

# Hydrogen-bonding, $\pi$ -stacking and $\text{Cl}^-$ -anion- $\pi$ interactions of linear bipyridinium cations with phosphate, chloride and $[\text{CoCl}_4]^{2-}$ anions

Thomas Dorn, Christoph Janiak\* and Khalid Abu-Shandi

Received 23rd June 2005, Accepted 3rd November 2005

First published as an Advance Article on the web 11th November 2005

DOI: 10.1039/b508944a

A series of protonated bipyridinium compounds has been synthesized and their crystal packing is discussed in terms of  $\text{N-H}\cdots\text{X}$  contacts ( $\text{X} = \text{O}, \text{Cl}$ ) together with  $\pi$ - $\pi$  and  $\text{Cl}^- \cdots \pi$  interactions of the positively charged aromatic nitrogen heterocycles. The bipyridinium-anion combinations are diprotonated 4,4'-bipyridin-1,1'-ium bis(dihydrogenphosphate) dihydrate (**3**), 4,4'-bipyridin-1,1'-ium bis(1,1'-binaphthalene-2,2'-diyl phosphate) $\cdot 2.5\text{H}_2\text{O}$  (**4**), 6,6'-diisoquinolin-2,2'-ium dichloride dihydrate (**5**), 2,2'-bi-1,6-naphthyridin-6,6'-ium dichloride dihydrate (**6**) and triprotonated 2,2'-bi-1,6-naphthyridin-1,6,6'-ium-tetrachlorocobaltate(II)-chloride (**7**). In all structures  $\text{N}^+\text{-H}$  hydrogen bonding occurs only to the anion and not to water of crystallization. The packing in **3-6** can be rationalized by a separation of the hydrophobic C-H backbone of the bipyridines from the hydrophilic N-H, phosphate or chloride and water part.  $\text{N}^+\text{-H}\cdots\text{Cl/O}$  hydrogen bonding and  $\pi$ - $\pi$ -stacking are identified as the major packing interactions in **3-6**. In **7** the  $\pi$ -stacking is replaced by remarkably short  $\text{Cl}^-$ -anion- $\pi$  interactions.

## Introduction

A key objective in the field of crystal engineering is the control and manipulation of weak interactions in order to tune the properties of the bulk material. Classical O/N-H $\cdots$ O/N hydrogen bonds are of course the predominant supramolecular interaction<sup>1</sup> followed by O/N-H $\cdots$ halide hydrogen bonds.<sup>2-6</sup> Even weaker control forces are C-H $\cdots$ O/N hydrogen bonds,<sup>7,8</sup>  $\pi\cdots\pi$  interactions,<sup>9,10</sup> C-H $\cdots\pi$ ,<sup>11</sup> (halide-)anion $\cdots\pi$ <sup>12</sup> and even C-H $\cdots$ C interactions.<sup>13,14</sup> Estimates for interaction energies are 16–60 kJ mol<sup>-1</sup> for O/N-H $\cdots$ O/N hydrogen bonds, <16 kJ mol<sup>-1</sup> for C-H $\cdots$ O hydrogen bonds, <2–20 kJ mol<sup>-1</sup> for  $\pi\cdots\pi$  interactions and 4–10 kJ mol<sup>-1</sup> for C-H $\cdots\pi$  interactions.<sup>1,9,11,15,16</sup>

Following the seminal work on hydrogen bonding from bipyridinium cations to perhalometallate anions by Orpen *et al.*,<sup>2</sup> Brammer *et al.*,<sup>3,17</sup> and related work on  $\text{N}^+\text{-H}\cdots[\text{MCl}_n]^{m-}$  interactions by others,<sup>4,5,18</sup> we were intrigued by a recent paper by Hubberstey *et al.* on hydrogen bonding between bipyridinium cations and nitrate anions.<sup>19</sup> Hubberstey *et al.* discussed the relative importance of  $\text{N}^+\text{-H}\cdots\text{O}$  and C-H $\cdots\text{O}$  hydrogen bonds in these compounds. It became apparent that such “simple” salts are attractive candidates to assess the significance of different types of supramolecular interactions. Furthermore a constant interest in hydrogen bonding patterns together with  $\pi$ - $\pi$ -stacking of protonated, cationic nitrogen heterocycles can be noted.<sup>20</sup>

Here we report the structures of (diprotonated) bipyridinium (di-)cations with phosphate anions, the structures of the more lengthy diprotonated 6,6'-diisoquinolinium and 2,2'-bi-1,6-naphthyridinium cations with chloride anions and

the triprotonated 2,2'-bi-1,6-naphthyridinium trication with chloride and tetrachlorocobaltate(II) anions. The supramolecular inter-cation-anion and inter-cation interactions, such as  $\text{N}^+\text{-H}\cdots\text{O}$ ,  $\text{N}^+\text{-H}\cdots\text{Cl}^-$ ,  $\pi$ - $\pi$  and  $\text{Cl}^- \cdots \pi$  are analyzed.

## Results and discussion

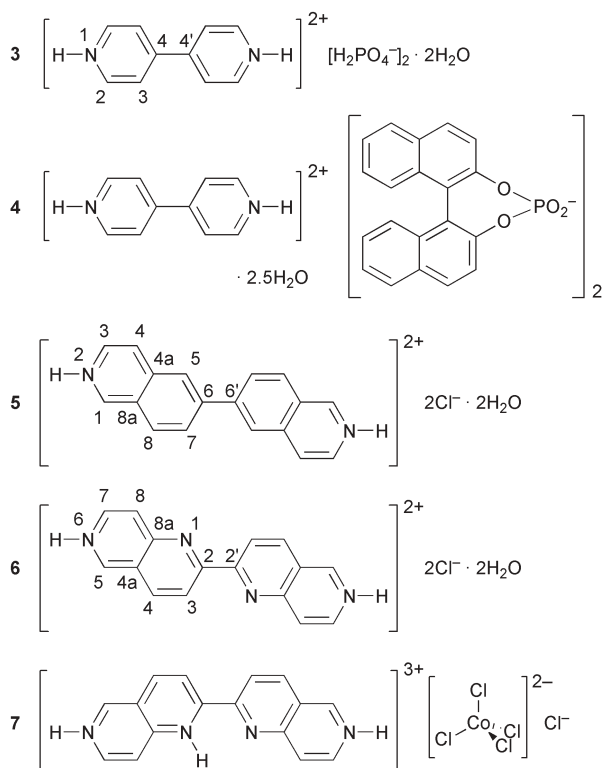
The bipyridinium salts (Scheme 1) are prepared as crystals through slow solvent evaporation from aqueous bipyridine solutions with the respective acid within a week.

The protonation could be followed by UV-Vis spectroscopy through a (bathochromic) shift of the  $\pi$ - $\pi^*$  transitions<sup>21</sup> to a longer wavelength (Fig. 1). A new UV-absorption peak emerges at 211–216 nm, possibly stemming from  $n$ - $\pi^*$  transitions below 200 nm.

Attempts to follow the protonation by <sup>15</sup>N NMR spectroscopy using the INEPT sequence,<sup>22</sup> relying on <sup>1</sup>H-<sup>15</sup>N coupling and polarization transfer, have failed in our hands as no <sup>15</sup>N signals could be observed for the bipyridines in acidic solutions.

In all salts at least diprotonation is achieved through the action of the phosphoric or hydrochloric acid. To reach triprotonation in the binaphthyridine in **7** the concentration of hydrochloric acid had to be increased from 6 mol l<sup>-1</sup> for **6** to 12 mol l<sup>-1</sup> for **7**. In all structures the additional electrostatic attraction enables N-H hydrogen bonding only to the anion, *i.e.* an O atom of the phosphate or a  $\text{Cl}^-$  ion, and not to water of crystallization (Table 1 and 2). The compounds adopt different packing arrangement, due to the difference in the anions.<sup>19</sup> Only compounds **5** and **6** crystallize isomorphously, that is, the additional N1 and N1' atoms of the binaphthyridine in **6** do not participate in intermolecular interactions to affect the packing. The phosphate and chloride salts **3-6** form as (di-)hydrates. The crystal water is, however, lost upon drying as evidenced by the elemental analyses. A Cambridge

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany.  
E-mail: janiak@uni-freiburg.de; Fax: 49 761 2036147;  
Tel: 49 761 2036127



**Scheme 1** Molecular composition of the prepared bipyridinium salts 3–7 with part of the nomenclature numbering scheme.

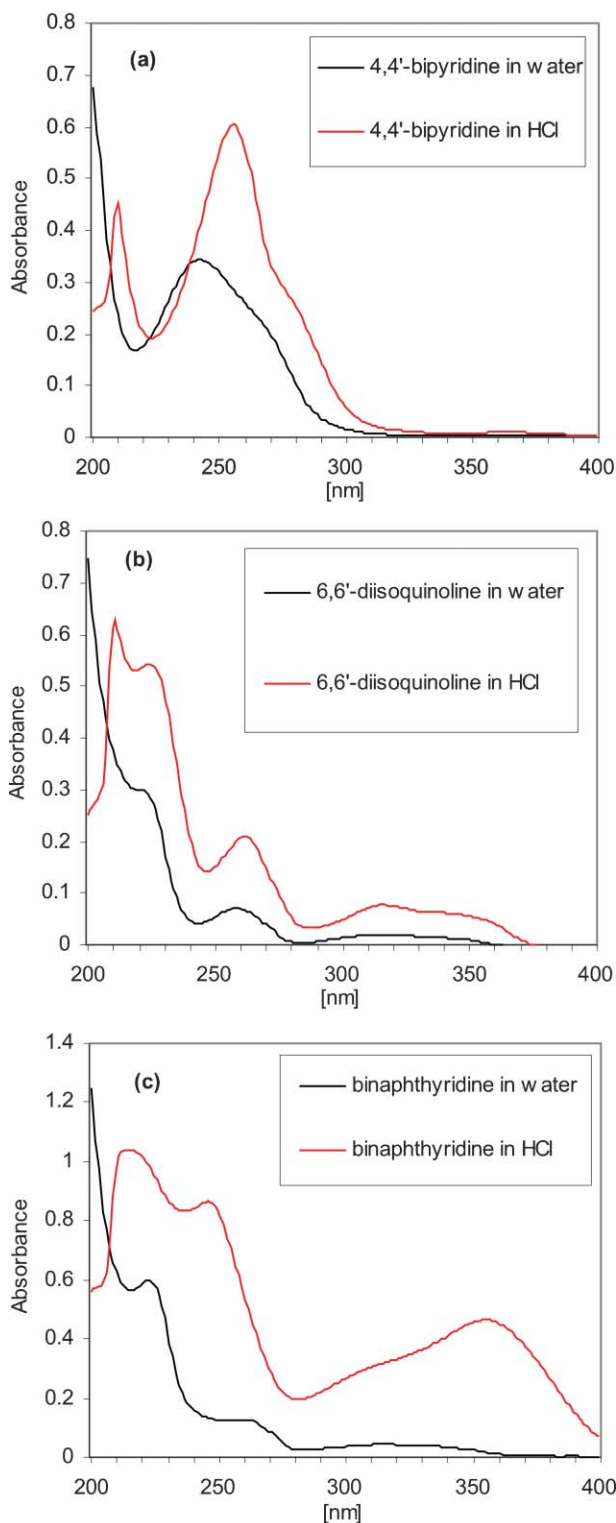
Structure Database study has recently shown that hydrate formation is above average (*ca.* 40 and 36%) for pyridinium chloride and phosphate salt structures, respectively, when compared to the total of pyridinium salts (22% hydrate formation).<sup>23</sup> In the following we will compare and interpret the crystal packing based on the supramolecular interactions.

### Crystal packing and hydrogen bonding

Generally, the packing arrangements found in 3–6 can be rationalized by a separation of the hydrophobic C–H backbone of the bipyridines from the hydrophilic N–H, phosphate or chloride and water part.<sup>24</sup>

In the structure of 3 the bipyridinium cations stack in columns along the *c* direction (Fig. 2). Within these columns the bipyridine exhibits  $\pi$ -stacking interactions (see below). These columns are separated through the 3-D hydrogen bonding framework of the phosphate ions and water molecules (Fig. 3). The phosphate ions form 2-D layers in the (1 0 0) and (2 0 0) plane which are interconnected by the chains of water molecules running parallel to the *c* direction (Fig. 3). Here again, the additional electrostatic attraction leads to shorter H...O or O...O contacts between phosphate ions than between water and phosphate (Table 1).

In the structure of 4 the bipyridinium cations are separated from each other both through the hydrophilic phosphate–water strands and the  $\pi$ – $\pi$  interactions to the naphthyl groups of the anion (Fig. 4, Table 3). In 4 the phosphate moieties and the water molecules form strands along the *a* direction with the water bridging between the deprotonated (RO)<sub>2</sub>PO<sub>2</sub><sup>−</sup> groups (Fig. 5). 4,4'-Bipyridin-1,1'-ium salts have been structurally



**Fig. 1** UV-Vis spectra of (a) 4,4'-bipyridine, (b) 6,6'-diisoquinoline and (c) 2,2'-bi-1,6-naphthyridine in water or 12 mol l<sup>−1</sup> HCl. Peak shift through protonation from 243 to 257 nm in (a), from 222 to 225 and 259 to 261 nm in (b) and from 224 to 246 nm in (c). New sharp peak at 211 nm in (a) and (b) and at 216 nm in (c).

characterized with the mineral acid anions chloride,<sup>2,25</sup> bromide,<sup>26</sup> nitrate,<sup>25,27</sup> as well as perchlorate<sup>28</sup> and *trans*-hyponitrite.<sup>29</sup> From these, the structures of 3 and 4 with the

**Table 1** Hydrogen bonding interactions in **3** and **4**<sup>a</sup>

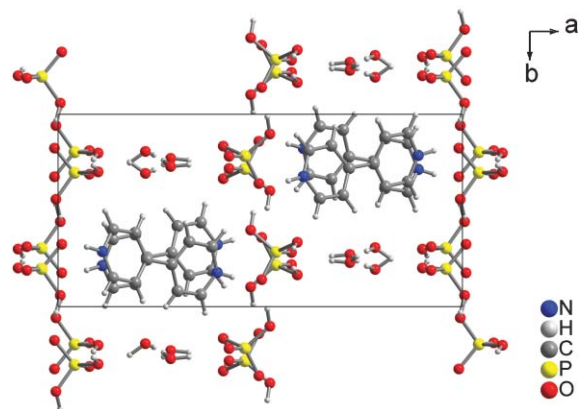
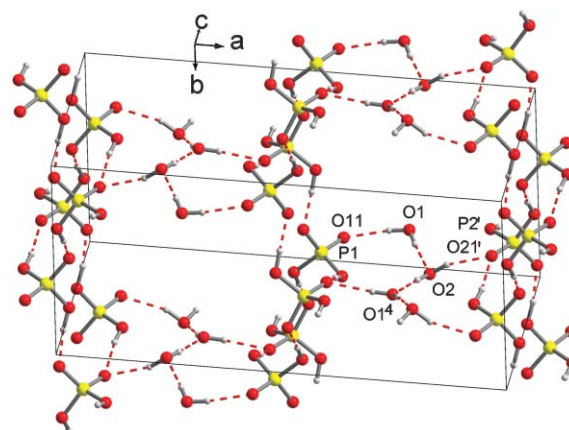
D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
<b>3</b> N–H···O(phosphate):				
N1–H···O22	1.01(3)	1.58(3)	2.588(2)	172(2)
N2–H···O12	0.94(3)	1.69(3)	2.615(2)	171(2)
O–H···O inter-phosphate (cf. Fig. 3):				
O13–H···O12 <sup>2</sup>	0.93(3)	1.60(3)	2.529(2)	178(3)
O14–H···O11 <sup>4</sup>	0.71(3)	1.89(3)	2.590(2)	169(3)
O23–H···O22 <sup>2'</sup>	0.95(4)	1.53(3)	2.471(2)	171(3)
O24–H···O21 <sup>4'</sup>	0.82(3)	1.76(3)	2.574(2)	171(3)
O–H···O(water, phosphate) (cf. Fig. 3):				
O1–H···O2	0.79(4)	1.92(4)	2.704(2)	171(3)
O1–H···O11	0.85(4)	1.93(4)	2.777(2)	173(3)
O2–H···O21'	0.91(4)	1.96(4)	2.829(2)	160(3)
O2–H···O1 <sup>4'</sup>	0.92(4)	1.79(4)	2.703(3)	175(3)
Symmetry transformations: <sup>1</sup> = 1 + x, y, 1 + z; <sup>2</sup> = 1 – x, y + 1/2, –z + 3/2; <sup>2'</sup> = –x, y – 1/2, –z – 1/2; <sup>4</sup> = x, –y + 3/2, z – 1/2; <sup>4'</sup> = x, –y + 3/2, z + 1/2.				
<b>4</b> N–H···O(phosphate):				
N1–H···O8	0.95(2)	1.74(2)	2.686(3)	179(2)
N2–H···O3	0.99(2)	1.62(2)	2.606(3)	173(2)
O–H···O(water, phosphate) (cf. Fig. 5):				
O9–H···O7	0.92(3)	1.92(3)	2.801(3)	160(2)
O9–H···O8 <sup>3</sup>	0.88(2)	1.97(3)	2.786(3)	154(2)
O10 <sup>2</sup> –H···O9	0.99(3)	1.98(3)	2.942(3)	166(2)
O10–H···O3	1.03(3)	1.84(3)	2.864(3)	175(2)
O11–H···O4	0.80	2.02	2.798(3)	164
O11 <sup>4</sup> –H···O4 <sup>2</sup>	0.85	1.94	2.789(4)	180
Symmetry transformations: <sup>2</sup> = 1/2 – x, 1/2 + y, 1/2 – z; <sup>3</sup> = 1 – x, 1 – y, 1 – z; <sup>4</sup> = 3/2 + x, 1/2 – y, 1/2 + z.				
<sup>a</sup> D = Donor, A = acceptor. For found and refined atoms the standard deviations are given.				

**Table 2** Hydrogen bonding interactions in **5**–**7**<sup>a</sup>

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
<b>5</b>				
N–H···Cl	0.98(5)	2.04(5)	3.019(4)	175(4)
O–H···Cl	1.03(6)	2.23(7)	3.195(5)	155(7)
O–H···O <sup>2</sup>	0.85	1.95	2.81(1)	180
O–H···O <sup>2'</sup>	0.80	1.88	2.676(9)	180
Symmetry transformations: <sup>2</sup> = –1 – x, 2 – y, 3 – z; <sup>2'</sup> = –x, 2 – y, 3 – z.				
<b>6</b> (cf. Fig. 6)				
N1–H···Cl	0.91(2)	2.10(2)	2.998(1)	171(2)
O–H···Cl	0.88(3)	2.38(3)	3.256(2)	174(3)
O–H···O <sup>2</sup>	0.99	1.79	2.729(4)	157
O–H···O <sup>2'</sup>	0.95	1.92	2.767(4)	147
Symmetry transformations: <sup>2</sup> = –x, 1 – y, 1 – z; <sup>2'</sup> = 1 – x, 1 – y, 1 – z.				
<b>7</b> (cf. Fig. 7)				
N1–H···Cl2 <sup>2m</sup>	0.83(2)	2.49(2)	3.131(2)	135(2)
N1–H···Cl1 <sup>2r</sup>	0.83(2)	2.87(2)	3.557(2)	142(2)
N2–H···Cl5	0.82(2)	2.33(2)	3.128(2)	164(2)
N4–H···Cl2 <sup>2r</sup>	0.80(2)	2.64(2)	3.217(2)	131(2)
N4–H···Cl1 <sup>2</sup>	0.80(2)	2.69(2)	3.381(2)	145(2)
N2–H···N3	0.82(2)	2.24(2)	2.592(2)	106(2)
Symmetry transformations: <sup>2</sup> = –x, 1 – y, 1 – z; <sup>2'</sup> = –x, 2 – y, –z; <sup>2''</sup> = 1 – x, 1 – y, 1 – z; <sup>2'''</sup> = 1 – x, 2 – y, –z.				
<sup>a</sup> D = Donor, A = acceptor. For found and refined atoms the standard deviations are given.				

phosphate anions differ, in that both structures crystallized as hydrates, thereby creating extended hydrogen bonding patterns. In **3** the dihydrogenphosphate is also an H-bond donor besides the bipyridinium dication.

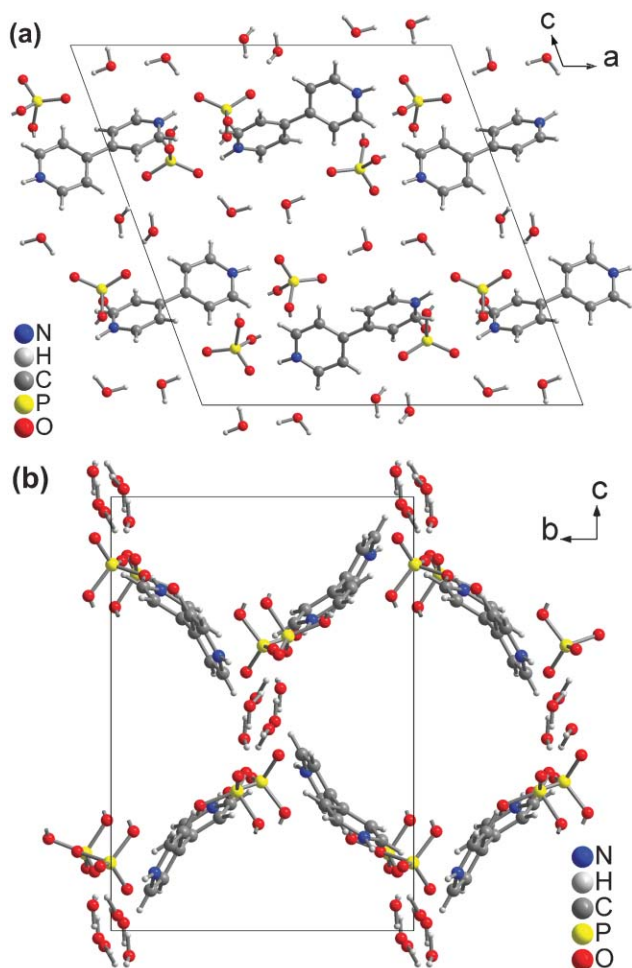
The idea of using the enantiomeric *R*-binaphthalenediylphosphate as a building block in **4** failed, to the extent

**Fig. 2** Projection of the crystal packing in **3** onto the (0 0 1) plane. Hydrogen bonds are not shown for clarity. Click here to access a 3D view of Fig. 2**Fig. 3** Phosphate and water hydrogen bonding network in **3**. See Table 1 for details. Click here to access a 3D view of Fig. 3

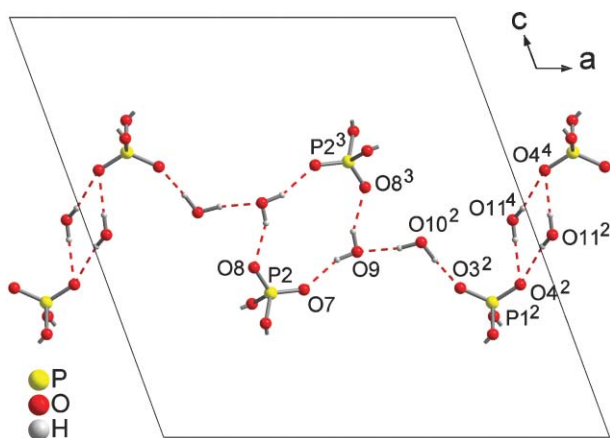
that crystallization experiments with the *R*-hydrogenphosphate were unsuccessful, yielding only oils. A variety of solvents, such as MeOH, EtOH, ethyl acetate, acetone, water and combinations thereof, were tried in these crystallization experiments. This failure is contrary to the use of *S*-binaphthalenediyl hydrogenphosphate as a good optical resolution agent of amines and its application in the resolution of pharmaceutical intermediates by fractional crystallization.<sup>30</sup> This failure is, however, consistent with difficulties we experienced when trying to crystallize *R*- or *S*-1,1'-bi-2-naphtholate metal salts<sup>31</sup> or *R*-binaphthalenediylphosphate amines<sup>32</sup> compared to the facile crystallization of the racemic mixtures.

The isomorphous compounds **5** and **6** feature the elongated bipyridine analogs 6,6'-diisoquinoline and 2,2'-bi-1,6-naphthyridine. There is a crystallographically imposed inversion symmetry on the isoquinolinium and naphthyridinium systems. Similar to the structure of **3** the bipyridinium-analog cations stack in columns along the *a* direction (Fig. 6). Within these columns the aromatic moieties exhibit  $\pi$ -stacking interactions (see below). These columns are separated through the “chains” of chloride anions and a chain of water molecules both running colinear to *a*.

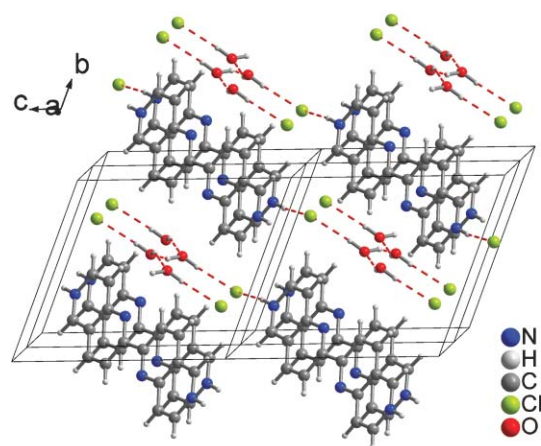




**Fig. 4** Projection of the crystal packing in **4** onto the (0 1 0) plane (a) and the (1 0 0) plane (b). Hydrogen bonds and naphthyl moieties are not shown for clarity. The voids along *a* in (b) are occupied by the naphthyl groups. Click here to access a 3D view of Fig. 4a. Click here to access a 3D view of Fig. 4b.



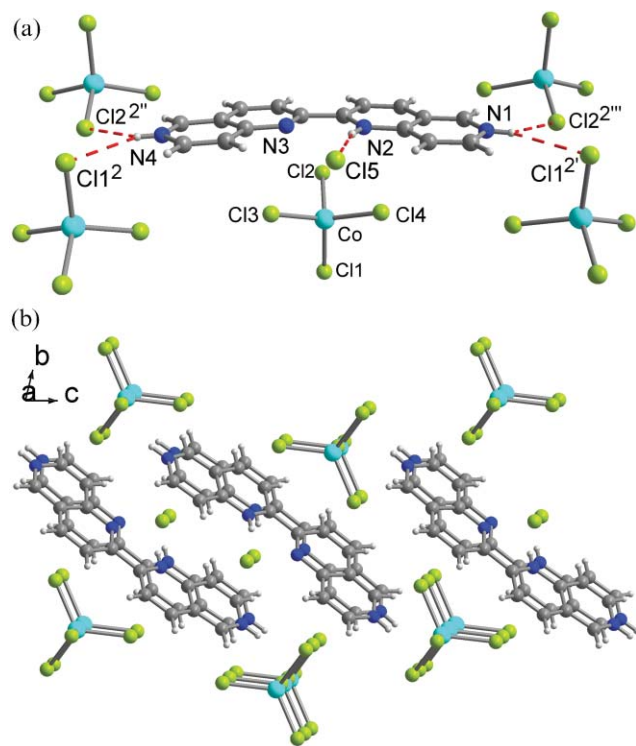
**Fig. 5** Phosphate and water hydrogen bonding network in **4**. See Table 1 for details. O11 is crystallographically disordered around a center of inversion. Hence, only one of two O11 positions shown is occupied. Click here to access a 3D view of Fig. 5



**Fig. 6** Crystal packing in isomorphous **5** and **6** (with **6** shown), viewed approximately along *a*. See Table 2 for hydrogen-bonding details, Table 3 for  $\pi$ -stacking. Click here to access a 3D view of Fig. 6

In the structure of **7** the triprotonated 2,2'-bi-1,6-naphthridin-1,6,6'-ium trication crystallizes with a chloride and a tetrachlorocobaltate(II) anion. The trications are fully separated from each other in terms of  $\pi$ - $\pi$ -stacking interactions (see below) by the surrounding anions (Fig. 7). The anion  $\text{CoCl}_4^{2-}$  has also been described with the 4,4'-bipyridin-1,1'-ium cation.<sup>33</sup>

The (N-)H $\cdots$ Cl $^-$  distances in **5** and **6** lie to the very short end (2.0 Å) of what is typically observed between N-H donors and chloride (Cl $^-$ ) acceptors, based on an analysis of the



**Fig. 7** Hydrogen bonding (a) and crystal packing (b) in **7**. See Table 2 for hydrogen-bonding details, Table 3 for  $\pi$ -interactions. Click here to access a 3D view of Fig. 7a. Click here to access a 3D view of Fig. 7b.

**Table 3** Distances ( $d/\text{\AA}$ ) and angles ( $^\circ$ ) for the strongest  $\pi$ -contacts in the crystal structures<sup>a</sup>

Compound, $\pi$ - $\pi$ interactions	ring(I)···ring(J)	$d[\text{Cg(I)}\cdots\text{Cg(J)}]^b$	$\alpha^c$	$\beta^d$	$\gamma^e$	$d[\text{Cg(I)}\cdots\text{P(J)}]^f$	$d[\text{Cg(J)}\cdots\text{P(I)}]^g$	$d[a]^h$
3, py-N1···py-N2 <sup>i</sup>		3.91	4.81	17.0	21.8	3.63	3.74	1.14, 1.45
4, py-N1···naphthyl_1		3.65	9.45	23.4	16.1	3.51	3.35	1.01, 1.45
py-N1···naphthyl_2		3.94	5.09	22.3	26.7	3.52	3.65	1.49, 1.77
5, C <sub>6</sub> ···C <sub>6</sub> of isoquinoline <sup>ii</sup>		3.72	0.0	18.9	18.9	3.52	3.52	1.20
py-N···C <sub>6</sub> <sup>iii</sup>		3.71	1.44	23.8	22.4	3.43	3.40	1.41, 1.50
6, inner ring···inner ring <sup>iv</sup>		3.66	0.0	19.0	19.0	3.46	3.46	1.19
outer ring···inner ring <sup>v</sup>		3.71	1.47	24.9	23.5	3.41	3.37	1.48, 1.56
7 no meaningful $\pi$ - $\pi$ interactions found								

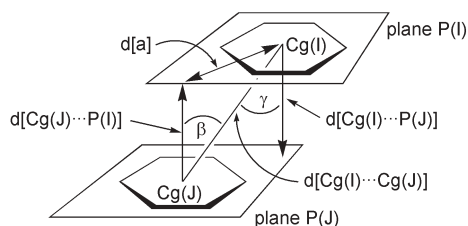
Compound, Cl- $\pi$ interactions	$d[\text{Cl}\cdots\text{Cg}]^i$	$d[\text{Cl}\cdots\perp]^j$	$\gamma^e$	$\angle[\text{Co}-\text{Cl}\cdots\text{Cg}]^k$	$\angle[\text{Co}-\text{Cl}\cdots\pi]^l$
5, Cl <sup>-</sup> ···ring-N <sup>v</sup>	3.529	3.420(3)			
(Individual Cl···atom distances of ring N1 <sup>v</sup> : to N1 3.577(1), C1 4.010(1), C2 4.273(1) C3 4.177(2), C8 3.750(1), C9 3.425(1))					
6, Cl <sup>-</sup> ···ring-N1 <sup>iii</sup>	3.557	3.3571(5)			
(Individual Cl···atom distances of ring N1 <sup>iii</sup> : to N1 3.5242(3), C1 3.3607(3), C2 3.6753(4), C6 4.0971(5), C7 4.2085(4), C8 3.9471(3))					
7, Co-Cl1···ring-N4 <sup>vi</sup>	3.334(1)	3.312	6.47	165.03(3)	81.0
Co-Cl3···ring-N3	3.417(1)	3.379	8.55	106.21(2)	17.6
Co-Cl4···ring-N2	3.379(1)	3.311	11.46	102.74(2)	18.6
anion Cl5···ring-N1 <sup>vii</sup>	3.346(5)	3.233(5)			
(Individual Cl5···atom distances of ring N1 <sup>vii</sup> : to C4 3.304(2), C5 3.357(2), N1 3.649(2), C6 3.909(2), C7 3.877(2), C8 3.565(2))					

<sup>a</sup> For a graphical depiction of distances and angles in the assessment of the  $\pi$ -contacts, see Scheme 2. Pyridyl rings of the bipy ligands are differentiated by their nitrogen atoms; the two rings of the isoquinoline moiety are differentiated as C<sub>6</sub> and py-N, the two rings of the naphthyridine moiety are differentiated as inner or outer ring in **6** or by their nitrogen atom in **7**. <sup>b</sup> Centroid-centroid distance. <sup>c</sup> Dihedral angle between the ring planes. <sup>d</sup> Angle between the centroid vector Cg(I)···Cg(J) and the normal to the plane I. <sup>e</sup> Angle between the centroid vector Cg(I)···Cg(J) or Cl···Cg and the normal to the plane J. <sup>f</sup> Perpendicular distance of Cg(I) on ring plane J. <sup>g</sup> Perpendicular distance of Cg(J) on ring plane I. <sup>h</sup> Vertical displacement between ring centroids; two values if the two rings are not exactly parallel (*i.e.*  $\alpha \neq 0^\circ$ ) because of the two reference planes P(J,I). <sup>i</sup> Cl-centroid distance. <sup>j</sup> Perpendicular distance of Cl on ring plane. <sup>k</sup> Co-Cl-centroid angle. <sup>l</sup> Angle of Co-Cl bond with ring plane. <sup>m</sup> Symmetry transformations: i =  $x, 3/2 - y, -1/2 + z$ ; ii =  $1 - x, 1 - y, 1 - z$ ; iii =  $-1 + x, y, z$ ; iv =  $-1 - x, 2 - y, 3 - z$ ; v =  $1 + x, y, z$ ; vi =  $-1 + x, 1 + y, z$ ; vii =  $1 - x, 1 - y, -z$ .

Cambridge Structural Database.<sup>2</sup> From the structure of **7** it is also evident that the hydrogen bond acceptor strength of Cl follows the sequence Cl<sup>-</sup> > Cl-M (here M = Co).<sup>34,35</sup> In comparison between the shorter (and stronger) N-H···Cl<sup>-</sup> contacts and the weaker N-H···Cl-Co contacts, the former also feature larger (more linear) N-H···Cl bond angles (Fig. 8). The more bent N-H···Cl-M contacts are rationalized with a higher basicity of p-type lone pairs over sp-type lone pairs.<sup>34,36</sup> The presence of a strongly bent intramolecular N-H···N hydrogen contact between N2 and N3 (Fig. 7a—not drawn, Table 2) is probably the origin for the binaphthyridinium to assume the otherwise less preferred *s-cis* conformation in **7**, compared to the *s-trans* conformation in **6**.<sup>37</sup>

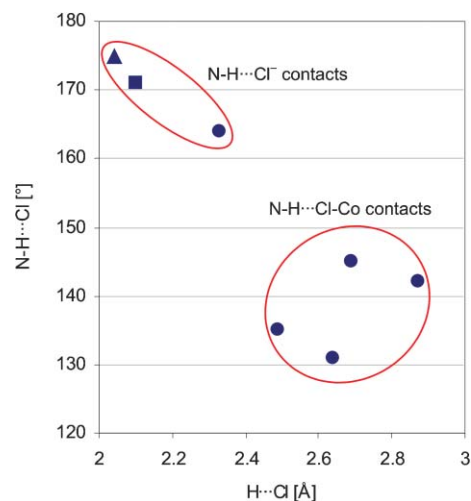
### $\pi$ - and C-H···X interactions

The aromatic nitrogen ligand systems in **3–7** let one expect the presence of supramolecular  $\pi$ - $\pi$  and C-H··· $\pi$  interactions.<sup>9–11</sup> Indeed in **4**, **5** and **6** are found rather short centroid-centroid contacts ( $\text{Cg}\cdots\text{Cg} < 3.8 \text{\AA}$ ), small slip angles ( $\beta, \gamma < 25^\circ$ ) and vertical displacements ( $d[a] < 1.5 \text{\AA}$ ) which translate into a

**Scheme 2** Graphical presentation of the parameters used in Table 3 for the description of  $\pi$ - $\pi$  stacking.

sizeable overlap of the pyridyl-plane areas and are indicative of strong  $\pi$ -stacking interactions (Table 3).<sup>9,10</sup> In **3** the  $\pi$ -interaction is still medium to strong, since weak  $\pi$ -interactions would have rather long centroid-centroid distances ( $>4.7 \text{\AA}$ ) together with large slip angles ( $>35^\circ$ ) and vertical displacements ( $>3.0 \text{\AA}$ ) between the ring centroids.<sup>9</sup>

Remarkably, no  $\pi$ - $\pi$  interactions are found in **7**. They appear to be replaced by Cl··· $\pi$  interactions both from the  $[\text{CoCl}_4]^{2-}$  and Cl<sup>-</sup> anion (Table 3). Such anion- $\pi$  interactions are a matter of current interest with few examples, so far.<sup>12</sup> Similar Cl<sup>-</sup>··· $\pi$  interactions are also observed in **5** and **6**, albeit

**Fig. 8** Scattergram N-H···Cl angles vs. H···Cl distances in the structures of **5** (▲), **6** (■) and **7** (●).

of greater distance than in **7**. The  $\text{Cl}^- \cdots \pi$  interactions in **7** are shorter than those reported to the pyridyl rings in  $[\text{Cu}_4(\text{azadendtriz})\text{Cl}_4](\text{Cl})_4(\text{H}_2\text{O})_{13}$ .<sup>38</sup> Only with more electron deficient  $\pi$ -systems, such as triazine the  $\text{Cl}^- \cdots \pi$ -ring distances are still shorter, as in  $[\text{L}_2(\text{CuCl})_3][\text{CuCl}_4]\text{Cl}$  ( $\text{L}$  = hexakis (pyridin-2-yl)-[1,3,5]-triazine-2,4,6-triamine).<sup>39</sup>

With respect to  $\text{C}-\text{H} \cdots \pi$  interactions, in **4** a single  $\text{C}-\text{H} \cdots \pi$  contact is found with  $\text{H} \cdots \text{Cg} < 3.0 \text{ \AA}$  and  $\gamma < 30.0^\circ$ . In all the other structures  $\text{C}-\text{H} \cdots \pi$  interactions within these limits (set by PLATON) are absent.

In **5** and **6**  $\text{C}-\text{H} \cdots \text{Cl}$  interactions with  $\text{H} \cdots \text{Cl}$  contacts between 2.65–2.78  $\text{Å}$  and  $\text{C}-\text{H} \cdots \text{Cl}$  angles between 148–162° add to the supramolecular  $\text{N}/\text{O}-\text{H} \cdots \text{Cl}$ ,  $\text{O}-\text{H} \cdots \text{O}$  and  $\pi-\pi$  interactions.

In **7**  $\text{C}-\text{H} \cdots \text{Cl}$  interactions to  $[\text{CoCl}_4]^{2-}$  and  $\text{Cl}^-$  with  $\text{H} \cdots \text{Cl}$  contacts between 2.65–2.80  $\text{Å}$  and  $\text{C}-\text{H} \cdots \text{Cl}$  angles between 115–161° complement the other supramolecular  $\text{N}-\text{H} \cdots \text{Cl}$  and  $(\text{Co})-\text{Cl} \cdots \pi$  interactions. The  $\text{C}-\text{H} \cdots \text{Cl}$  ranges correspond to values reported for  $[\text{Cu}_2(\text{HB}(\text{triazolyl})_3)(\text{OH})_2]\text{Cl} \cdot 6\text{H}_2\text{O}$  and  $[\text{CuCl}(\text{HB}(\text{triazolyl})_3)] \cdot \text{H}_2\text{O}$ <sup>8</sup> and are somewhat longer than for  $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ <sup>40</sup> and  $[\text{Pt}(1-\text{O}_2\text{N}-9\{(2-\text{Me}_2\text{N}-\text{ethyl})\text{amino}\}\text{acridinato})\text{Cl}]$ .<sup>6</sup>

A few (five and eight)  $\text{C}-\text{H} \cdots \text{O}$  interactions with  $\text{H} \cdots \text{O}$  contacts between 2.17–2.56  $\text{Å}$ ,  $\text{C} \cdots \text{O}$  contacts between 2.930 and 3.374  $\text{Å}$  and  $\text{C}-\text{H} \cdots \text{O}$  angles between 112–162° are observed in **3** and **4**, respectively, whereas in **5** and **6** no  $\text{C}-\text{H} \cdots \text{O}$  contacts are seen.

## Conclusions

The principal interactions controlling the structures of the bipyridinium salts are  $\text{N}^+-\text{H} \cdots \text{anion}$  hydrogen bonds. In the structures reported here  $\text{N}^+-\text{H}$  hydrogen bonding occurs only to the chloride or phosphate anion and not to water of crystallization, despite the formation of dihydrates. The packing in the diprotonated bipyridines **3–6** can be rationalized by a separation of the hydrophobic  $\text{C}-\text{H}$  backbone of the bipyridines from the hydrophilic  $\text{N}-\text{H}$ , phosphate or chloride and water part. Thus, the role of  $\pi-\pi$  stacking is significant in **3–6**. In the triprotonated binaphthyridinium salt **7** the  $\pi$ -stacking is replaced by remarkably short  $\text{Cl}^-$ -anion- $\pi$  interactions. Furthermore, weaker  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds in **3** and **4** and  $\text{C}-\text{H} \cdots \text{Cl}$  contacts in **5–7** add to the supramolecular forces.

## Experimental

Elemental analyses were obtained on a VarioEL from Elementaranalysensysteme GmbH. IR spectra (2–4 mg compound/300 mg KBr pellet) were measured on a Bruker Optik IFS25. NMR spectra were collected on a Bruker ARX200 (200 MHz for  $^1\text{H}$ , 50.3 MHz for  $^{13}\text{C}$  and 81 MHz for  $^{31}\text{P}$ , both with  $^1\text{H}$  broad band decoupling) with calibration against the residual protonated solvent signal ( $\text{CDCl}_3$   $^1\text{H}$  NMR 7.26 ppm,  $^{13}\text{C}$  NMR 77.0 ppm;  $d_6$ -DMSO  $^1\text{H}$  NMR 2.52 ppm,  $^{13}\text{C}$  NMR 39.5 ppm) or against an external standard of 85%  $\text{H}_3\text{PO}_4$ . Proton NMR multiplicities are stated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). UV/Vis spectra were measured on Jasco V570 UV-VIS-NIR

spectrometer. The UV/Vis spectra in the range of 200–400 nm were measured against a 12 mol  $\text{l}^{-1}$  HCl reference solution in the second beam line of the instrument. Mass spectra were obtained with a GC-MS Finnigan MAT in solid probe electron impact mode (ionization energy 70 eV).

4,4'-Bipyridine and  $\text{PPh}_3$  were purchased from Aldrich. *rac*-1,1'-Bi-2-naphthol was prepared by the oxidative coupling of 2-naphthol through  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  at 50 °C and recrystallized from toluene. The analytical data matched the literature values.<sup>41</sup> 6-Bromoisoquinoline was prepared from 4-bromobenzaldehyde and aminoacetaldehyde dimethylacetal, followed by reaction with ethylchloroformate, trimethylphosphine and  $\text{TiCl}_4$  and purified by sublimation with the analytical data in agreement with the literature values.<sup>42</sup> 2,2'-Bi-1,6-naphthyridine was prepared by a literature procedure.<sup>43</sup> Other chemicals were of reagent grade or better and used without further purification. The silica gel drying agent was "KC-Trockenperlen (drying pearls) Orange<sup>®</sup>" from Engelhard-Process Chemicals GmbH, Nienburg, Germany.

## Syntheses

**6,6'-Diisoquinoline (1).** A 250 ml Schlenk flask was charged with 2.37 g (10 mmol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 10.50 g (40 mmol) of  $\text{PPh}_3$  in 100 ml of anhydrous dimethylformamide. The deep blue solution was carefully degassed and saturated with argon (5.0 grade). The solution was warmed to 50 °C and 0.70 g (11 mmol) of zinc dust were added under argon. After stirring the mixture for 1 h, accompanied by a color change to red-brown, 2.07 g (10 mmol) of 6-bromoisoquinoline<sup>42</sup> were added and stirring was continued for 24 h at 50 °C. For workup the solution was narrowed to half of its original volume in vacuum, poured in 100 ml of conc. ammonia and stirred for 24 h at room temperature. Formation of the complex  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  gave rise to a deep blue color. The mixture was extracted five times with 100 ml each of diethyl ether. The combined organic phase was extracted three times with 80 ml each of 6 mol  $\text{l}^{-1}$  hydrochloric acid to separate the product as the hydrochloric salt from triphenyl phosphine. The combined aqueous phases were made alkaline by careful addition of solid  $\text{Na}_2\text{CO}_3$  and extracted five times with 80 ml each of diethyl ether. The combined ether phase was dried over  $\text{MgSO}_4$  and the solvent removed with a rotary evaporator to leave a yellow oil which crystallized after some time. The raw product was washed with 20 ml of cold (0 °C) diethyl ether to give 2.0 g (80%) of a pale yellow solid (mp 146 °C).

$\text{C}_{18}\text{H}_{12}\text{N}_2$  (256.1): calc. C 84.35, H 4.72, N 10.93; found C 84.54, H 4.84, N 9.87%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 9.36 (s, 2H, H1, H1'), 8.64 (d, 2H,  $J = 5.8 \text{ Hz}$ , H3, H3'), 8.16 (d, 4H,  $J = 8.7 \text{ Hz}$ , H5, H5', H8, H8'), 8.02 (dd, 2H,  $J_1 = 8.5 \text{ Hz}$ ,  $J_2 = 1.68 \text{ Hz}$ , H7, H7'), 7.76 (d, 2H,  $J = 5.8 \text{ Hz}$ , H4, H4').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 152.4 (C1, C1'), 143.8 (C3, C3'), 142.1 (C6, C6'), 136.1 (C4a, C4a'), 128.5 (C8, C8'), 128.0 (C8a, C8a'), 127.1 (C7, C7'), 125.2 (C5, C5'), 120.7 (C4, C4'). IR ( $\text{cm}^{-1}$ ) 1627, 877, 827, 643 (strong signals only). MS ( $m/z$ ) 256.1 (100% [ $\text{M}]^+$ )

## 1,1'-Binaphthalene-2,2'-diyl phosphate (2)

The compound was synthesized by a modified literature procedure.<sup>44</sup> A 250 ml Schlenk flask was evacuated, refilled



with argon and charged under argon with a solution of 10 g (35 mmol) of *rac*-1,1'-bi-2-naphthol in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> and 30 ml of pyridine. The solution was cooled to 0 °C in an ice bath and 4 ml (6.6 g, 4.3 mmol) of POCl<sub>3</sub> were added dropwise. The mixture was heated to reflux for 3 h, then the solvent completely (to avoid pyridine and POCl<sub>3</sub> residues) removed in vacuum. The residue was dissolved in a hot sodium carbonate solution prepared from 15 g Na<sub>2</sub>CO<sub>3</sub> in 400 ml of H<sub>2</sub>O. Finely powdered activated carbon (5 g) was added to the solution, the mixture heated to reflux for 20 min in an open flask (to remove any residual pyridine) and filtered hot through a paper filter. After cooling to 5 °C, the solution was acidified dropwise with 12 mol l<sup>-1</sup> hydrochloric acid to yield a colorless precipitate. (Without pre-cooling a yellow rather impure oil instead of a colorless powder was obtained.) After stirring for 12 h at room temperature the precipitate was separated by filtration and dried in vacuum to yield 10.3 g (85%) of a finely powdered colorless solid (mp >180 °C). C<sub>20</sub>H<sub>13</sub>O<sub>4</sub>P (348.3): calc. C 68.97, H 3.76; found C 67.79, H 3.89%. <sup>31</sup>P NMR (d<sub>6</sub>-DMSO) 4.5.

**4,4'-Bipyridin-1,1'-ium bis(dihydrogenphosphate) dihydrate, (C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (3).** 4,4'-Bipyridine (0.468 g, 3.0 mmol) and H<sub>3</sub>PO<sub>4</sub> (85%, 1.1 ml, 9.0 mmol) were dissolved in 25 ml of distilled water. The pH value for the clear solution was adjusted to 3.1 using triethylamine. The solution was stirred for 6 h at room temperature. Colorless crystals were collected after 3 d of slow solvent evaporation (yield 0.75 g, 71%). C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>·2H<sub>2</sub>O (388.20): calc. C 30.94, H 4.67, N 7.22; C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub> (352.17): calc. C 34.10, H 4.01, N 7.95; found C 34.10, H 4.13, 8.10%. IR (cm<sup>-1</sup>): 3444 (br, OH), 1631 (C=N), 1592 (C=C), 1482 (P=O), 1031 (P-O).

**4,4'-Bipyridin-1,1'-ium bis(1,1'-binaphthalene-2,2'-diyl phosphate)·2.5H<sub>2</sub>O, (C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>)(C<sub>20</sub>H<sub>12</sub>PO<sub>4</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (4).** 1,1'-Binaphthalene-2,2'-diyl phosphate (2) (0.174 g, 0.50 mmol) and 4,4'-bipyridine (0.039 g, 0.25 mmol) were dissolved in 10 ml of methanol and 10 ml of water. Evaporation of the solvent at room temperature yielded bright-yellow crystals after 5–7 d (yield 0.16–0.18 g, 72–80% from different batches) (mp > 180 °C). C<sub>50</sub>H<sub>39</sub>N<sub>2</sub>O<sub>10.5</sub>P<sub>2</sub> (897.77): calc. C 66.89, H 4.38, N 3.12; found C 66.70, H 4.31, N 3.10% (measured within 30 min after sample taken from mother liquor). IR (cm<sup>-1</sup>): 3480 (br), 3165 (br), 1634 (m), 1589 (m), 1507 (m), 1491 (m), 1463 (m), 1431 (w), 1362 (w), 1328 (m), 1269 (m), 1213 (s), 1213 (s), 1067 (s), 1030 (m), 989 (s), 956 (m), 833 (m), 811 (m), 753 (m), 716 (m), 695 (m), 658 (m), 632 (m), 615 (m), 581 (m), 567 (m) 536 (m), 536 (m), 490 (m). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 8.80 (s, 4H, bipy-H2/2'/6/6'), 8.10 (d, 2H, H4,4', <sup>3</sup>J<sub>3,4</sub> = 9 Hz), 8.04 (s, 4H, bipy-H3/3'/5/5'), 8.03 (d, 2H, H5,5', <sup>3</sup>J<sub>5,6</sub> = 12 Hz), 7.53 (d, 2H, H3/3', <sup>3</sup>J<sub>3,4</sub> = 8 Hz), 7.46 (t, 2H, H6/6', <sup>3</sup>J<sub>5,6,7</sub> = 5 Hz), 7.31 (t, 2H, H7/7', <sup>3</sup>J<sub>6,7,8</sub> = 8 Hz), 7.22 (d, 2H, H8/8', <sup>3</sup>J<sub>7,8</sub> = 8 Hz). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): 148.3 (C2/2'), 147.2 (bipy-C2/2'), 146.6 (bipy-C4/4'), 131.7 (C8a/8a'), 130.7 (C4a/4a'), 130.6 (C4/4'), 128.5 (C5/5'), 126.6 (bipy C3/3'), 126.0 (C7/7', C8/8'), 125.1 (C6/6'), 121.6 (C3/3'), 121.2 (C1/C1').

**6,6'-Diisoquinolin-2,2'-ium dichloride dihydrate, (C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O (5).** In a 100 ml one-necked flask 6,6'-diisoquinoline (1) (0.10 g, 0.39 mmol) was dissolved in 25 ml of hydrochloric acid (8 mol l<sup>-1</sup>). The flask was connected through a short bridge to a second 100 ml flask containing about 100 g of the silica gel drying agent KC-Trockenperlen Orange<sup>®</sup>. After about 7 d the product was obtained as light-yellow crystals (yield 0.068 g, 46%) (mp > 180 °C). C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (361.23): calc. C 59.85, H 5.02, N 7.75; found C 60.12, H 5.38, N 6.77% (measured within 30 min after sample taken from mother liquor). IR (cm<sup>-1</sup>): 1646 (s), 1437 (m), 1404 (m), 1174 (w), 1120 (m), 893 (m), 826 (m), 724 (s), 696 (s), 512 (s), 467 (m)

**2,2'-Bi-1,6-naphthyridin-6,6'-ium dichloride dihydrate, (C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>)Cl<sub>2</sub>·2H<sub>2</sub>O (6).** In a 100 ml one-necked flask 2,2'-bi-1,6-naphthyridine<sup>43</sup> (0.10 g, 0.39 mmol) was dissolved in 25 ml of hydrochloric acid (6 mol l<sup>-1</sup>). The flask was connected through a short bridge to a second 100 ml flask containing about 100 g of the silica gel drying agent KC-Trockenperlen Orange<sup>®</sup>. After about 7 d the product was obtained as light-yellow crystals (yield 0.09 g, 63%) (mp > 180 °C). C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (367.23): calc. C 54.61, H 3.06, N 15.95; C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub> (331.21): calc. C 58.02, H 3.65, N 16.92; found C 57.61, H 3.60, N 16.72%. IR (cm<sup>-1</sup>): 3040 (m), 2346 (br), 2092 (s), 1982 (s), 1890 (m), 1644 (s), 1464 (m), 1440 (s), 1390 (w), 1348 (s), 1300 (m), 1201 (s), 1067 (w), 1028 (m), 927 (m), 840 (s), 826 (s), 783 (m), 649 (w), 634 (w), 540 (m), 524 (s).

**2,2'-Bi-1,6-naphthyridin-1,6,6'-ium-tetrachlorocobaltate(II)-chloride, (C<sub>16</sub>H<sub>13</sub>N<sub>4</sub>)[CoCl<sub>4</sub>]Cl (7).** In a 100 ml one-necked flask 2,2'-bi-1,6-naphthyridine (0.10 g, 0.39 mmol) was dissolved in 25 ml of hydrochloric acid (12 mol l<sup>-1</sup>) and anhydrous CoCl<sub>2</sub> (0.50 g, 0.39 mmol) were added. The flask was connected through a short bridge to a second 100 ml flask containing about 100 g of the silica gel drying agent KC-Trockenperlen Orange<sup>®</sup>. After about 7 d the product was obtained as pale-green crystals (yield 0.12 g, 16%) (mp > 180 °C). C<sub>16</sub>H<sub>13</sub>Cl<sub>5</sub>CoN<sub>4</sub> (497.48): calc. C 38.79, H 2.69, N 11.28; found C 38.63, H 2.63, N 11.26%. IR (cm<sup>-1</sup>): 3445 (br), 3120 (br), 2360 (w), 2001 (w), 1642 (s), 1612 (s), 1560 (m), 1496 (m), 1474 (m), 1445 (m), 1381 (s), 1308 (w), 1248 (m), 1184 (s), 1130 (m), 1027 (w), 948 (w), 845 (s), 810 (m), 527 (w), 471 (w).

#### X-Ray crystallography

*Data Collection:* Bruker AXS with CCD area-detector, temperature 205(2) K, Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), graphite monochromator,  $\omega$ -scans, data collection and cell refinement with SMART,<sup>45</sup> data reduction with SAINT,<sup>45</sup> experimental absorption correction with SADABS except for **5**.<sup>46</sup> *Structure Analysis and Refinement:* The structure was solved by direct methods (SHELXS-97);<sup>47</sup> refinement was done by full-matrix least squares on  $F^2$  using the SHELXL-97 program suite.<sup>47</sup> All non-hydrogen positions were found and refined with anisotropic temperature factors.

Hydrogen atoms on the aromatic rings were placed at calculated positions with an appropriate riding model (AFIX

**Table 4** Crystal data and structure refinement for **3** to **7**

Compound	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
Empirical formula	C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>50</sub> H <sub>39</sub> N <sub>2</sub> O <sub>10.5</sub> P <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>13</sub> Cl <sub>5</sub> CoN <sub>4</sub>
<i>M</i> /g mol <sup>-1</sup>	388.20	897.77	365.24	367.23	497.48
Crystal size/mm	0.50 × 0.50 × 0.40	0.20 × 0.20 × 0.10	0.18 × 0.09 × 0.01	0.40 × 0.40 × 0.40	0.40 × 0.40 × 0.40
$\theta$ range/ $^\circ$	2.15–27.10	1.86–26.60	2.12–26.20	2.14–26.39	1.37–27.35
<i>h</i> ; <i>k</i> ; <i>l</i> range	–20, 24; –11, 8; –12, 12–23, 23; –14, 15; –24, 24	–6, 6; –11, 11; –12, 12–6, 6; –11, 10; –12, 12–8, 8; –13, 13; –19, 19			
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	18.937(2)	19.004(16)	4.9715(19)	4.9382(6)	6.2231(5)
<i>b</i> /Å	9.0233(9)	12.519(11)	9.162(4)	9.1344(11)	10.3057(8)
<i>c</i> /Å	9.4739(9)	19.141(18)	10.233(4)	10.2335(12)	15.4812(11)
$\alpha$ / $^\circ$	90	90	109.757(7)	110.667(2)	75.295(1)
$\beta$ / $^\circ$	92.801(2)	110.093(17)	92.325(7)	91.904(2)	79.299(1)
$\gamma$ / $^\circ$	90	90	98.082(7)	98.093(2)	74.715(1)
<i>V</i> /Å <sup>3</sup>	1616.9(3)	4277(7)	432.4(3)	425.88(9)	918.84(12)
<i>Z</i>	4	4	1	1	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.595	1.394	1.403	1.432	1.798
<i>F</i> (000)	808	1868	190	190	498
$\mu$ /mm <sup>-1</sup>	0.324	0.168	0.388	0.398	1.670
Max/min transmiss.	0.8813/0.8547	0.9834/0.9671	0.9961/0.9334	0.8571/0.8571	0.5548/0.5548
Reflections collected	9392	23013	3520	3470	7958
Indep. reflections	3556 ( <i>R</i> <sub>int</sub> = 0.0261)	8811 ( <i>R</i> <sub>int</sub> = 0.0286)	1725 ( <i>R</i> <sub>int</sub> = 0.2267) <sup>e</sup>	1724 ( <i>R</i> <sub>int</sub> = 0.0152)	4072 ( <i>R</i> <sub>int</sub> = 0.0175)
Obs. refl. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2360	6039	768	1500	3452
Parameters refined	247	607	116	115	244
Max./min. $\Delta\rho$ /e Å <sup>-3</sup>	0.464/–0.486	0.233/–0.392	0.329/–0.287	0.244/–0.184	0.555/–0.530
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0409/0.1039	0.0376/0.0905	0.0686/0.1079	0.0334/0.0938	0.0261/0.0657
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all reflect.) <sup>b</sup>	0.0668/0.1148	0.0610/0.0988	0.1561/0.1355	0.0386/0.0976	0.0320/0.0681
Goodness-of-fit on <i>F</i> <sup>2c</sup>	0.941	0.936	0.815	1.076	1.031
Weight. scheme <i>w</i> ; <i>a</i> / <i>b</i> <sup>d</sup> /0.0647/0.0000		0.0561/0.0000	0.0000/0.0000	0.0640/0.0151	0.0403/0.0000

<sup>a</sup> Largest difference peak and hole. <sup>b</sup>  $R_1 = [\sum(|F_o| - |F_c|)]/\sum|F_o|$ ;  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ . <sup>c</sup> Goodness-of-fit =  $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ . <sup>d</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$ . <sup>e</sup> Traced to crystal shape, very thin plate with the third crystal dimension only 0.01 mm.

43) and an isotropic temperature factor of Ueq(H) = 1.2 Ueq(C).

The protic hydrogen atoms on the pyridyl N atoms were found and refined with Ueq(H) = 1.5 Ueq(N) for all structures. All the protic hydrogen atoms on O (water or phosphate) were found and refined with Ueq(H) = 1.5 Ueq(O) for the structures of **3** and **7**. In the structures of **5** and **6** only one of the H atoms on O was found and refined. The other H-atom of the water molecule was disordered over two positions, found in either direction of the water chain but had to be fixed upon further refinement. In the structure of **4** both H atoms on O9 and O10 could be found and refined with Ueq(H) = 1.5 Ueq(O). The water molecule of O11 is crystallographically disordered with occupation factor 0.5 around a center of inversion to give a symmetry related water molecule with an unrealistic O...O separation of 2.11 Å. Together, this yields a single water molecule around this special position. The H-atoms of the half-occupied water molecule with O11 could be found but had to be fixed upon further refinement.

Details of the X-ray structure determinations and refinements are provided in Table 4. Graphics were drawn with DIAMOND (Version 3.0d).<sup>48</sup> Computations on the supramolecular interactions were carried out with PLATON for Windows.<sup>49</sup> CCDC reference numbers 276033 for **3**, 276030 for **4**, 276031 for **5**, 276032 for **6** and 276029 for **7**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b508944a

## Acknowledgement

We are greatly thankful to the University of Freiburg for financial assistance.

## References

- Reviews: L. Brammer, *Chem. Soc. Rev.*, 2004, **43**, 476; C. B. Aakeröy and A. M. Beatty, *Aust. J. Chem.*, 2001, **54**, 409; G. R. Desiraju, *Acc. Chem. Res.*, 1999, **35**, 565; D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; M. B. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283; S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; M. B. J. Zaworotko, *Chem. Commun.*, 2001, 1; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- B. Dolling, A. L. Gillon, A. G. Orpen, J. Starbuck and X.-M. Wang, *Chem. Commun.*, 2001, 567; A. Angeloni and A. B. G. Orpen, *Chem. Commun.*, 2001, 343; A. L. Gillon, A. B. G. Orpen, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín and C. Ruiz-Pérez, *Chem. Commun.*, 1999, 2287; G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653; G. R. Lewis and A. G. Orpen, *Chem. Commun.*, 1998, 1873.
- J. C. Marque Rivas and L. Brammer, *Inorg. Chem.*, 1998, **37**, 4756.
- S. Haddad and R. D. Willett, *Inorg. Chem.*, 2001, **40**, 2457.
- W. Frank and G. J. Reiß, *Inorg. Chem.*, 1997, **36**, 4593; W. Frank and G. J. Reiß, *Chem. Ber.*, 1996, **129**, 1355; W. Frank and G. B. J. Reiß, *Z. Naturforsch., B*, 1996, **51**, 1459; W. Frank and G. B. J. Reiß, *Z. Naturforsch., B*, 1996, **51**, 1464; W. Frank, G. B. J. Reiß and I. Kleinwächter, *Z. Anorg. Allg. Chem.*, 1996, **622**, 729.
- E. Ceci, R. Cini, J. Konopa, L. Maresca and G. Natile, *Inorg. Chem.*, 1996, **35**, 876.
- G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565; M. Mascal, *Chem. Commun.*, 1998, 303; T. Steiner, *Chem. Commun.*, 1997, 727; G. B. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.



- 8 C. Janiak and T. G. Scharmann, *Polyhedron*, 2003, **22**, 1123.
- 9 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- 10 Recent  $\pi$ -interactions for comparison: X.-J. Yang, F. Drepper, B. Wu, W.-H. Sun, W. Haehnel and C. Janiak, *Dalton Trans.*, 2005, 256 and supplementary material thereof; K. Abu-Shandi, H. Winkler, H. Paulsen, R. Glaum, B. Wu and C. Janiak, *Z. BAnorg. Allg. Chem.*, 2005, **631**, 2705; S. Banerjee, A. Ghosh, B. Wu, P.-G. Lassahn and C. Janiak, *Polyhedron*, 2005, **24**, 593; S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak and A. Ghosh, *Inorg. Chim. Acta*, 2005, **358**, 535; C. Zhang, G. Rheinwald, V. Lozan, B. Wu, P.-G. Lassahn, H. Lang and C. Janiak, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1259; E. Craven, E. Mutlu, D. Lundberg, S. Temizdemir, S. Dechert, H. Brombacher and C. Janiak, *Polyhedron*, 2002, **21**, 553; C. Zhang and C. Janiak, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1972; C. Zhang and C. Janiak, *J. Chem. Crystallogr.*, 2001, **31**, 29; C. Zhang, C. Janiak and H. Brombacher, *Z. Naturforsch., B*, 2001, **56**, 1205; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173.
- 11 M. Nishio, *CrystEngComm*, 2004, **6**, 130; M. Nishio, M. Hirota and Y. Umezawa, *The CH $\pi$  interaction (Evidence, Nature and consequences)*, Wiley-VCH, New York, 1998; Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207; C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann and O. M. Zipffel, *Eur. J. Inorg. Chem.*, 2000, 1229.
- 12 M. Mascal, A. Armstrong and M. D. Bartberger, *J. Am. Chem. Soc.*, 2002, **124**, 6274.
- 13 A. S. Batsanov, M. G. Davidson, J. A. K. Howard, S. Lamb and C. Lustig, *Chem. Commun.*, 1996, 1791.
- 14 J. A. Platts, S. T. Howard and K. Wozniak, *Chem. Commun.*, 1996, 63.
- 15 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, 2000.
- 16 H.-J. Schneider and A. Yatsimirski, *Principles and Methods in Supramolecular Chemistry*, Wiley, New York, 2000.
- 17 L. Brammer, *Dalton Trans.*, 2003, 3145; L. Brammer, J. B. K. Swearingen, E. A. Burton and P. Sherwood, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4956.
- 18 B. Antonioli, K. Gloe, K. Gloe, G. Goretzki, M. Grotjahn, H. HeBke, M. Langer, L. F. Lindoy, A. M. Mills and T. Söhnel, *Z. BAnorg. Allg. Chem.*, 2004, **630**, 998.
- 19 M. Felloni, A. J. Blake, P. Hubberstey, C. Wilson and M. Schröder, *CrystEngComm*, 2002, **4**, 483.
- 20 Recent examples: A. Moghimi, S. Sheshmani, A. Shokrollahi, M. Shamsipur, G. Kickelbick and H. Aghabozorg, *Z. Anorg. Allg. Chem.*, 2005, **631**, 160; Y.-Q. Sun, J. Zhang, Z.-F. Ju and G.-Y. Yang, *Aust. J. Chem.*, 2005, **58**, 572; M. Hemamalini, P. B. T. Muthiah, U. Rychlewska and A. Plutecka, *Acta Crystallogr.*, 2005, **C61**, 095; M. Du and X.-J. Zhao, *Acta Crystallogr.*, 2004, **E60**, o439; T. Akutagawa, T. Hasegawa, T. Nakamura and G. Saito, *CrystEngComm*, 2003, **5**, 54; S. Kawata, K. Adachi, Y. Sugiyama, M. K. Kabir and S. Kaizaki, *CrystEngComm*, 2002, **4**, 496.
- 21 M. S. Henry and M. Z. Hoffman, *J. Am. Chem. Soc.*, 1977, **99**, 5201.
- 22 C. Janiak, T. G. Scharmann, J. C. Green, R. P. G. Parkin, M. B. J. Kolm, E. Riedel, W. Mickler, J. Elguero, R. M. Claramunt and D. Sanz, *Chem. Eur. J.*, 1996, **2**, 992.
- 23 D. A. Haynes, W. Jones and W. D. S. Motherwell, *CrystEngComm*, 2005, **7**, 342.
- 24 Compare to the structure of [C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>(NH<sub>3</sub>)<sup>+</sup>]ClO<sub>4</sub>·H<sub>2</sub>O: P. Raghavaiah, S. Supriya and S. K. Das, *CrystEngComm*, 2005, **7**, 167.
- 25 P. A. Iyere, W. Y. Boadi, D. Atwood and S. Parkin, *Acta Crystallogr.*, 2003, **B59**, 664.
- 26 B. Mestvedt, *Acta Crystallogr.*, 1960, **13**, 1043; Bi-Song Zhang and Yue-Qing Zheng, *Z. Kristallogr. - New Cryst. Struct.*, 2003, **218**, 421.
- 27 T. G. R. Weakley, *Acta Crystallogr.*, 1987, **C43**, 2144; D. J. Barker, J. S. Buckleton, G. R. Clark, R. P. Cooney and C. E. F. Rickard, *J. BMol. Struct.*, 1990, **239**, 249.
- 28 S. W. Ng, *Acta Crystallogr.*, 1999, **C55**, 2105.
- 29 N. Arulsamy, D. S. Bohle, J. A. Imonigie and E. S. Sagan, *Inorg. Chem.*, 1999, **38**, 2716.
- 30 I. Fuji and N. Hirayama, *Helv. Chim. Acta*, 2002, **85**, 2946.
- 31 B. Paul, C. Näther, K. M. Fromm and C. Janiak, *CrystEngComm*, 2005, **7**, 309; B. Paul, C. Näther, B. Walfort, K. M. Fromm, B. Zimmermann, H. Lang and C. Janiak, *CrystEngComm*, 2004, **6**, 293.
- 32 T. Dorn, A.-C. Chamayou and C. Janiak, *New J. Chem.*, DOI: 10.1039/b510617f.
- 33 L. J. Barbour, L. R. MacGillivray and J. L. Atwood, *Supramol. Chem.*, 1996, **7**, 167; 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.
- 34 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, IUCr Oxford Science, 1999, ch. 3.2.1.2, p. 215ff.
- 35 F. Zordan, S. L. Purver, H. Adams and L. Brammer, *CrystEngComm*, 2005, **7**, 350.
- 36 G. Yap, A. L. Rheingold, P. Das and R. H. Crabtree, *Inorg. Chem.*, 1995, **34**, 3474.
- 37 H.-P. Wu, C. Janiak, L. Uehlin, P. Klüfers and P. Mayer, *Chem. Commun.*, 1998, 2637; C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121.
- 38 P. de Hoog, P. Gamez, I. Mutikainen, U. Turpeinen and J. Reedijk, *Angew. Chem., Int. Ed.*, 2004, **43**, 5815.
- 39 S. Demeshko, S. Dechert and F. Meyer, *J. Am. Chem. Soc.*, 2004, **126**, 4508.
- 40 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 540.
- 41 K. Ding, Y. Wang, L. Zhang, Y. Wu and T. Matura, *Tetrahedron*, 1996, **52**, 1005; E. Yashima, C. Yamamoto and Y. Okamoto, *J. Am. Chem. Soc.*, 1996, **118**, 17, 4036.
- 42 H. Nerenz, M. Meier, W. Grahn, A. Reisner, E. Schmäzlin, S. Stadler, K. Meerholz, C. Bräuchle and P. G. Jones, *J. Chem. Soc., Perkin Trans. 2*, 1998, 437.
- 43 C. Janiak, S. Deblon and L. Uehlin, *Synthesis*, 1999, **6**, 956.
- 44 S. Miyano, M. Tobita and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3522; Y. Y. Hoyano and R. E. Pincock, *Can. J. Chem.*, 1980, **58**, 134.
- 45 SMART, Data Collection Program for the CCD Area-Detector System; SAINT, Data Reduction and Frame Integration Program for the CCD Area-Detector System. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, 1997.
- 46 G. Sheldrick, Program SADABS: Area-detector absorption correction, University of Göttingen, Germany, 1996.
- 47 G. M. Sheldrick, SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.
- 48 DIAMOND 3.0d for Windows. Crystal Impact Gbr, Bonn, Germany; <http://www.crystalimpact.com/diamond>.
- 49 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34; PLATON – A multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, A. L. Spek, 2005; Windows implementation: L. B. J. Furrugia, University of Glasgow, Scotland, 2005. Version 80205.