A. L. Gillon, G. R. Lewis, A. G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodriguez-Martin and C. Ruiz-Perez, *J. Chem. Soc., Dalton Trans.*, 2000, 3897.

13 B. Dolling, A. L. Gillon, A. G. Orpen, J. Starbuck and X.-M. Wang, *Chem. Commun.*, 2001, 567.

14 A. Angeloni and A. G. Orpen, *Chem. Commun.*, 2001, 343.

15 (*a*) T. J. Podesta and A. G. Orpen, *CrystEngComm*, 2002, **12**, 336; (*b*) C. J. Adams, P. C. Crawford, A. G. Orpen and T. J. Podesta, *Dalton Trans.*, 2006, DOI: 10.1039/b604319d.

16 P. C. Crawford, A. L. Gillon, J. Green, A. G. Orpen, T. J. Podesta and S. V. Pritchard, *CrystEngComm*, 2004, 419.

17 A. Angeloni, P. C. Crawford, A. G. Orpen, T. J. Podesta and B. J. Shore, *Chem.–Eur. J.*, 2004, **10**, 3783.

18 (*a*) R. Enjalbert, A. Gleizes, J.-C. Trombe, M. L. Gutierrez-Campo and P. Roman, *J. Mol. Struct.*, 1985, **131**, 1; (*b*) P. Roman, C. Bao, J. M. Gutierrez-Zorrilla and A. Vegas, *J. Crystallogr. Spectrosc. Res.*, 1988, **18**, 207; (*c*) P. Roman, A. Luque, J. I. Beitia and C. Guzman-Miralles, *Polyhedron*, 1992, **11**, 1883.

19 T. J. Podesta and A. G. Orpen, *Cryst. Growth Des.*, 2005, **5**, 681.

20 (*a*) *SMART*, Bruker AXS, Madison, WI, USA, Copyright 1989–1999; (*b*) *SAINT*, Bruker AXS, Madison, WI, USA; (*c*) *SHELXTL, Rev. 5.0*, Bruker AXS, Madison, WI, USA.

21 A. P. Gray, R. D. Platz, T. R. Henderson, C. P. Timothy, K. Takahashi and K. L. Dretchen, *J. Med. Chem.*, 1988, **31**, 807.