

# Oxo-anion binding by protonated (dimethylphenyl)(pyridyl)ureas†

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The anion coordination chemistry of two protonated urea-based ligands, *N*-(2,4-dimethylphenyl)-*N'*-(3-pyridyl)urea (**1**) and *N*-(2,6-dimethylphenyl)-*N'*-(3-pyridyl)urea (**2**) is reported. Reaction of **1** or **2** with inorganic oxo-acids such as perchloric, nitric or sulfuric acid affords the adducts (**3–6**) of the corresponding anions with protonated ligands ( $1\text{H}^+$  and  $2\text{H}^+$ ). The solid-state structures of the anion complexes display a rich variety of hydrogen bond motifs involving the urea NH groups, carbonyl, protonated pyridyl  $\text{NH}^+$  fragment, water molecules, and the anions. While complexes with ligand **1** (**3** and **4**) crystallize as monohydrate, compounds with **2** (**5** and **6**) are solvent-free, which leads to notable differences in their hydrogen bond patterns. When crystallized from the acid mixture  $\text{HClO}_4/\text{HNO}_3$  or  $\text{HClO}_4/\text{H}_2\text{SO}_4$  both **1** and **2** selectively bind the perchlorate anion.

## Introduction

Anion binding is an important aspect in supramolecular chemistry and continues to attract much research interest.<sup>1–3</sup> In a recent review Bowman-James<sup>4</sup> has summarized the definition and geometrical features of anion coordination chemistry by an extension of the concept of coordination number, which is well established in the classical transition metal coordination chemistry developed by Werner. Hydrogen bonding is one of the dominant interactions in anion complexation, *i.e.*, the ligands act as hydrogen bond donors and “coordinate” to the anion *via* hydrogen atoms. Organic compounds that are capable of hydrogen bond formation (*e.g.*, those containing NH fragments) have been widely studied for coordination with anions.<sup>5</sup> In particular, urea-based ligands are a group of good hydrogen bond donors to anions, and the two NH groups in ureas can participate in the binding of anions with various H-bond motifs.<sup>6</sup>

Very recently, Gale *et al.*<sup>7</sup> and Steed *et al.*<sup>8</sup> have developed some urea-based monodentate pyridyl ligands which are capable of simultaneous coordination with transition metal ions and anions. In the metal–ligand–anion systems, there are several factors that can affect the binding properties of anions, such as the hydrogen bond donors, electrostatic interactions

between the positively charged metal-bound ligand moieties and anion, and the geometrical conformation of the metal–ligand fragments. It is found that the coordination geometry of the transition metal and the orientation and topology of the urea subunits considerably determine the hydrogen bond pattern.<sup>9</sup> In order to further understand the anion coordination chemistry of the ureidopyridyl ligands without the restriction of the dimensionality of metal coordination, we have established a new ternary system of such ligands, *i.e.*, the proton–ligand–anion system. Two phenylpyridylurea ligands bearing methyl groups at different positions on the phenyl ring (**1** and **2**, Chart 1) have been synthesized, and the binding properties of the protonated ligands with inorganic oxo-anions studied. In these ternary compounds, the electrostatic interaction ability of the positively charged ligand moieties similar to the metal-bound hosts is maintained upon protonation of the ligands. Moreover, incorporation of  $\text{H}^+$  ions instead of transition metals provides more flexible coordination geometries and more possible H-bonding modes for anion complexation.

Co-binding and co-transport of  $\text{H}^+$ /anion is of importance in some biological processes and two amidopyrrole-based ligands have recently been reported to co-transport  $\text{HCl}$ .<sup>10</sup> Furthermore, the charge-assisted anion binding property of a protonated tripodal amide has been studied.<sup>11</sup> In the present work, we report the detailed structural aspects, especially the

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† Electronic supplementary information (ESI) available: Molecular structures of compounds **1–6** with atomic labeling, a table of the intramolecular C–H...O bonds in **3–6**, and <sup>1</sup>H NMR data for compounds **3** and **4** at different concentrations. See DOI: 10.1039/b702278f

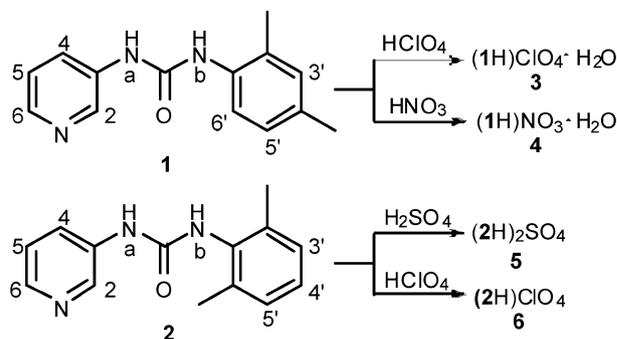
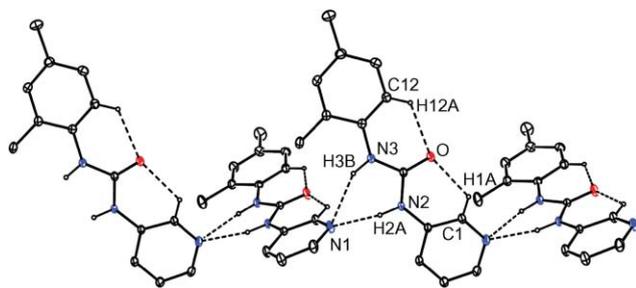


Chart 1



**Fig. 1** ORTEP view of the hydrogen bonded chain of ligand **1** showing the  $R_2^1(6)$  motif of  $N-H\cdots N_{py}$  contacts and the intramolecular  $C-H\cdots O_{C=O}$  interactions as dashed bonds. Hydrogen atoms not involved in these interactions are omitted for clarity.

hydrogen bond motifs of the two ligands (**1** and **2**) and their “complexes” (**3–6**, Chart 1) with inorganic oxo-acids such as sulfuric acid, perchloric acid and nitric acid, as well as the solution behavior of these salts.

## Results and discussion

### Synthesis

The urea-based pyridyl ligands **1** and **2** were synthesized by a method similar to literature reports.<sup>12</sup> The hydrogen bonded supramolecular networks of the ligands with  $H^+$ /anion (**3–6**) were obtained by co-crystallization of **1** or **2** with diluted acid ( $H_2SO_4$ ,  $HClO_4$  or  $HNO_3$ ) in aqueous or methanol/water

solution. Colorless crystals of **1–6** were grown by slow evaporation of the corresponding solutions. All new compounds were characterized by NMR and IR spectra, and their structures were studied by X-ray crystal diffraction.

### Structures

**1.** The ligand crystallizes in the monoclinic space group  $P2_1/c$  with an almost planar conformation. The phenyl  $C_6$  ring, pyridyl  $C_5N$  moiety, and urea  $N_2CO$  are coplanar with each other (largest deviation:  $0.15 \text{ \AA}$ ; torsion angle between pyridyl  $C1-C2$  and urea  $N2-C6$ :  $4.0^\circ$ ; torsion angle between phenyl  $C7-C8$  and urea  $N3-C6$ :  $4.4^\circ$ ). However, this planarity is not retained in the acid adducts,  $(1H)^+ClO_4^- \cdot H_2O$  (**3**) and  $(1H)^+NO_3^- \cdot H_2O$  (**4**) (*vide infra*). The urea NH groups form two hydrogen bonds with a pyridine nitrogen acceptor of another molecule with an  $R_2^1(6)$  motif,<sup>13</sup> which is repeated along the  $c$  axis to form an infinite chain with two adjacent molecules arranged in a nearly orthogonal orientation (Fig. 1). This  $N-H\cdots N_{py}$  hydrogen bond pattern is similar to that observed for *N*-phenyl-*N'*-(3-pyridyl)urea and other related systems,<sup>14</sup> but is different from the typical urea tape  $\alpha$ -network found in a variety of diarylureas, which feature a chain of bifurcated  $N-H\cdots O$  hydrogen bonds.<sup>15</sup> The 2-methyl substituent on the phenyl ring is *anti* to the  $C=O$  unit, and there are two intramolecular  $C-H\cdots O$  hydrogen bonds (see Fig. 1), both of which are part of a six-membered ring ( $S(6)$  motif).<sup>13</sup> The hydrogen bond parameters for **1**, as well as for **2–6**, are summarized in Table 1.

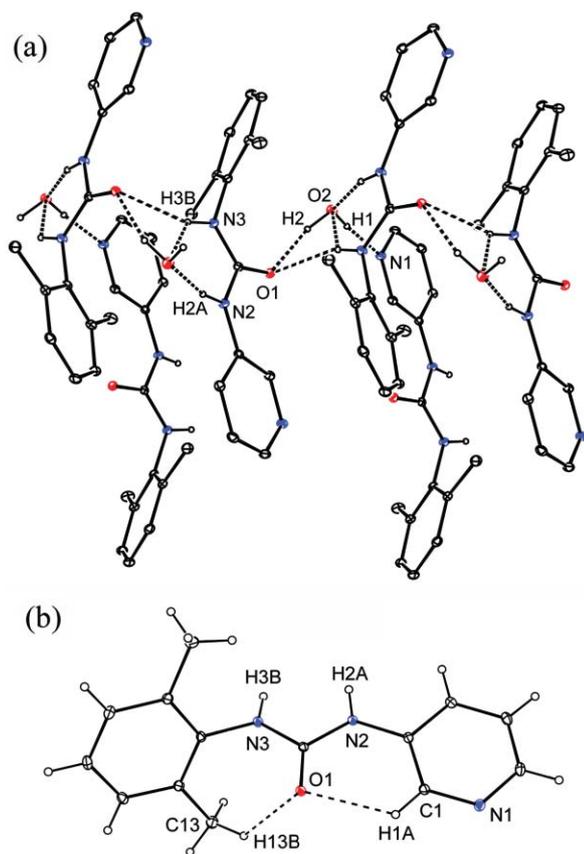
**Table 1** Selected hydrogen bond parameters for **1–6**

Compound	D–H $\cdots$ A	Symmetry code	D–H/ $\text{\AA}$	H $\cdots$ A/ $\text{\AA}$	D $\cdots$ A/ $\text{\AA}$	$\angle D-H\cdots A/^\circ$
<b>1</b>	N2–H2A $\cdots$ N1	$x, 0.5 - y, -0.5 + z$	0.86	2.06	2.913(2)	168.8
	N3–H3B $\cdots$ N1	$x, 0.5 - y, -0.5 + z$	0.86	2.49	3.265(3)	150.3
	C1–H1A $\cdots$ O <sup>a</sup>		0.93	2.25	2.868(3)	122.9
	C12–H12A $\cdots$ O <sup>a</sup>		0.93	2.26	2.878(3)	123.2
	N2–H2A $\cdots$ O2		0.86	2.01	2.854(2)	165.3
<b>2</b> ·H <sub>2</sub> O	N3–H3B $\cdots$ O2		0.86	2.72	3.363(2)	132.8
	N3–H3B $\cdots$ O1	$1.5 - x, 0.5 + y, -0.5 - z$	0.86	2.13	2.9292(19)	153.9
	O2–H2 $\cdots$ O1	$1.5 - x, 0.5 + y, -0.5 - z$	0.86(1)	2.102(15)	2.9037(17)	156(3)
	O2–H1 $\cdots$ N1	$0.5 + x, 0.5 - y, 0.5 + z$	0.86(1)	1.955(10)	2.813(2)	177(3)
	C1–H1A $\cdots$ O1 <sup>a</sup>		0.93	2.26	2.879(2)	123.2
<b>3</b>	C13–H13B $\cdots$ O1 <sup>a</sup>		0.96	2.55	3.244(2)	128.9
	N1–H1A $\cdots$ O1	$-x, -0.5 + y, 0.5 - z$	0.86	1.95	2.727(5)	149.7
	O6–H1 $\cdots$ O2	$1 + x, y, z$	0.85(1)	2.09(5)	2.779(13)	139(6)
	O6–H2 $\cdots$ O5		0.85(1)	2.10(4)	2.872(10)	151(7)
	O6–H1 $\cdots$ O5	$0.5 + x, 0.5 - y, 1 - z$	0.85(1)	2.50(6)	2.968(12)	116(6)
<b>4</b>	N2–H2A $\cdots$ O6	$-0.5 + x, 0.5 - y, 1 - z$	0.86	1.94	2.778(7)	163.0
	N3–H3A $\cdots$ O6	$-0.5 + x, 0.5 - y, 1 - z$	0.86	2.41	3.171(10)	147.1
	O5–H1 $\cdots$ O1	$-0.5 + x, 1.5 - y, -0.5 + z$	0.85(1)	2.088(16)	2.909(3)	162(4)
	N1–H1B $\cdots$ O3	$x, 2 - y, 0.5 + z$	0.86	1.89	2.752(4)	174.3
	O5–H2 $\cdots$ O3		0.84(1)	1.955(14)	2.781(3)	166(4)
<b>5</b>	N2–H2A $\cdots$ O5	$0.5 + x, 0.5 + y, z$	0.86	1.99	2.818(3)	161.4
	N3–H3B $\cdots$ O5	$0.5 + x, 0.5 + y, z$	0.86	2.34	3.121(3)	151.1
	N1–H1B $\cdots$ O4	$-0.5 + x, y, 1.5 - z$	0.86	1.79	2.640(3)	169.4
	N2–H2A $\cdots$ O6		0.86	1.99	2.835(3)	166.9
	N3–H3B $\cdots$ O3		0.86	2.22	3.021(3)	154.5
<b>6</b>	N4–H4B $\cdots$ O3	$1.5 - x, -0.5 + y, z$	0.86	1.87	2.723(3)	171.4
	N5–H5B $\cdots$ O5		0.86	1.95	2.786(3)	164.3
	N6–H6A $\cdots$ O6		0.86	2.13	2.952(3)	158.5
	N3–H3B $\cdots$ O2	$0.5 + x, 0.5 - y, 1 - z$	0.86	2.21	3.037(4)	160.0
	N1–H1B $\cdots$ O3		0.86	2.00	2.853(4)	171.8
	N2–H2A $\cdots$ O4	$0.5 + x, 0.5 - y, 1 - z$	0.86	2.23	3.072(5)	166.5

<sup>a</sup> Intramolecular  $C-H\cdots O$  bonds. For **3–6** these data are given as Electronic Supplementary Information (Table S1).

**2·H<sub>2</sub>O.** The ligand **2** crystallizes (space group  $P2_1/n$ ) with one water molecule. Unlike the planar conformation of the 2,4-disubstituted ligand **1**, the 2,6-disubstituted **2** shows a twisted structure. Although the pyridyl moiety is coplanar with the urea carbonyl (torsion angle C1–C<sub>2</sub><sub>py</sub>–N2–C6<sub>urea</sub> 3.3°), the aryl ring lies in a nearly perpendicular position relative to the pyridyl–urea plane, with a torsion angle of 74.7° (C7–C8<sub>aryl</sub>–N3–C6<sub>urea</sub>), caused by steric repulsion of the two *ortho*-methyl groups. The twisted conformation of the ligand persists in its complexes with H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>, as will be described later. Interestingly, while ligand **2** contains a crystal water molecule, both of its adducts (**5** and **6**) do not include any water or other solvent during the assembly process, although they were crystallized from water-containing solutions (*vide infra*).

As shown in Fig. 2a, the crystal structure of monohydrate **2** contains multiple intermolecular hydrogen bonds. Again, the urea tape N–H···O synthon is absent. Instead, the urea group and pyridine nitrogen are hydrogen-bonded to the crystalline water molecule, which binds three ligand molecules *via* four hydrogen bonds. Among these H-bond interactions, H<sub>2</sub>O acts either as a hydrogen bond acceptor, in the formation of the N–H···O R<sub>2</sub><sup>1</sup>(6) ring with the urea NH groups, or as a donor, in the O–H···N<sub>py</sub> and O–H···O<sub>C=O</sub> bonds. The hydrogen bonding between the urea NH donors and solvent O atom is common when such ligands or their complexes are



**Fig. 2** (a) Hydrogen bonding interactions in **2**·H<sub>2</sub>O, including the R<sub>2</sub><sup>1</sup>(6) motif, the O–H···N<sub>py</sub> and O–H···O<sub>C=O</sub> bonds around H<sub>2</sub>O, and the N–H···O<sub>C=O</sub> bond. CH hydrogens are omitted for clarity. (b) The intramolecular C–H···O<sub>C=O</sub> bonds with an S(6) and an S(7) motif.

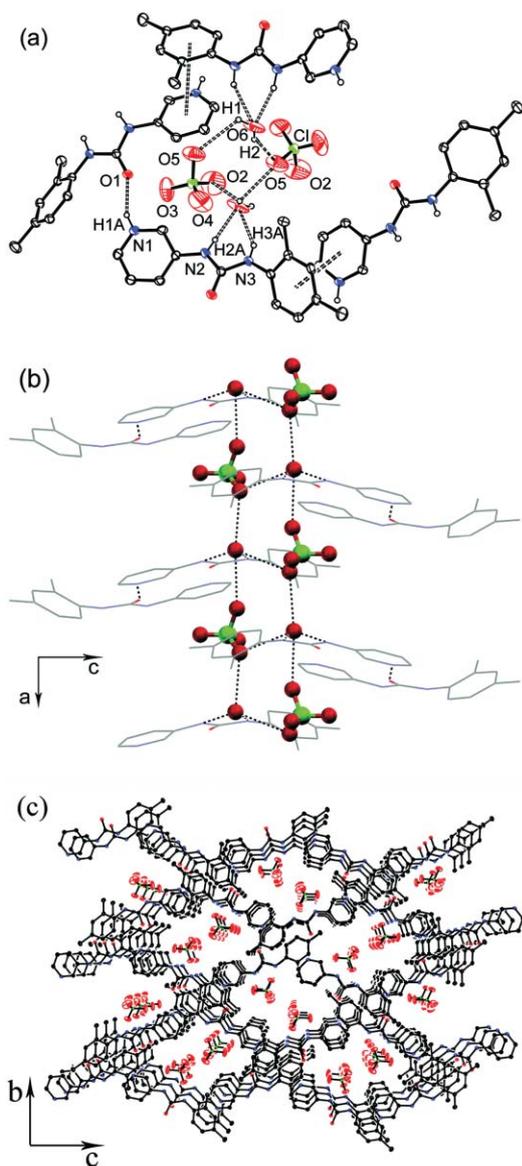
hydrated or solvated.<sup>14</sup> There is an interligand N–H···O contact in **2**, which is from one of the NH groups to the carbonyl oxygen of another ligand, thus forming an R<sub>2</sub><sup>2</sup>(4) ring together with the O–H···O<sub>C=O</sub> interaction. The crystal packing is directed by these hydrogen bonds and a  $\pi$ – $\pi$  stacking interaction between a pyridine ring and an adjacent aryl unit (centroid–centroid separation 3.780 Å; dihedral angle 14.2°; vertical displacements between ring centroids 1.292 and 0.604 Å, respectively).<sup>16</sup> The intramolecular C–H···O hydrogen bonds found in **1** also exist in this compound. However, one of them is formed between the O atom and an H atom of the CH<sub>3</sub> group *syn* to C=O, completing a seven-membered ring (S(7) motif),<sup>13</sup> Fig. 2b and Table 1.

**(1H)ClO<sub>4</sub>·H<sub>2</sub>O (3).** The perchlorate salt **3** crystallizes in the orthorhombic space group  $P2_12_12_1$ . The asymmetric unit contains a protonated ligand (1H<sup>+</sup> cation), a ClO<sub>4</sub><sup>−</sup> anion, and a H<sub>2</sub>O molecule. The ligand molecule in this compound adopts a non-planar conformation (torsion angle C1–C<sub>2</sub><sub>py</sub>–N2–C6<sub>urea</sub> 27.0°, C7–C8<sub>aryl</sub>–N3–C6<sub>urea</sub> 43.1°) rather than a flat one, as seen in the free ligand **1**. In compound **3**, the water molecule acts as a bridge between the ureidopyridyl ligand and the perchlorate anion in the formation of the hydrogen bonded network, and there is no direct N–H···O<sub>anion</sub> contact. The urea NH moieties donate two N–H···O bonds to the water molecule, forming an R<sub>2</sub><sup>1</sup>(6) motif. In addition, the pyridinium nitrogen donor is involved in an interligand N<sub>py</sub>–H···O<sub>C=O</sub> bond (Fig. 3a).

The double stranded structure formed between the water molecule and the perchlorate anion is very interesting. As shown in Fig. 3b, each water molecule links two perchlorate ions through two single O–H···O hydrogen bonds, resulting in a linear arrangement with H<sub>2</sub>O and ClO<sub>4</sub><sup>−</sup> alternating along the *a* axis. A pair of such strands is oriented parallel, with a short O···O contact (O6···O5, 2.968(12) Å) between a H<sub>2</sub>O molecule and an anion in another strand. Hydrogen bonding between the strands may be possible through disorder in the H<sub>2</sub>O hydrogen positions. We note that the thermal ellipsoids of ClO<sub>4</sub> indicate a high rotational mobility of this anion.

There is a  $\pi$ – $\pi$  stacking interaction between the pyridyl ring and the aryl ring of an adjacent ligand (dihedral angle 13.3°, centroid–centroid separation 3.696 Å, and vertical displacements between ring centroids 1.838 and 1.094 Å).<sup>16</sup> The compound is packed to a 3-D network with roughly rhombic channels running parallel to the *a* axis, which are filled with the double strands of the water molecules and perchlorate anions (Fig. 3c). Two opposite edges of these cavities are composed of ligands with the NH groups pointing toward the inside space to hydrogen-bond with the guest water molecules, while the other two ligands are oriented such that the NH groups point outwards to other channels.

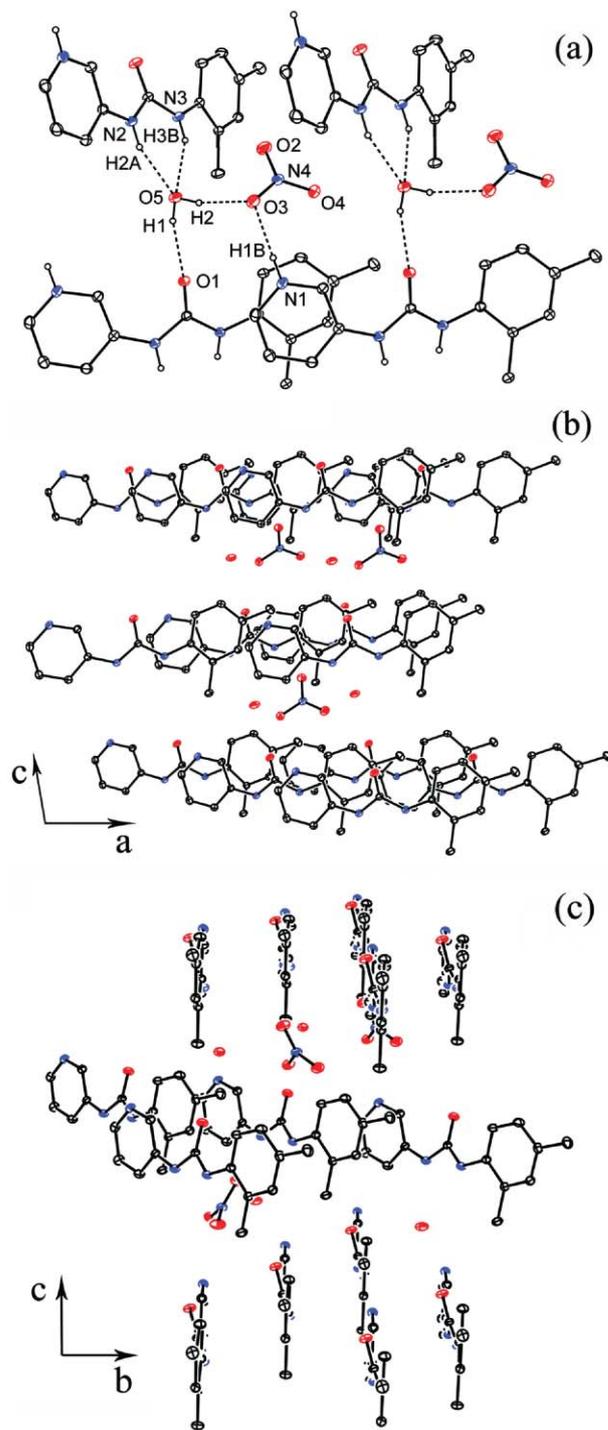
**(1H)NO<sub>3</sub>·H<sub>2</sub>O (4).** The nitrate compound **4** also crystallizes as monohydrate. The conformation of the ligand molecule is only slightly twisted (8.2° for C1–C<sub>2</sub><sub>py</sub>–N2–C6<sub>urea</sub> and 19.2° for C7–C8<sub>aryl</sub>–N3–C6<sub>urea</sub>) compared to **3**. In **4**, each NO<sub>3</sub><sup>−</sup> anion forms two hydrogen bonds with the water molecule (O5–H2···O3) and one protonated pyridine N atom (N1–H1B···O3), respectively, through the same O3 atom,



**Fig. 3** (a) Hydrogen bonding and the  $\pi$ - $\pi$  stacking interaction in (1H)ClO<sub>4</sub>·H<sub>2</sub>O (**3**), including the R<sub>2</sub><sup>1</sup>(6) motif of N-H...O bonds, the O-H...O contacts between H<sub>2</sub>O and ClO<sub>4</sub><sup>-</sup>, and the N<sub>py</sub>-H...O<sub>C=O</sub> bonds. (b) The double-stranded structure formed by the anion and water molecules. Hydrogen atoms not shown. (c) Packing diagram showing the large size channels formed by the ligands and the encapsulated anion/water strands.

and the other two oxygen atoms remain intact (Fig. 4a). As in the perchlorate analog **3**, there is no hydrogen bonding between the urea NH donors and the nitrate anion in **4**.

The co-crystallized water molecule plays an important role in the assembly of the solid-state structure of **4**, and the multiple hydrogen bonding interactions around the water molecule are particularly interesting. Each H<sub>2</sub>O, behaving as both H-bond donor and acceptor, is involved in as many as four H-bonds, including a bifurcated N-H...O R<sub>2</sub><sup>1</sup>(6) motif with the two urea NH donors, a single O-H...O contact with the NO<sub>3</sub><sup>-</sup> anion (as mentioned above), and an O-H...O<sub>C=O</sub> bond to the carbonyl oxygen of an adjacent ligand, Fig. 4a and



**Fig. 4** (a) Hydrogen bonds in **4**, showing the R<sub>2</sub><sup>1</sup>(6) motif and the single N-H...O and O-H...O contacts around NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O. CH hydrogen atoms are omitted for clarity. (b) Packing diagram along the *b*-axis showing the layered structure. (c) Tilted orientations of the ligands in the alternative layers viewed along the *a*-axis.

Table 1. The ligands are stacked on top of each other along the *a* and *b* axis to form layers (Fig. 4b) through  $\pi$ - $\pi$  stacking interactions between the pyridine and aryl rings (dihedral angles of the two planes 2.6 and 2.6°, centroid-centroid separation 3.648 and 3.917 Å, and vertical displacements

between ring centroids 1.154 and 1.067 Å; 1.994 and 1.839 Å, respectively).<sup>16</sup> Along the *c* axis the ligands are tilted towards each other, with the water molecules and nitrate anions located between the ligand layers (Fig. 4b and c).

**(2H)<sub>2</sub>SO<sub>4</sub> (5).** Co-crystallization of *N*-(2,6-dimethylphenyl)-*N'*-(3-pyridyl)urea (ligand **2**) with inorganic oxo-acids yielded the sulfate **5** and perchlorate **6**. In contrast to the monohydrate composition of **3** and **4** (with ligand **1**), neither **5** nor **6** enclathrate any crystal water or methanol. This difference leads to dramatic changes in the hydrogen bonding mode of the ligands with anions, as the NH donors of the urea group in **5** and **6** are freed from solvation, allowing for the formation of direct N<sub>urea</sub>-H...O<sub>anion</sub> bonds.

Compound **5** contains two protonated 2H<sup>+</sup> cations and one SO<sub>4</sub><sup>2-</sup> anion. Similar to the free ligand **2**, the pyridinium moiety in the ligand molecules is coplanar with the urea group (torsion angle C-C<sub>py</sub>-N-C<sub>urea</sub> 5.4 and 3.0°), and the phenyl ring is nearly perpendicular to the urea group (torsion angle C-C<sub>aryl</sub>-N-C<sub>urea</sub> 80.6 and 65.0°). In the packed structure, each SO<sub>4</sub><sup>2-</sup> ion is coordinated *via* six N-H...O interactions with four pyridinium ligands, including two R<sub>2</sub><sup>2</sup>(8) motifs<sup>17</sup> formed by the urea NH groups of 2H<sup>+</sup> and two oxygen atoms of SO<sub>4</sub><sup>2-</sup>, and two single hydrogen bonds from pyridinium nitrogen (NH<sup>+</sup>) to an oxygen atom of the anion (Fig. 5a, Table 1). The R<sub>2</sub><sup>2</sup>(8) motif generated by the NH donors and O

atoms has been observed in the binding of sulfate ion by some metal complexes bearing urea-based ligands.<sup>6d,17</sup> In the present compound, both of the urea NH groups and pyridinium nitrogen donate hydrogen bonds to the sulfate ion, making a coordination number of six. A higher coordination number of sulfate ion has been reported in a MOF compound of a tripodal tris-urea ligand, which features a coordinatively saturated sulfate with twelve hydrogen bonds.<sup>6d</sup>

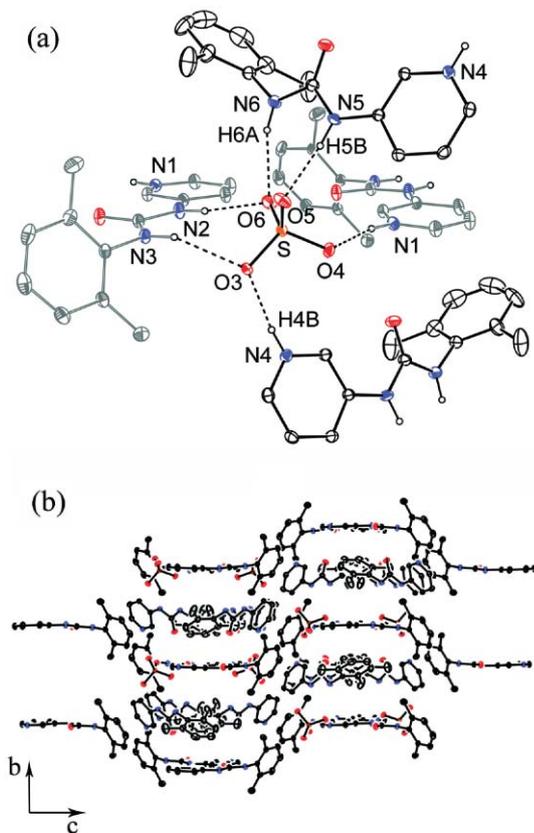
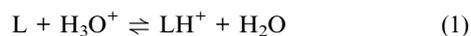
There is a π-π stacking interaction between a pyridine ring and an adjacent aryl unit (centroid-centroid separation 3.563 Å; dihedral angle 4.6°; vertical displacements between ring centroids 0.851 and 0.568 Å).<sup>16</sup> The supramolecular 3-D network is held together by the H-bonds and π stacking interaction. Viewed along the *a*-axis, the packing diagram shows a ladder-like structure with the ligand molecules, arranged head-to-tail, being the steps and the stacked aryl and pyridyl rings being the bars (Fig. 5b).

**(2H)ClO<sub>4</sub> (6).** The adduct of perchloric acid with **2** has a 1 : 1 ratio of the protonated pyridinium ligand, (2H)<sup>+</sup>, and perchlorate ion. The ligand molecule of this compound displays the twisted conformation as in **2** and **5** (torsion angle of phenyl-urea and pyridyl-urea, 63.7 and 4.2°, respectively). There are fewer hydrogen bonds in the crystal structure of **6** than in the sulfate analog **5** (see Table 1). Each ClO<sub>4</sub><sup>-</sup> anion receives three N-H...O hydrogen bonds from two (2H)<sup>+</sup> ligands. These include an R<sub>2</sub><sup>2</sup>(8) motif with the urea NH groups, and a single contact with the protonated pyridine (NH<sup>+</sup>) donor (Fig. 6a). The packed structure of this compound shows parallel zigzag arrays in the *ac* plane, and the ClO<sub>4</sub><sup>-</sup> anions lie in the trigonal clefts of the zigzag structure (Fig. 6b).

Although both complexes **5** and **6** feature multisite hydrogen bonding interactions around the anions, the H-bond numbers and modes of the urea (HNCONH) groups of the two compounds are different: The sulfate adduct **5** has six hydrogen bonds including two R<sub>2</sub><sup>2</sup>(8) motifs, whereas the perchlorate compound **6** forms three hydrogen bonds with only one R<sub>2</sub><sup>2</sup>(8) ring, and the N<sub>py</sub>-H...O<sub>C=O</sub> bond is absent in **6**.

### NMR spectra

The solution behavior of the hydrogen-bonded compounds (**3**–**6**) was studied by <sup>1</sup>H NMR spectroscopy. All anion complexes show a significant downfield shift of the urea NH and pyridyl protons compared to the free ligand **1** or **2**. As shown in Fig. 7, with decreasing concentration, the Δδ value also decreases and the chemical shift becomes closer to the free ligands. This can be explained by the equilibrium of the protonation of the pyridyl nitrogen (eqn (1), the water in the equilibrium is part of the hygroscopic DMSO-*d*<sub>6</sub>). In a more diluted solution the protolysis is increased and the equilibrium shifts to the left, with the chemical shift approaching the free ligand. Since the urea NH shifts display similar trends as the pyridyl protons with changing concentration, it may be concluded that the protonation/deprotonation processes are dominant for the anion complexes, and the NMR spectra do not imply significant cation-anion interactions in DMSO-*d*<sub>6</sub> solution.



**Fig. 5** (a) The coordination sphere around the sulfate anion with four ligands and six hydrogen bonds, including two R<sub>2</sub><sup>2</sup>(8) motifs and two single N<sub>py</sub>-H...O bonds. (b) Packing diagram viewed down the *a*-axis showing the π-π stacking interactions and the ladder-like structure.

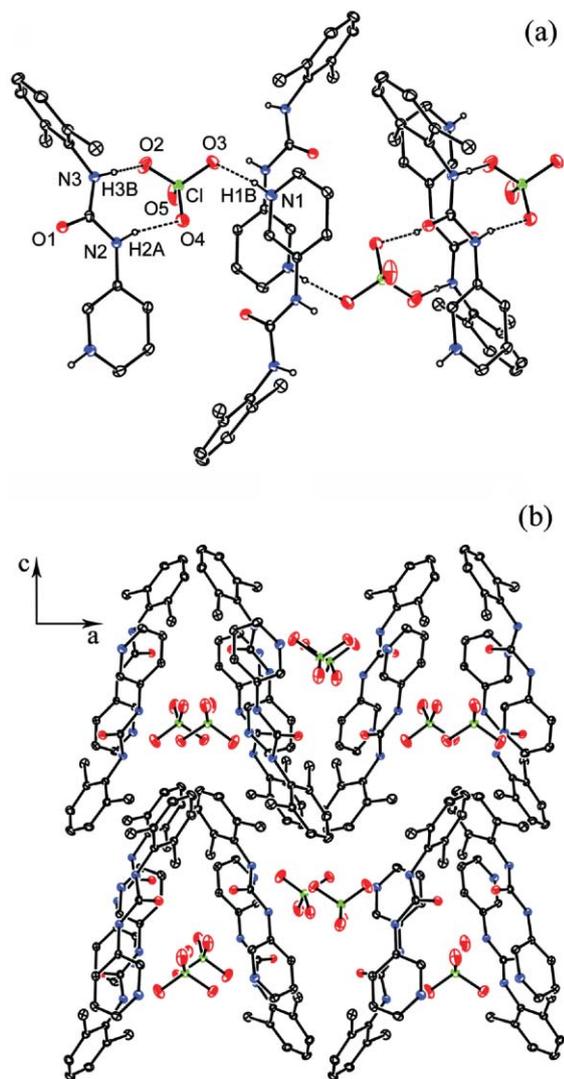


Fig. 6 (a) The  $R_2^2(8)$  motif and N-H...O contact around the  $\text{ClO}_4^-$  anion in **6**. (b) The zigzag arrangement along the  $a$ -axis.

### Anion selectivity

We obtained the adducts of ligand **1** with perchloric acid or nitric acid, and those of ligand **2** with sulfuric acid or perchloric acid. In order to examine the selectivity of the ligands between the two different anions/acids, the following experiments have been done. Ligand **1** was crystallized from a mixture of  $\text{HClO}_4/\text{HNO}_3$  (1 : 1), and ligand **2** from  $\text{H}_2\text{SO}_4/\text{HClO}_4$  (1 : 2) under the same conditions as in the preparation of the complexes **3–6**. Colorless crystals were isolated after several days and tested by X-ray powder diffraction. The adduct of ligand **1** with  $\text{HClO}_4/\text{HNO}_3$  shows a diffraction pattern almost identical to that simulated for complex **3**,  $(1\text{H})\text{ClO}_4$ , indicating that the protonated ligand selected the perchlorate ion from the mixed acids. The ligand **2** also picked  $\text{H}^+/\text{ClO}_4^-$  from the  $\text{H}_2\text{SO}_4/\text{HClO}_4$  mixture, as the XRPD diffraction of the product is essentially the same as that simulated for complex **6**,  $(2\text{H})\text{ClO}_4$  (Fig. 8 and 9). Thus, both ligands display some preference for perchlorate ion over nitrate or sulfate ion in the solid state. This perchlorate

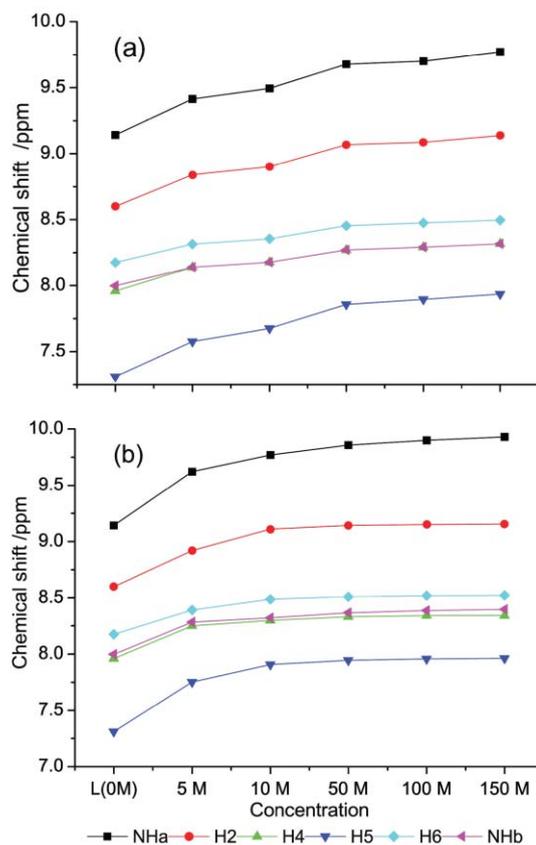


Fig. 7 The relationship of chemical shift vs concentration. (a) Compound **3** and (b) compound **4**, at 0 (ligand **1**), 5, 10, 50, 100, and 150 M in  $\text{DMSO-}d_6$ .

selectivity is remarkable in view of the smaller number of hydrogen bonds formed to this anion when compared to sulfate. Perchlorate is usually viewed as a weakly coordinating

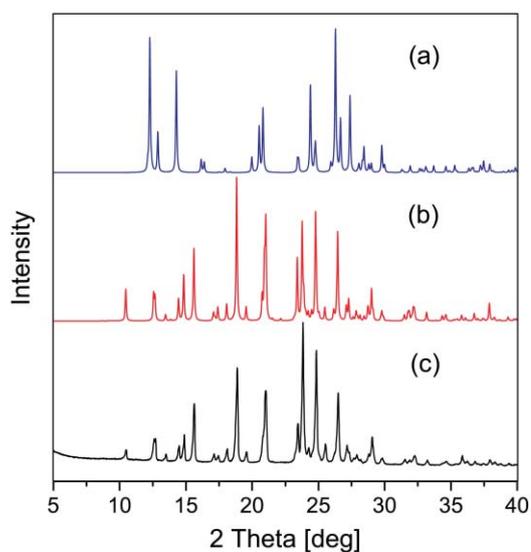
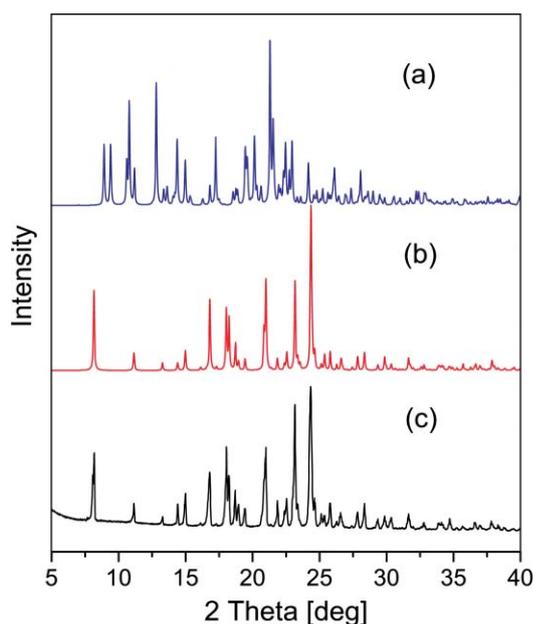


Fig. 8 XRPD patterns of the adducts of ligand **1** with different acids. (a) Simulated for **4**,  $(1\text{H})\text{NO}_3$ ; (b) simulated for **3**,  $(1\text{H})\text{ClO}_4$ ; (c) product from the mixture of  $\text{HClO}_4/\text{HNO}_3$ , showing identical diffraction as **3**.

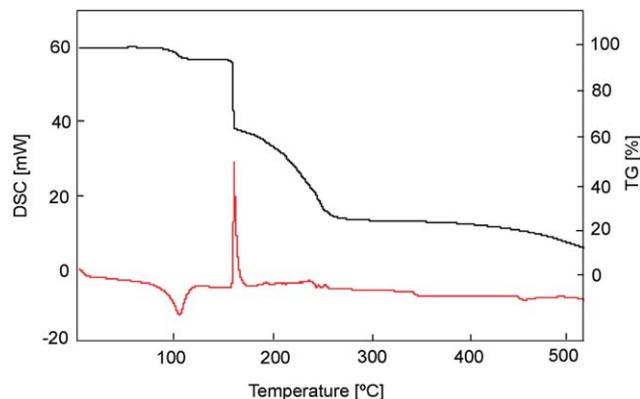


**Fig. 9** XRPD patterns of the adducts of ligand **2** with different acids: (a) simulated for **5**, (2H)<sub>2</sub>SO<sub>4</sub>; (b) simulated for **6**, (2H)ClO<sub>4</sub>; (c) a product from the mixture of HClO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>, showing identical diffraction as **6**.

anion. A qualitative test indicated a lower solubility for the ClO<sub>4</sub><sup>-</sup> than the NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> compounds. Thus, we reason the perchlorate selectivity on the basis of their higher lattice energy/lower solubility due to stronger lattice forces, *i.e.* more favorable packing interactions.

#### TG/DSC analysis

The perchlorate (**3**) and nitrate (**4**) compounds of ligand **1** crystallize with a molecule of water, which forms multiple hydrogen bonds with the ligands and anions. Thermal analysis (TG/DSC) was then performed for these two samples at 20–700 °C with a heating rate of 5 °C min<sup>-1</sup>, and the TG/DSC curves of compound **4** are depicted in Fig. 10. Both compounds show a clear mass loss at around 100 °C corresponding to the removal of water; however, the temperature ranges for the loss are different. In the TG curve of **3**, a slow mass decrease is observed at 99–153 °C with a percentage of 4.7%



**Fig. 10** The TG and DSC curves of compound **4**.

(calculated 5.01% for a water), while compound **4** displays a rather sharp water loss (5.6%; calculated 5.59%) at 97–108 °C. This could be attributed to the different melting points of the two samples, namely 130–131 °C for **3**, and 160–161 °C for the nitrate **4**. During the water loss step of **3**, melting of the sample also occurs, which may significantly prolong the process. Compound **4** has a higher melting point and the loss of water is completed around 50 °C before melting of the sample, resulting in a narrow temperature range. The explanation is well supported by the DSC results: in the range of 99–153 °C the DSC curve of compound **3** shows two partly overlapping endothermic peaks (centered at 126 and 149 °C), and **4** has only one endothermic process at 106 °C. It is noted that the solvent-free compound **6** (with ligand **2**) has a much higher melting point (219–220 °C) compared to **3**. Moreover, the crystals of **3** and **4** were heated to examine the possible phase change. At around 100 °C, both samples became opaque. This is in accordance with the water loss process of the TG results. It is thus concluded that the water molecule is essential to the crystal structures of **3** and **4**, and removal of water can lead to the collapse of the crystals.

At a higher temperature the compounds decompose in two (**3**) or three (**4**) stages. From 215 to 318 °C, compound **3** shows a rapid mass loss (*ca.* 52%) corresponding to an exothermic reaction, followed by another slower mass loss starting at 318 °C with no obvious endo- or exothermic peak. The mass loss is complete at 538 °C. The TG curve of compound **4** has a very sharp mass loss (*ca.* 25%) at 161–168 °C, corresponding to an exothermic process in the DSC curve (Fig. 10). This can be attributed to the decomposition of HNO<sub>3</sub> → NO<sub>2</sub> + 1/2 H<sub>2</sub>O + 1/4 O<sub>2</sub> (20%). However, there are several changes at this temperature range, including the melting of the sample as well as effusion of the gaseous species. The second and third mass loss steps occur in the temperature range of 168–251 °C (47%) and 251–571 °C (22%), respectively, due to the decomposition of the ligand.

#### Conclusions

Upon addition of inorganic acids, the ligands **1** and **2** are protonated and coordinate with the anions through multiple hydrogen bonds. The perchlorate (**3**) and nitrate (**4**) compounds of ligand **1** contain a crystal water molecule, while the sulfate (**5**) and perchlorate (**6**) of ligand **2** are both solvent-free. The co-crystallized water molecule plays an important role in the building of the H-bonded networks. When the H<sub>2</sub>O molecule is in presence, as in 2·H<sub>2</sub>O, **3** and **4**, the urea NH donors prefer to bind with the water oxygen to form an R<sub>2</sub><sup>1</sup>(6) motif with two N–H···O contacts. In contrast, when there is no water molecule in the structure, the NH groups of urea can form R<sub>2</sub><sup>2</sup>(8) motifs composed of two direct N–H···O bonds between the urea NHs and the anion oxygens, as described for **5** and **6**.

The overall coordination number (*i.e.*, number of hydrogen bonds) of the anions is two for the perchlorate **3**, two for the nitrate **4**, six for the sulfate **5**, and three for the perchlorate **6**. Crystal packing of complexes **3–6** is directed by electrostatic forces and the aforementioned hydrogen bonds together with some π–π stacking interactions. The packing diagrams display

interesting supramolecular networks, such as the channels of **3**, the layers of **4**, the ladder-like **5**, and zigzag arrangement in **6**.  $^1\text{H}$  NMR spectra of the compounds show a concentration-dependent downfield shift of NH and pyridyl protons upon protonation. Crystallization from acid mixtures demonstrates a remarkable preference for the perchlorate ion over sulfate or nitrate ion for both ligands **1** and **2**.

## Experimental

### General

2,4-Dimethylphenyl isocyanate, 2,6-dimethylphenyl isocyanate, and 3-aminopyridine were purchased from Alfa Aesar. All other chemicals and solvents were of reagent grade or better and were used without further purification unless otherwise specified.  $^1\text{H}$  NMR spectra were recorded on a Mercury plus-400 spectrometer using tetramethylsilane (TMS) as an internal standard. Numbering of the protons on the pyridyl and phenyl rings is shown in Chart 1. Elemental analysis was performed on a VarioEL instrument from Elementar Analysensysteme GmbH. IR spectra were measured with an HP5890II GC/NEXUS870. ESI-MS measurements were performed with a Waters ZQ4000 mass spectrometer. X-Ray powder diffraction data were recorded with an X'Pert PRO instrument. TG-DSC analysis was carried out with a Pyris diamond (Perkin Elmer).

### Synthesis

Ligand **2**, *N*-(2,6-dimethylphenyl)-*N'*-(3-pyridyl)urea, is a known compound and was prepared following literature procedures.<sup>12</sup> The colorless block crystal of **2** was obtained by evaporation of its methanol/water (1 : 1 v/v) solution at room temperature. The new ligand (*N*-(2,4-dimethylphenyl)-*N'*-(3-pyridyl)urea) (**1**) was synthesized by a similar method and was crystallized in acetone/petroleum ether (1 : 1 v/v).

The anion "complexes" **3–6** were synthesized by the reaction of ligand **1** or **2** with the corresponding dilute acid,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  or  $\text{HClO}_4$ . In a typical experiment, the ligand (48.5 mg, 0.20 mmol) was dissolved in diluted acid (1N,  $\sim 2$  mL,  $\sim 2$  mmol) by addition of methanol (1 mL), in some cases, to give a clear solution. Colorless cubic crystals were obtained by slow evaporation of the solution at rt for several days.

***N*-(2,4-Dimethylphenyl)-*N'*-(3-pyridyl)urea (**1**)**. A solution of 2,4-dimethylphenyl isocyanate (1.47 g, 0.01 mol) in anhydrous THF (20 mL) was treated with a solution of 3-aminopyridine (0.92 g, 0.01 mol) in anhydrous THF (20 mL). The mixture was refluxed under nitrogen for 3 h with stirring and then cooled to rt. The resulting white precipitate was filtered and washed with THF,  $\text{Et}_2\text{O}$  and dried *in vacuo* to give a white powder. Yield: 2.15 g (90%). Mp: 180–181 °C. ESI-MS:  $m/z = 242.4$  [ $\text{M} + \text{H}$ ] $^+$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta = 9.14$  (s, 1H, NHa), 8.60 (d, 1H,  $J = 2.4$  Hz, Py-H2), 8.18 (dd, 1H,  $J = 4.4, 3.6$  Hz, Py-H6), 8.00 (s, 1H, NHb), 7.96 (ddd, 1H,  $J = 8.4, 3.6, 2.0$  Hz, Py-H4), 7.63 (d, 1H,  $J = 8.0$  Hz, Ar-H6'), 7.31 (dd, 1H,  $J = 8.4, 4.4$  Hz, Py-H5), 7.00 (s, 1H, Ar-H3'), 6.96 (d, 1H,  $J = 8.0$  Hz, Ar-H5'), 2.23 (s, 3H,  $\text{CH}_3$ ), 2.20 (s, 3H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$  (241.29): C, 69.69; H,

6.27; N, 17.41%. Found: C, 70.12; H, 5.99; N, 17.99%. IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3296 (N-H), 3033, 1639 (C=O), 1589, 1557, 1479, 811, 708.

**(1H)ClO<sub>4</sub>·H<sub>2</sub>O (**3**)**. Yield: 40%. Mp: 130–131 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta = 9.77$  (s, 1H, NHa), 9.14 (d, 1H,  $J = 2.4$  Hz, Py-H2), 8.50 (d, 1H,  $J = 5.2$  Hz, Py-H6), 8.32 (m, 2H, NHb + Py-H4), 7.94 (dd, 1H,  $J = 8.4, 5.2$  Hz, Py-H5), 7.51 (d, 1H,  $J = 8.4$  Hz, Ar-H6'), 7.04 (s, 1H, Ar-H3'), 6.99 (d, 1H,  $J = 8.4$  Hz, Ar-H5'), 2.25 (s, 3H,  $\text{CH}_3$ ), 2.21 (s, 3H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_5\text{Cl}\cdot\text{H}_2\text{O}$  (359.77): C, 46.74; H, 5.04; N, 11.68%. Found: C, 47.15; H, 4.68; N, 11.41%; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3238 (N-H), 3042, 2980, 1722 (C=O), 1614, 1588, 1089 (Cl-O), 763, 701.

**(1H)NO<sub>3</sub>·H<sub>2</sub>O (**4**)**. Yield: 38%. Mp: 160–161 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta = 9.83$  (s, 1H, NHa), 9.13 (d, 1H,  $J = 2.4$  Hz, Py-H2), 8.50 (d, 1H,  $J = 5.2$  Hz, Py-H6), 8.35 (s, 1H, NHb), 8.33 (dd, 1H,  $J = 8.4, 1.2$  Hz, Py-H4), 7.93 (dd, 1H,  $J = 8.4, 5.2$  Hz, Py-H5), 7.51 (d, 1H,  $J = 8.4$  Hz, Ar-H6'), 7.03 (s, 1H, Ar-H3'), 6.99 (d, 1H,  $J = 8.4$  Hz, Ar-H5'), 2.24 (s, 3H,  $\text{CH}_3$ ), 2.20 (s, 3H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_4$  (304.30) (a powder sample was used after carefully drying over  $\text{P}_4\text{O}_{10}$ ): C, 55.26; H, 5.30; N, 18.41%. Found: C, 55.10; H, 5.10; N, 18.40%. IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3358 (N-H), 3099, 3040, 1704 (C=O), 1574, 1538, 1384, 1304 (N-O), 796.

**(2H)<sub>2</sub>SO<sub>4</sub> (**5**)**. Yield: 35%. Mp: 165–166 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta = 9.50$  (s, 1H, NHa), 8.88 (d, 1H,  $J = 2.0$  Hz, Py-H2), 8.33 (d, 1H,  $J = 4.4$  Hz, Py-H6), 8.19 (s, 1H, Py-H4), 8.17 (s, 1H, NHb), 7.63 (dd, 1H,  $J = 8.4, 4.8$  Hz, Py-H5), 7.09 (s, 3H, Ar), 2.20 (s, 6H, 2 $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}\cdot 0.5\text{H}_2\text{SO}_4$  (290.33): C, 57.92; H, 5.55; N, 14.47%. Found: C, 57.46; H, 5.78; N, 13.84%. IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3253 (N-H), 3046, 3020, 1685 (C=O), 1570, 1469, 1178 (S-O), 881, 780.

**(2H)ClO<sub>4</sub> (**6**)**. Yield: 45%. Mp: 219–220 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta = 9.82$  (s, 1H, NHa), 9.12 (d, 1H,  $J = 2.0$  Hz, Py-H2), 8.49 (d, 1H,  $J = 5.6$  Hz, Py-H6), 8.38 (d, 1H,  $J = 8.0$  Hz, Py-H4), 8.27 (s, 1H, NHb), 7.94 (dd, 1H,  $J = 8.4, 5.6$  Hz, Py-H5), 7.11 (s, 3H, Ar), 2.21 (s, 6H, 2 $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_5\text{Cl}$  (341.75): C, 49.20; H, 4.72; N, 12.30%. Found: C, 48.23; H, 4.76; N, 11.72%. IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3358 (N-H), 3062, 1708 (C=O), 1569, 1517, 1146, 1079 (Cl-O), 792, 780.

### X-Ray crystal structure determination

Diffraction data for the complexes were collected on a Rigaku RAXIS-RAPID IP diffractometer (ligands **1** and **2**), a Bruker SMART CCD area detector (complexes **4–6**), or a Bruker SMART APEX II diffractometer equipped with a CCD area detector (complex **3**), at room temperature (293 K) with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction using SADABS<sup>18</sup> was applied for all data. The structures were solved by direct methods using the SHELXS program.<sup>19</sup> All non-hydrogen

**Table 2** Crystallographic data and refinement details for compounds 1–6

	1	2	3	4	5	6
Empirical formula	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>6</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>28</sub> H <sub>32</sub> N <sub>6</sub> O <sub>6</sub> S	C <sub>14</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>5</sub>
<i>M<sub>r</sub></i>	241.29	259.31	359.76	322.32	580.66	341.75
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
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> 2 <sub>1</sub> 2 <sub>1</sub>	<i>Cc</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> /Å	8.642(2)	13.241(3)	7.6682(6)	10.023(2)	14.118(3)	11.659(2)
<i>b</i> /Å	13.656(3)	7.926(2)	12.761(1)	10.816(2)	16.665(3)	12.283(3)
<i>c</i> /Å	11.778(2)	13.576(3)	16.895(1)	14.610(2)	25.163(5)	21.669(4)
$\alpha$ /°	90.00	90.00	90.00	90.00	90.00	90.00
$\beta$ /°	109.65(3)	110.66(3)	90.00	99.832(3)	90.00	90.00
$\gamma$ /°	90.00	90.00	90.00	90.00	90.00	90.00
<i>V</i> /Å <sup>3</sup>	1309.2(5)	1333.2(5)	1653.2(2)	1560.6(5)	5920(2)	3103(1)
<i>Z</i>	4	4	4	4	8	8
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.224	1.292	1.445	1.372	1.303	1.463
crystal size/mm <sup>3</sup>	0.41 × 0.30 × 0.06	0.45 × 0.32 × 0.22	0.17 × 0.13 × 0.12	0.42 × 0.40 × 0.32	0.26 × 0.23 × 0.09	0.21 × 0.20 × 0.17
<i>F</i> (000)	512	552	752	680	2448	1424
$\mu$ /mm <sup>-1</sup>	0.080	0.089	0.267	0.106	0.160	0.276
$\theta$ range	2.37–27.48	1.85–27.48	2.00–27.48	2.79–25.10	1.62–28.16	2.57–28.18
Reflns collected	11749	12236	10337	3889	36104	18593
Independent reflns	3134	3280	3760	2114	7206	3782
Observed reflns	1585	2223	2377	1743	2455	1511
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]						
<i>R</i> (int)	0.0579	0.0521	0.0378	0.0223	0.1254	0.0762
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0597; 0.1321	0.0482; 0.1292	0.0725; 0.2053	0.0354; 0.0977	0.0532; 0.1272	0.0567; 0.1642
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> (all data)	0.1191; 0.1508	0.0722; 0.1378	0.1087; 0.2416	0.0441; 0.1021	0.1799; 0.1567	0.1432; 0.1922
GOF ( <i>F</i> <sup>2</sup> )	0.947	1.065	1.054	1.051	0.797	0.850

atoms were refined anisotropically by full-matrix least-squares on *F*<sup>2</sup> by the use of the program SHELXL.<sup>19</sup> The hydrogen atoms bonded to carbon and nitrogen were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms on O (water) were located from the difference Fourier map with O–H ≈ 0.85(1) Å and U(H) = 0.08 Å<sup>2</sup>, and were refined isotropically. Complex 3 crystallizes in the non-centrosymmetric space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, and its absolute configuration was confirmed by a Flack factor refinement.<sup>20</sup> Complex 4 was found to crystallize in the non-centrosymmetric space group *Cc*. For a compound of composition C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>5</sub> the absolute structure or Flack-parameter is, however, meaningless in the absence of a heavy atom and the use of anomalous dispersion so that the correct absolute structure or twin law could not be determined. The thermal ellipsoids of ClO<sub>4</sub><sup>-</sup> in compounds 3 and 6 may suggest unresolved disorder of this anion. Crystallographic data for 1–6 are listed in Table 2, and graphics generated using ORTEP-3 for Windows<sup>21</sup> are shown in Figs. 1–6. CCDC reference numbers 636992–636997. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702278f

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## References

- (a) *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. García-España, Wiley-VCH: New York, 1997; (b) *Coord. Chem. Rev.*, 2003, **240**(1–2): 35 Years of synthetic anion receptor chemistry 1968–2003; (c) V. Amendola, D. Esteban-Gómez, L. Fabbrizzi and M. Licchelli, *Acc. Chem. Res.*, 2006, **39**, 343; (d) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465.
- (a) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (b) D. A. Haynes, W. Jones and W. D. S. Motherwell, *CrystEngComm*, 2005, **7**, 342; (c) T. Dorn, C. Janiak and K. Abushandi, *CrystEngComm*, 2005, **7**, 633; (d) E. C. Alyea, D. Craig, I. Dance, K. Fisher, G. Willett and M. Scudder, *CrystEngComm*, 2005, **7**, 491; (e) S. A. Bourne and L. J. Moitsheki, *CrystEngComm*, 2005, **7**, 674; (f) D. Pocic, J.-M. Planeix, N. Kyritsakas, A. Jouaiti and M. W. Hosseini, *CrystEngComm*, 2005, **7**, 624; (g) F. Zordan, S. L. Purver, H. Adams and L. Brammer, *CrystEngComm*, 2005, **7**, 350.
- (a) G. W. Bates, M. Kostermans, W. Dehaen, P. A. Gale and M. E. Light, *CrystEngComm*, 2006, **8**, 445; (b) Y.-H. Wang, K.-L. Chu, H.-C. Chen, C.-W. Yeh, Z.-K. Chan, M.-C. Suen, J.-D. Chen and J.-C. Wang, *CrystEngComm*, 2006, **8**, 84; (c) F. S. Delgado, C. Ruiz-Pérez, J. Sanchiz, F. Lloret and M. Julve, *CrystEngComm*, 2006, **8**, 530; (d) K.-T. Youm, H. K. Woo, J. Ko and M.-J. Jun, *CrystEngComm*, 2007, **9**, 30.
- K. Bowman-James, *Acc. Chem. Res.*, 2005, **38**, 671.
- (a) P. A. Gale, J. L. Sessler, V. Kral and V. Lynch, *J. Am. Chem. Soc.*, 1996, **118**, 5140; (b) S. G. Telfer, X. J. Yang and A. F. Williams, *Dalton Trans.*, 2004, 699; (c) L. H. Uppadine, M. G. B. Drew and P. D. Beer, *Chem. Commun.*, 2001, 291; (d) B. Wu, X. J. Yang, C. Janiak and P. G. Lassahn, *Chem. Commun.*, 2003, 902; (e) C. Schmuck and M. Schwegmann, *J. Am. Chem. Soc.*, 2005, **127**, 3373; (f) P. A. Gale, M. E. Light, B. McNally, K. Navakhun, K. E. Sliwinski and B. D. Smith, *Chem. Commun.*, 2005, 3773; (g) M. D. Lankshear, A. R. Cowley and P. D. Beer, *Chem. Commun.*, 2006, 612; (h) L. S. Evans, P. A. Gale, M. E. Light and R. Quesada, *Chem. Commun.*, 2006, 965.
- For ureas and thioureas, see (a) S. J. Brooks, P. A. Gale and M. E. Light, *CrystEngComm*, 2005, **7**, 586; (b) D. K. Kumar, A. Das and P. Dastidar, *CrystEngComm*, 2006, **8**, 805; (c) J. M. Russell, A. D. M. Parker, I. Radosavljevic-Evans, J. A. K. Howard and J. W. Steed, *CrystEngComm*, 2006, **8**, 119; (d) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon and K. C. Nam, *J. Am. Chem. Soc.*, 2003, **125**, 12376; (e) M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507; (f) R. Custelcean, B. A. Moyer and B. P. Hay, *Chem. Commun.*, 2005, 5971; (g) P. Diaz, J. Benet-Buchholz, R. Vilar and

- 
- A. J. P. White, *Inorg. Chem.*, 2006, **45**, 1617; (h) D. Meshcheryakov, V. Böhmer, M. Bolte, V. Hubscher-Bruder, F. Arnaud-Neu, H. Herschbach, A. van Dorsselaer, I. Thondorf and W. Mögelin, *Angew. Chem., Int. Ed.*, 2006, **45**, 1648.
- 7 (a) C. R. Bondy, P. A. Gale and S. J. Loeb, *Chem. Commun.*, 2001, 729; (b) C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Supramol. Chem.*, 2002, **2**, 93; (c) C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030.
- 8 See, for example, (a) D. R. Turner, E. C. Spencer, J. A. K. Howard, D. A. Tocher and J. W. Steed, *Chem. Commun.*, 2004, 1352; (b) D. R. Turner, B. Smith, A. E. Goeta, I. R. Evans, D. A. Tocher, J. A. K. Howard and J. W. Steed, *CrystEngComm*, 2004, **6**, 633; (c) J. M. Russell, A. D. M. Parker, I. J. Radosavljevic-Evans, A. K. Howard and J. W. Steed, *Chem. Commun.*, 2006, 269.
- 9 D. R. Turner, B. Smith, E. C. Spencer, A. E. Goeta, I. R. Evans, D. A. Tocher, J. A. K. Howard and J. W. Steed, *New J. Chem.*, 2005, **29**, 90.
- 10 P. A. Gale, M. E. Light, B. McNally, K. Navakhun, K. E. Sliwinski and B. D. Smith, *Chem. Commun.*, 2005, 3773.
- 11 P. S. Lakshminarayanan, E. Suresh and P. Ghosh, *Inorg. Chem.*, 2006, **45**, 4372.
- 12 M. R. Pavia, S. J. Lobbstaël, C. P. Taylor, F. M. Hershenson and D. L. Miskell, *J. Med. Chem.*, 1990, **33**, 854.
- 13 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
- 14 L. S. Reddy, S. Basavoju, V. R. Vangala and A. Nangia, *Cryst. Growth Des.*, 2006, **6**, 161.
- 15 (a) X. Zhao, Y.-L. Chang, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1990, **112**, 6627; (b) J. J. Kane, R. F. Liao, J. W. Lauher and F. W. Fowler, *J. Am. Chem. Soc.*, 1995, **117**, 12003; (c) T. L. Nguyen, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 2001, **123**, 11057.
- 16 (a) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885; (b) X.-J. Yang, F. Drepper, B. Wu, W.-H. Sun, W. Haehnel and C. Janiak, *Dalton Trans.*, 2005, 256.
- 17 D. R. Turner, M. Henry, C. Wilkinson, G. J. McIntyre, S. A. Mason, A. E. Goeta and J. W. Steed, *J. Am. Chem. Soc.*, 2005, **127**, 11063.
- 18 G. Sheldrick, Program SADABS: Area-Detector Absorption Correction, University of Göttingen, Germany, 1996.
- 19 G. M. Sheldrick, SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.
- 20 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.
- 21 (a) M. N. Burnett and C. K. Johnson, ORTEP-III, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustration, Oak Ridge National Laboratory Report ORNL-6895, 1996; (b) L. J. Farrugia, ORTEP3 for Windows, Version 1.073, University of Glasgow, 1997; (c) L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.