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Binding of Polyatomic Anions with Protonated Ureido-pyridyl Ligands

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ABSTRACT: Two ureido-pyridyl ligands, 1-(4-nitro-phenyl)-3-pyridine-3-ylmethyl-urea (**L^1**) and 1-pentafluorophenyl-3-pyridine-4-yl-urea (**L^2**) were synthesized in good yields, and solid-state anion binding studies of (H**L^1**)$^+$ and (H**L^2**)$^+$ with polyatomic anions such as NO_3^-, AcO^-, ClO_4^-, SO_4^{2-}, and SiF_6^{2-} were carried out in detail. Protonation of the pyridyl nitrogen center of **L^1** with HNO_3, $HClO_4$, and HF in different solvent media yielded crystals of complexes **1** (H**L^1**·NO_3), **2** (H**L^1**·ClO_4), and **3** (H**L^1**·0.5SiF_6) suitable for single crystal X-ray diffraction studies, respectively. Similarly, protonation of **L^2** with HNO_3, CH_3COOH, and H_2SO_4 yielded single crystals of complexes **4** [2(H**L^2**·NO_3)·DMF], **5** (H**L^2**·AcO), and **6** [(H**L^2**)$_2$·SO_4], respectively. X-ray crystallographic analysis of all these six complexes has been carried out and the details of anion binding with the urea functionality of ureido-pyridyl ligands were investigated. In all the complexes, the pyridyl moiety of the ligands is found to be protonated and the binding of anions are observed at the urea functionality of the ligands through the $R_2^2(8)$ hydrogen bonding motif irrespective of sizes and shapes of anions or the electron withdrawing ability of aryl substitutions (*p*-nitro phenyl vs pentafluoro phenyl) or the position of the pyridyl nitrogen center (protonation site) of the designed ligands.

INTRODUCTION

Anion binding/recognition in synthetic receptors as well as in biological systems is one of the most frontier and emergent areas of research in supramolecular chemistry and it plays many significant roles in different areas of chemistry and biology.[1] Anions have shown enormous potential applications in medicine, catalysis, environment, ion exchange, anion separation in nuclear waste, water purification, etc.[1] In general, organic compounds that are capable of forming hydrogen bonds (e.g., those containing -NH fragments) have been widely studied for coordination of different anions. To date a number of anion recognition elements such as protonated amine,[2] amide,[3] urea,[4] pyrrole,[5] indole,[6] and guanidinium[7] have been developed. In particular, urea-based ligands, good hydrogen bond donors to anions, have attracted lots of interest toward the development of selective anion receptors as well as anion sensors.[4] Two -NH of urea can participate in the binding of anions with various H-bond motifs due to their unidirectional hydrogen bonding nature. It is evident from the crystal structures of many urea based ligands that the most prominent hydrogen bonding pattern is the robust α-network, a tape of bifurcated N−H···O hydrogen bonds between N−H donors and an oxygen acceptor.[8] On the other hand, the urea moiety has immense potential to interact with a variety of anions through the formation of different hydrogen bonding patterns $R_1^2(6)$ for halides, $R_2^2(8)$ for planar, tetrahedral, or octahedral anions (Scheme 1). Several ureido-pyridyl ligands have been utilized as synthons in crystal engineering as well as receptors for anion binding by different groups.[9] For example, Steed et al. have reported a range of anion binding coordination complexes of ureido-pyridyl ligands where the ligand complexes with a metal cation and its conjugate anion.[9a−c] In these cases, the metal-center plays the role in determining the orientation of the receptor units thus by changing the hydrogen bonding patterns. Study of anion binding and anion assisted formation of supramolecular architecture by protonated ureido-pyridyl ligands could be useful in the area of anion coordination chemistry.[9d−h] Thus, the interference of the cationic counterpart, such as metal ions or tetraalkylammonium ions, can be avoided in the anion binding event. An interesting contribution by Gale et al. has shown the importance of cobinding of proton and chloride toward transport of HCl with some amidopyrrole-based ligands in biological systems.[10] Herein we report two new ureido-pyridyl ligands, 1-(4-nitro-phenyl)-3-pyridine-3-ylmethyl-urea and 1-pentafluorophenyl-3-pyridine-4-yl-urea, and structurally demonstrate anion binding properties of these ligands in their protonated form with polyatomic anions such as NO_3^-, AcO^-, ClO_4^-, SO_4^{2-}, and SiF_6^{2-}. In all the complexes, ligands **L^1** and **L^2** were found to be protonated and the primary binding of anion always occurs at the urea moiety, through the $R_2^2(8)$ recognition patterns of strong N−H···O hydrogen bonds, even though the two-dimensional arrangement of the resulting product changing depending upon the substitution on the phenyl ring of ligand and the counteranion.

EXPERIMENTAL SECTION

Materials and Methods. 3-Picolylamine and 4-aminopyridine were purchased from Fluka and used as received. 4-Nitrophenyl

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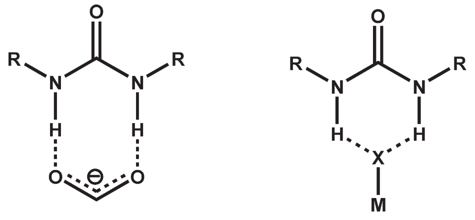
Scheme 1. (a) The R$_2^2$(8) and (b) R$_2^1$(6) Hydrogen Bonded Motifs Observed in the Urea Based Ligands with Oxy-Anions and Metal-Bound Halogens, Respectively



(a) (b)

isocyanate and pentafluorophenylisocyanate were purchased from Sigma-Aldrich and used as received. Methanol (MeOH), chloroform (CHCl$_3$), tetrahydrofuran (THF), acetone, dimethylformamide (DMF), and diethylether were purchased from Spectrochem-India and distilled prior to use. 48% Hydrofluoric acid, 69% nitric acid, 70% perchloric acid, glacial acetic acid, and sulphuric acid were purchased from Merck, India, and used as received without any further purification.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 and 75 MHz or Bruker 500 and 125 MHz FT-NMR spectrometers, respectively, and the chemical shifts are reported in parts per million. Elemental analyses for the synthesized ligands and complexes were carried out with a 2500 series II elemental analyzer (Perkin-Elmer, Waltham, MA).

Syntheses. *Synthesis of* ***L^1***. 3-Picolylamine (0.61 mL, 6 mmol) was dissolved in 50 mL of CHCl$_3$ and the mixture was stirred at RT for 10 min under nitrogen atmosphere. Then 4-nitrophenylisocyanate (0.985 g, 6 mmol) was added to the above solution with constant stirring. The formation of a yellow precipitate in the reaction mixture was observed immediately and was allowed to stir for 10 h. The precipitate was filtered, and the residue was washed with CHCl$_3$ (3 × 10 mL) and with diethyl ether. The product was dried in a vacuum to give a crystalline yellow powder of **1**. Yield: 72%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.35 (d, 2H, −CH_2), 7.02 (t, 1H, N*H*), 7.35 (t, 1H, Ar$_{-\mathrm{CH}}$), 7.63 (d, 2H, Ar$_{-\mathrm{CH}}$), 7.72 (d, 1H, Ar$_{-\mathrm{CH}}$), 8.13 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.45 (d, 1H Ar$_{-\mathrm{CH}}$), 8.54 (s, 1H, Ar$_{-\mathrm{CH}}$), 9.43 (s, 1H, -N*H*). ^{13}C NMR (75 MHz, D$_2$O): δ 41.17, 117.70, 124.13, 125.74, 135.71, 135.97, 141.15, 147.63, 148.75, 149.40, 155.16. Elemental analysis calcd: C, 57.35; H, 4.44; N, 20.58. Found: C, 57.27; H, 4.41; N, 20.52.

Synthesis of ***L^2***. 4-Aminopyridine (940 mg, 10 mmol) was dissolved in 50 mL of THF and the mixture was stirred for 10 min under a nitrogen atmosphere at RT. Pentafluoro phenylisocyanate (1.3 mL, 10 mmol, 1 equiv) was added through a syringe under nitrogen atmosphere with constant stirring. The formation of a white precipitate in the reaction mixture was observed immediately and was allowed to stir for 10 h. The precipitate was filtered, and the residue was washed thoroughly with THF (3 × 10 mL). Then the residue was further washed with diethyl ether and dried in air to give 2.6 g of white powder of **2**. Yield: 86%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.42 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.35 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.72 (b, 1H, -N*H*), 9.53 (b, 1H, -N*H*). ^{13}C NMR (125 MHz, DMSO): δ 112.44, 146.03, 150.17, 151.73. Elemental analysis calcd: C, 47.54; H, 1.99; N, 13.86. Found: C, 47.48; H, 1.91; N, 13.52.

*Synthesis of Complex H**L^1**·NO$_3$,* ***1***. Complex **1** was obtained by adding 0.2 mL of 69% nitric acid to 10 mL of methanolic solution of **L^1** (272.26 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Yellowish crystals suitable for X-ray crystallography were obtained after 2−3 days. Yield of **1**: 62%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm) 4.48 (d, 2H), 7.15 (t, 1H, -N*H*), 7.62 (d, 2H), 7.96 (t, 1H), 8.13 (d, 2H), 8.41 (1H), 8.77 (1H), 8.81 (s, 1H), 9.62 (s, -N*H*). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) 40.25, 117.15, 125.08, 126.40, 139.52, 140.73, 141.85, 143.35, 146.81, 154.71. Elemental analysis calcd: C, 46.57; H, 3.91; N, 20.89. Found: C, 46.23; H, 3.83; N, 20.92.

*Synthesis of Complex H**L^1**·ClO$_4$,* ***2***. Complex **2** was obtained by adding 0.2 mL of 70% perchloric acid to 10 mL acetone solution of **L^1** (272.26 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Pale-yellow crystals suitable for X-ray crystallography were obtained after 2−3 days. Yield of **2**: 71%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 4.52 (d, 2H), 7.15 (t, 1H, -N*H*), 7.62 (d, 2H), 8.06 (t, 1H), 8.13 (d, 2H), 8.54 (1H), 8.82 (1H), 8.86 (s, 1H), 9.64 (s, -N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 40.85, 117.80, 125.69, 127.48, 140.83, 141.03, 141.28, 145.41, 147.35, 155.30. Elemental analysis calcd: C, 41.89; H, 3.52; N, 15.03. Found: C, 41.26; H, 3.23; N, 15.28.

*Synthesis of Complex H**L^1**·0.5SiF$_6$,* ***3***. Complex **3** was obtained by adding 0.1 mL of 48% hydrofluoric acid to the acetone solution of **L^1** (272.26 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Pale-yellow crystals suitable for X-ray crystallography were obtained after 4−5 days. Yield of **3**: 38%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 4.51 (d, 2H), 7.15 (t, 1H, -N*H*), 7.65 (d, 2H), 8.04 (t, 1H), 8.14 (d, 2H), 8.50 (1H), 8.80 (1H), 8.84 (s, 1H), 9.63 (s, -N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 40.84, 117.73, 125.66, 127.32, 140.59, 141.30, 141.48, 144.93, 147.32, 155.29. Elemental analysis calcd: C, 45.35; H, 3.81; N, 16.27. Found: C, 45.16; H, 3.57; N, 16.21.

*Synthesis of Complex 2(H**L^2**·NO$_3$)·DMF,* ***4***. Complex **4** was obtained by adding 0.2 mL of 69% nitric acid to 10 mL dimethylformamide solution of **L^2** (303.19 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography were obtained after 4−5 days. Yield of **4**: 68%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm) 7.43 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.35 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.79 (b, 1H, -N*H*), 9.61 (b, 1H, -N*H*). ^{13}C NMR (125 MHz, DMSO): δ 112.49, 146.22, 150.09, 151.79. Elemental analysis calcd: C, 40.26; H, 2.63; N, 15.65. Found: C, 40.02; H, 2.12; N, 15.52.

*Synthesis of Complex H**L^2**·AcO,* ***5***. Complex **5** was obtained by adding 0.1 mL of glacial acetic acid to the 10 mL methanolic solution of **L^2** (303.19 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography were obtained after 3−4 days. Yield of **5**: 59%; ^{1}H NMR (MeOD, 500 MHz) δ (ppm) 2.01 (s, 3H, C*H*$_3$COO$^-$), 7.57 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.38 (d, 2H, Ar$_{-\mathrm{CH}}$). ^{13}C NMR (125 MHz, MeOD): δ 113.07, 148.99. Elemental analysis calcd: C, 46.29; H, 2.77; N, 11.57. Found: C, 46.10; H, 2.52; N, 11.23.

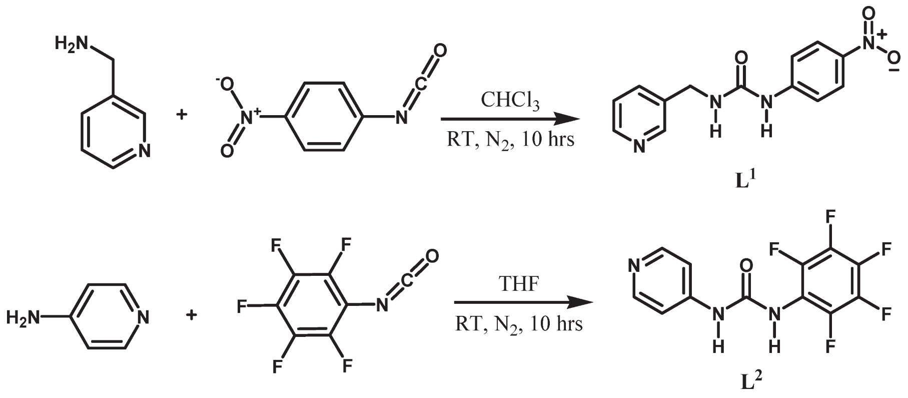
*Synthesis of Complex (H**L^2**)$_2$·SO$_4$,* ***6***. Complex **6** was obtained by adding 0.1 mL of conc. sulphuric acid to the 10 mL methanolic solution of **L^2** (303.19 mg, 1 mmol). After the addition of acid, the clear solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography were obtained after a week. Yield of **5**: 34%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 7.92 (d, 2H, Ar$_{-\mathrm{CH}}$), 8.64 (d, 2H, Ar$_{-\mathrm{CH}}$), 9.37 (s, -N*H*), 10.86 (s, -N*H*). ^{13}C NMR (755 MHz, DMSO-d_6,): δ 114.10, 142.71, 151.89, 154.28. Elemental analysis calcd: C, 40.92; H, 2.00; N, 11.93. Found: C, 40.76; H, 1.97; N, 11.79.

X-ray Measurement and Structure Determination. The crystallographic data and details of data collection for complexes **1**−**6** are given in Table 1. In each case, a crystal of suitable size was selected from the mother liquor, immersed in paratone oil, then mounted on the tip of a glass fiber, and cemented using epoxy resin. The intensity data for all six crystals were collected using MoKα (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with a CCD area detector at 100 K. The data integration and reduction were processed with SAINT[11a] software. An empirical absorption correction was applied to the collected reflections with SADABS.[11b] Structures were solved by direct methods using SHELXTL[12] and were refined on F^2 by a full-matrix

Table 1. Crystallographic Parameters of Complexes 1−6

parameters	1	2	3	4	5	6
formula	$C_{13}H_{13}N_5O_6$	$C_{13}H_{13}ClN_4O_7$	$C_{26}H_{26}F_6N_8O_6Si$	$C_{27}H_{21}F_{10}N_9O_9$	$C_{14}H_{10}F_5N_3O_3$	$C_{24}H_{14}F_{10}N_6O_6S$
M	335.28	372.72	344.32	805.53	363.25	704.47
crystal habit	block	needle	block	block	needle	block
crystal system	triclinic	triclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P2_12_12_1$
a/Å	8.256(10)	8.586(5)	6.3850(10)	10.198(2)	10.9560(10)	7.7890(10)
b/Å	9.084(10)	10.343(6)	7.8280(10)	10.250(2)	17.7010(10)	18.282(2)
c/Å	10.619(10)	10.905(11)	14.914(2)	16.458(3)	7.4980(10)	18.558(2)
α/°	103.73(10)	113.510(10)	104.360(10)	87.780(10)	90	90
β/°	102.17(10)	108.280(10)	100.100(10)	77.010(10)	90	90
γ/°	102.31(10)	99.450(10)	93.240(10)	72.990(10)	90	90
V/Å^3	726.62(14)	795.3(10)	707.03(17)	1602.3(5)	1454.1(2)	2642.6(5)
Z	2	2	2	2	4	4
D_c/g cm^{-3}	1.532	1.556	1.617	1.670	1.659	1.771
μ/mm^{-1}	0.124	0.287	0.182	0.163	0.160	0.249
2θ range [°]	50.00	45.00	50.00	50.00	49.96	49.88
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$F(000)$	348	384	354	816	736	1416
λ/Å	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
min/max/e Å^{-3}	0.154/−0.206	0.286/−0.364	0.196/−0.318	0.251/−0.282	0.127/−0.185	0.203/−0.260
total reflections	8465	3063	6850	24216	12548	14092
unique reflections	2545	1969	2496	8920	2514	4398
reflections used	2292	1515	2312	5998	2411	3940
R_1, $I > 2\sigma(I)$	0.0313	0.0511	0.0278	0.0439	0.0239	0.0328
wR, $I > 2\sigma(I)$	0.0910	0.1409	0.0736	0.0977	0.0609	0.0710

Scheme 2. Syntheses of Ureido-Pyridyl Ligands, L^1 and L^2



least-squares technique using the SHELXL-97[13] program package. Graphics were generated using PLATON[14] and MERCURY 2.3.[15] In all cases, non-hydrogen atoms were treated anisotropically, and all of the hydrogen atoms attached with carbon atoms were geometrically fixed. Hydrogen atoms attached with nitrogen atoms are located in electron Fourier map.

RESULTS AND DISCUSSION

Syntheses. We have designed and synthesized two different ureido-pyridyl ligands, 1-(4-nitro-phenyl)-3-pyridine-3-ylmethyl-urea, $\mathbf{L}^1$ and 1-pentafluorophenyl-3-pyridine-4-yl-urea, $\mathbf{L}^2$, with nitrophenyl and pentafluorophenyl as electron withdrawing substitutions, respectively. The synthetic procedures have been described in Scheme 2. Both the ligands, $\mathbf{L}^1$ and $\mathbf{L}^2$, can be considered as good candidates for the investigation of anion binding with various polyatomic-anions, as they have two different electron withdrawing substitutions in addition to a urea moiety as well as the pyridyl-N in two different positions (3-N and 4-N). Attached electron withdrawing groups and protonation sites in the ligand architecture can presumably play a role in changing the binding nature of the ligand toward anions as well as the variations in the two-dimensional molecular arrangement, upon protonation of the pyridyl group. We have attempted to isolate the protonated salt of $\mathbf{L}^1$ and $\mathbf{L}^2$ with anions of various geometries under different media of crystallization. We are able to isolate only these six complexes **1**−**6** as single crystals

Table 2. Characteristic Hydrogen Bonds Observed in the Complexes **1**−**3**

complex name	D−H···A	H···A/Å	D···A/Å	∠D−HA/°	symmetry code
1	N1−H1A···O6	1.98(2)	2.890(2)	164.4(2)	1 − *x*, 1 − *y*, 2 − *z*
	N2−H2A···O4	2.14(2)	3.019(2)	170.6(1)	1 − *x*, 1 − *y*, 1 − *z*
	N3−H3A···O5	1.99(2)	2.877(2)	178.1(1)	1 − *x*, 1 − *y*, 1 − *z*
	C1−H1···O5	2.55(2)	3.303(2)	136.1(1)	1 + *x*, *y*, *z*
	C3−H3···O2	2.42(2)	3.264(2)	147.4(1)	1 − *x*, −*y*, −*z*
	C5−H5···O4	2.44(2)	3.237(2)	140.6(1)	1 + *x*, 1 + *y*, *z*
2	N1−H11···O3	2.07(7)	2.793(8)	148(6)	−*x*, 1 − *y*, 1 − *z*
	N2−H21···O4	2.23(5)	2.988(7)	175(5)	−1 + *x*, *y*, *z*
	N3−H31···O5	2.12(6)	2.939(7)	173(5)	−1 + *x*, *y*, *z*
	C1−H1···O5	2.58(5)	3.257(7)	134(5)	
	C3−H3···O2	2.56(5)	3.243(8)	137(4)	−1 + *x*, −1 + *y*, −1 + *z*
	C5−H5···O1	2.44(6)	3.290(8)	159(5)	−1 + *x*, *y*, −1 + *z*
3	N1−H1A···F3	1.82(2)	2.741(1)	168.5(2)	−1 + *x*, *y*, *z*
	N2−H2A···F2	2.34(2)	3.056(1)	147.0(2)	*x*, 1 + *y*, *z*
	N2−H2A···F1	2.19(2)	2.926(1)	149.5(2)	1 − *x*, 1 − *y*, 1 − *z*
	N2−H3A···F2	2.09(2)	2.878(1)	158.8(2)	*x*, 1 + *y*, *z*
	C1−H1···F1	2.34(2)	3.113(2)	138.4(1)	−1 + *x*, *y*, *z*
	C5−H5···F3	2.27(2)	3.175(2)	161.7(1)	−*x*, 1 − *y*, 1 − *z*
	C3−H3···O2	2.43(2)	3.181(20	136.4(1)	1 − *x*, 1 − *y*, −*z*
	C12−H12···O3	2.49(2)	3.415(2)	159.7(1)	2 − *x*, 2 − *y*, −*z*

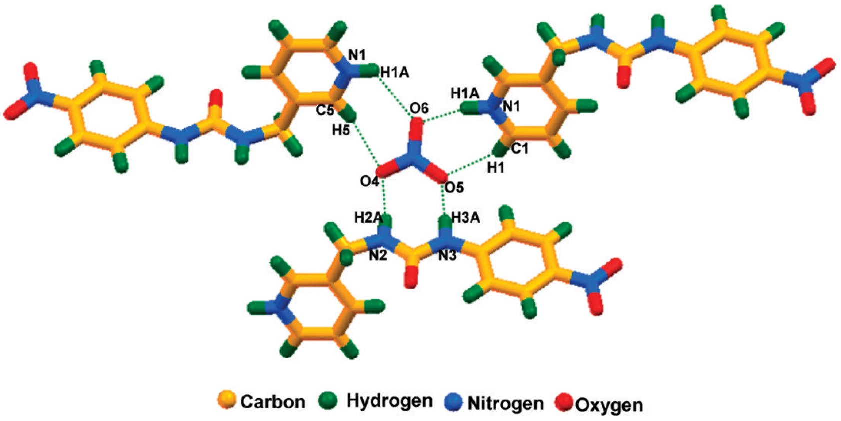


Figure 1. View depicting the interactions of the NO_3^- ion with $[HL^1]^+$ in complex **1**.

suitable for single crystal X-ray analysis. The detailed structural analyses of these complexes are described below.

Binding of Polyatomic Anions with $[HL^1]^+$. Protonated salts of L^1 with HNO_3, $HClO_4$, and HF have been isolated as complexes **1**, **2**, and **3**, respectively. All the crystals have been characterized by single crystal X-ray crystallography (Table 1). The structural analysis revealed that the anions coordinated with the receptors via various hydrogen bonding interactions. Detailed hydrogen bonding interactions of the complexes **1**, **2**, and **3** are given in Table 2.

*Binding of NO_3^- to $[HL^1]^+$ in Complex **1**.* Complex **1** was crystallized in $P\bar{1}$ space group and the asymmetric unit contains one molecule of L^1 and one nitrate anion. Structural analysis revealed that one NO_3^- ion is coordinated with three of the protonated L^1 units via strong N−H···O and C−H···O interactions as shown in Figure 1. The primary interactions are established through $R_2^2(8)$ N−H···O hydrogen bond with the hydrogen bonding parameters: N2−H2A···O4 (N2···O4 = 3.019 Å, ∠N2−H2A···O4 = 171°) and N3−H3A···O5 (N3···O5 = 2.877 Å, and ∠N3−H3A···O5 = 178°). In addition to the hydrogen bonding interactions with urea moieties, the coordinated NO_3^- ion is in strong hydrogen bonding interactions with pyridinium −NH protons and pyridinium −CH protons as shown in Figure 1. The detailed hydrogen bonding interactions are as follows: N1−H1A···O6 (N1···O6 = 2.890 Å, and ∠N1−H1A···O6 = 164°), C1−H1···O5 (C1···O5 = 3.303 Å, and ∠C1−H1···O5 = 136°), and C5−H5···O4 (C5···O4 = 3.237 Å, and ∠C5−H5···O4 = 141°). A complete list of hydrogen bonding interactions of complex **1** is given in Table 2.

Thus, in complex **1**, the NO_3^- ion is coordinated with three units of HL^1 units and is stabilized by two N−H···O interactions from urea, two $N-H_{py}$···O and C−H···O interactions

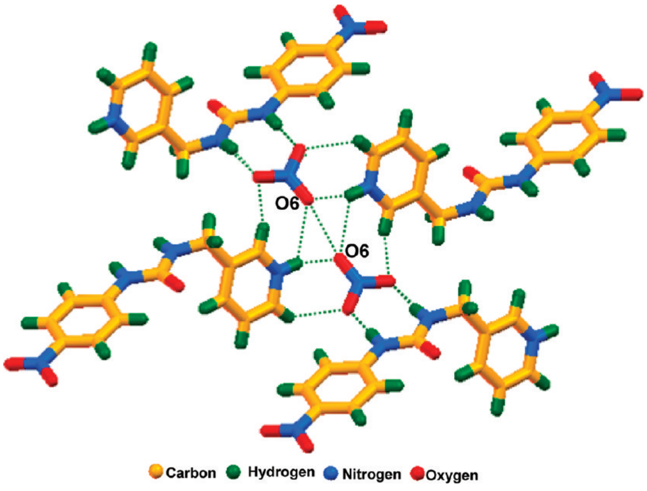


Figure 2. View showing the $NO_3^- \cdots NO_3^-$ interactions and the hydrogen bonding interactions of NO_3^- to the protonated receptor unit in complex **1**.

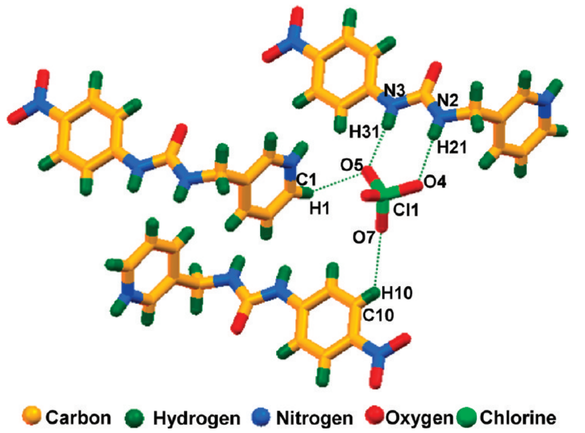


Figure 3. MERCURY diagram depicting the interactions of the ClO_4 ion with three units of $[HL^1]^+$ in complex **2**.

from pyridinium units of two different ligands. Thus, the overall coordination number of the NO_3^- ion is six in **1**. Further, such quadrate units are interconnected through $NO_3^- \cdots NO_3^-$ interactions (O6···O6, 2.77 Å) in two dimensions as shown in Figure 2. It is important to mention that $NO_3^- \cdots NO_3^-$ interactions in the solid state are quite interesting, and indeed it is known from the literature that $NO_3^- \cdots NO_3^-$ interactions have a great importance in describing the structural features of the corresponding salts.[16]

Upon protonation of the pyridine nitrogen atom, the aryl-CH protons of the pyridine units become more acidic due to the positive charge in the pyridinium ring, and hence the aryl −CH protons are more prone to form hydrogen bonding interactions with NO_3^- ion. Though the receptor possesses only one urea unit, to satisfy the number of coordination the nitrate anion interacted with two other protonated receptor molecules. Other than urea functionality, the protonated $\mathbf{L^1}$ possesses pyridinium -NH and -CH protons adjacent to a protonated pyridyl nitrogen center as a hydrogen bonding element which allow six coordination to the anion.

*Binding of ClO_4^- to $[H\mathbf{L^1}]^+$ in Complex **2**.* Complex **2** is crystallized in triclinic space group $P\bar{1}$. Crystal structure analysis shows that the asymmetric unit contains one protonated ligand, $[H\mathbf{L^1}]^+$, and a ClO_4^- anion. Structure analysis revealed that one ClO_4^- ion is coordinated with three of the protonated $\mathbf{L^1}$ units via strong N−H···O and C−H···O interactions as shown in Figure 3. Further, the primary interactions are established through $R_2^2(8)$ N−H···O hydrogen bonding interactions with urea −NH protons with following bonding parameters as observed in the case of complex **1**: N2−H21···O4 (N2···O4 = 2.9852 Å, and ∠N2−H21···O4 = 173°), N3−H31···O5 (N3···O5 = 2.9344 Å, and ∠N3−H31···O5 = 173°), C1−H1···O5 (C1···O5 = 3.257 Å, ∠C1−H1···O5 = 133.85°) and C10−H10···O7 (C10···O7 = 3.286 Å, ∠C10−H10···O7 = 125.29°). A complete list of hydrogen bonding interactions of complex **2** is given in Table 2.

Here the ClO_4^- ion is hydrogen bonded with receptor units by four hydrogen bonding interactions (two from urea −NH protons and another two from pyridinium −CH protons of two different ligands). The ClO_4^- ion interacts with the pyridinium -NH protons as observed in the case of **1**. Thus, the cocrystallization of ligand $\mathbf{L^1}$ with oxy-acids such nitric and perchloric acids yielded complexes **1** and **2** in which the corresponding anions were bound with the urea functionality of the ligand via the same binding topology.

*Binding of SiF_6^{2-} to $[H\mathbf{L^1}]^+$ in Complex **3**.* Complex **3** crystallized in triclinic $P\bar{1}$ space group. Structural analysis revealed that one SiF_6^{2-} ion is hydrogen bonded with four units of protonated receptor $\mathbf{L^1}$ via N−H···F hydrogen bonds as shown in Figure 4a. Two of the $\mathbf{L^1}H^+$ units are in coordination with SiF_6^{2-} through their two urea moieties and four F atoms of SiF_6^{2-} through the formation of cyclic N−H···F hydrogen bonds, whereas remaining two F atoms are in hydrogen bonding interaction with the pyridinium hydrogen of two other $\mathbf{L}^1H^+$.

Detailed hydrogen bonding interactions are as follows: N1−H1A···F3 (N1···F3 = 2.741(1) Å, ∠N1−H1A···F3 = 168.5(2)°), N2−H2A···F1 (N2···F1 = 2.926(1) Å, ∠N2−H2A···F1 = 149.5(2)), N3−H3A···F2 (N3···F2 = 2.878(1)Å, ∠N3−H3A···F2 = 158.8(2)), and C1−H1···F1 (C1···F1 = 3.175(2) Å, ∠C1−H1···F1 = 138.4(1)). Complete list of hydrogen bonding interactions of complex **3** are given in Table 2. Thus, one SiF_6^{2-} anion was strongly bound with four $\mathbf{L}^1H^+$ ligands leading to the formation of a square as depicted in Figure 4b. Further, such adjacent squares are aggregated to yield a two-dimensional sheet and the sheets are stacked along the *a*-axis in three dimensions.

Binding of Polyatomic Anions with $[H\mathbf{L^2}]^+$. Binding of polyatomic anions have also been performed with the ureido-pyridyl ligand $\mathbf{L^2}$ which possesses a strong electron withdrawing pentafluorophenyl group without any spacer. Several attempts have been made to isolate the protonated salts of $\mathbf{L^2}$ under different mediums of crystallization. However, we could isolate only HNO_3, CH_3COOH, and H_2SO_4 complexes of $\mathbf{L^2}$ as complexes **4**, **5**, and **6**, respectively, as crystals suitable for single crystal X-ray analysis. All these complexes have been characterized structurally and anions are coordinated with the protonated receptor units via various hydrogen bonding interactions. Detailed hydrogen bonding interactions are given in Table 3.

*Binding of NO_3^- to $[H\mathbf{L^2}]^+$ in Complex **4**.* Protonation of $\mathbf{L^2}$ with HNO_3 in a solution of dimethylformamide (DMF) afforded complex **4** as colorless block crystals which are suitable for single crystal X-ray crystallographic analysis. Solid state structure of **4** revealed that the complex crystallized in triclinic $P\bar{1}$ space group, and there are two protonated molecules of $\mathbf{L^2}$ ($\mathbf{L}^2H^+$), two nitrate anions, and one DMF molecule present in the asymmetric

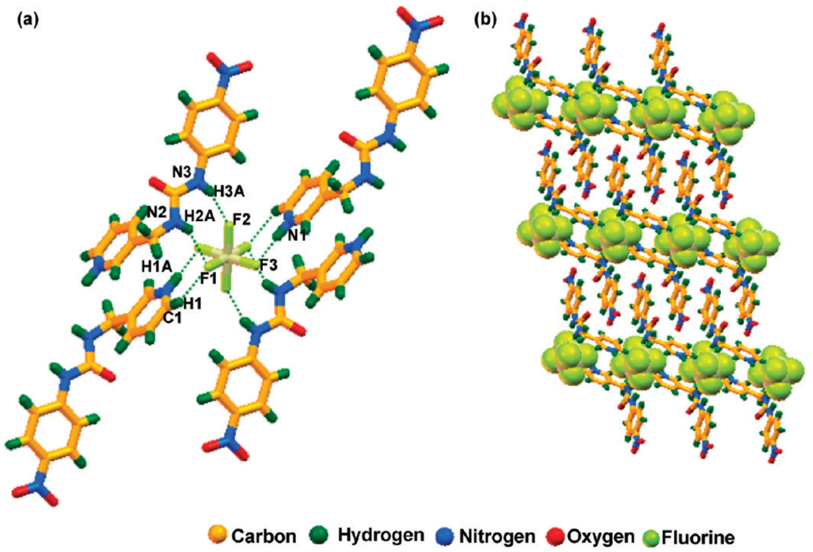


Figure 4. (a) MERCURY diagram depicting the N−H···F and C−H···F interactions of the SiF_6^{2-} ion with four units of $[HL^1]^+$ in complex **3** and (b) the three-dimensional stacked sheets formed by the aggregation of adjacent molecular squares.

Table 3. Characteristic Hydrogen Bonds Observed in the Complexes 4−6

complex name	D−H···A	H···A/Å	D···A/Å	∠D−H···A/°	symmetry code
4	N1−H1···O3	1.98(2)	2.839(2)	168.2(2)	1 − *x*, 1 − *y*, 1 − *z*
	N2−H21···O2	1.99(2)	2.823(2)	166.6(2)	1 − *x*, 2 − *y*, 1 − *z*
	N3−H31···O1	2.09(2)	2.914(2)	173.9(2)	1 − *x*, 2 − *y*, 1 − *z*
	N4−H41···O4	1.93(2)	2.826(2)	176.8(1)	−1 + *x*, *y*, *z*
	N5−H51···O6	2.01(2)	2.859(2)	171(2)	−1 + *x*, 1 + *y*, *z*
	N6−H61···O5	2.02(2)	2.836(2)	171.9(2)	−1 + *x*, 1 + *y*, *z*
	C3−H3···O1	2.41(2)	3.153(2)	133.5(2)	
	C3−H3···O7	2.43(2)	3.190(2)	135.6(1)	
	C4−H4···O6	2.55(2)	3.367(2)	144.3(1)	1 − *x*, 1 − *y*, −*z*
	C5−H5···O2	2.48(2)	3.240(2)	137.3(1)	*x*, 1 + *y*, *z*
	C13−H13···O2	2.48(2)	3.222(2)	148.2(1)	−*x*, 1 − *y*, −*z*
	C13−H13···O3	2.51(2)	3.261(2)	136.7(1)	−*x*, 1 − *y*, −*z*
	C14−H14···O6	2.54(2)	3.31292)	137.6(1)	−1 + *x*, 1 + *y*, *z*
	C26−H26···O4	2.57(2)	3.424(2)	140.9(2)	
5	N1−H1A···O3	1.64(2)	2.609(2)	169.8(2)	1/2 − *x*, 1/2 + *y*, 1/2 + *z*
	N2−H2A···O2	1.81(2)	2.681(2)	167(2)	
	N3−H3A···O3	2.04(2)	2.858(2)	178(3)	
	C1−H1···F2	2.48(2)	3.456(2)	171.9(2)	3/2 − *x*, 1/2 + *y*, 1/2 + *z*
	C5−H5···F1	2.55(2)	3.36(2)	150.1(5)	
	C4−H4···O2	2.56(2)	3.233(2)	134.0(1)	
	C5−H5...O1	2.24(2)	3.005(2)	141.2(1)	−1/2 + *x*, 1/2 − *y*, *z*
6	N1−H1A···O5	1.61(3)	2.617(3)	175(2)	−*x*, −1/2 + *y*, 1/2 − *z*
	N2−H2A···O3	2.06(3)	2.897(3)	170(3)	
	N3−H3A···O4	2.01(3)	2.776(3)	177(3)	
	N4−H4A···O4	1.80(3)	2.750(3)	163(3)	1 − *x*, −1/2 + *y*, 1/2 − *z*
	N5−H5A···O3	2.00(3)	2.912(3)	166(3)	1 − *x*, 1/2 + *y*, 1/2 − *z*
	N6−H6A···O6	1.84(3)	2.732(3)	179(4)	1 − *x*, 1/2 + *y*, 1/2 − *z*
	C1−H1···O2	2.48	3.247(3)	139	1/2 − *x*, −*y*, −1/2 + *z*
	C16−H16···O3	2.47	3.231(3)	139	
	C13−H13···F5	2.40	3.312(4)	167	1 − *x*, −1/2 + *y*, 1/2 − *z*
	C17−H17···F10	2.46	3.386(4)	171	1 − *x*, −1/2 + *y*, 1/2 − *z*

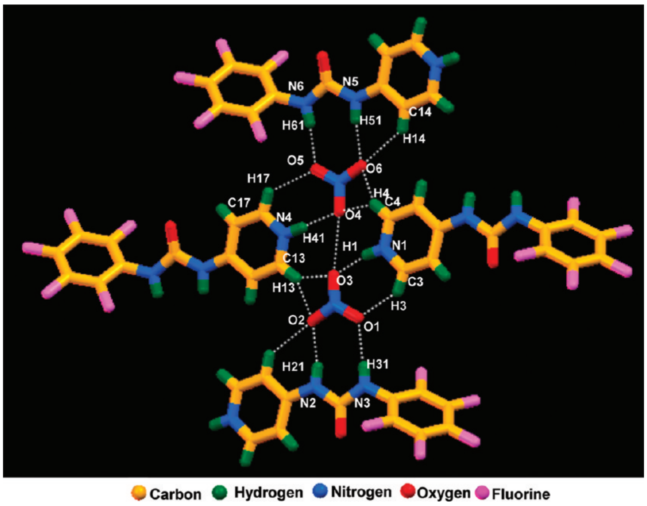


Figure 5. (a) MERCURY diagram depicting the N−H···O and C−H···O interactions of the NO_3^-···NO_3^- dimer with four units of $[HL^1]^+$ in complex **4**.

unit. The molecular packing analysis shows that $\mathbf{L}^2\mathrm{H}^+$ is coordinated with a NO_3^- ion through cyclic N−H···O hydrogen bonding interactions. In addition to the hydrogen bonding with urea −NH protons, the coordinated NO_3^- ion is in strong interaction with −NH protons as well as −CH protons of pyridinium moieties. Detailed hydrogen bonding interactions and bond parameters are as follows: N1−H1···O3 (N1···O3 = 2.839(2) Å, ∠N1−H1···O3 = 168.2(2)), N2−H21···O2 (N2···O2 = 2.823(2) Å, ∠N2−H21···O2 = 2.823(2) Å), N3−H31···O1 (N3···O1 = 2.914(2) Å, ∠N3−H31···O1 = 173.9(2)°), N4−H41···O4 (N4...O4 = 2.826(2) Å, ∠N4−H41···O4 = 176.8(1)°), N5−H51···O6 (N5···O6 = 2.859(2) Å, ∠N5−H51···O6 = 171(2) °), N6−H61···O5 (N6···O5 = 2.836(2) Å, ∠N6−H61···O5 = 171.9(2) °). In addition to the above-described conventional hydrogen bonding interactions, in complex **4**, NO_3^- is also involved in C−H···O interactions with pyridinium moieties. A complete list of hydrogen bonding interactions and the bond parameters are given in Table 3. As observed in the case of complex **1**, in complex **4** also, the nitrate ion exists as a NO_3^-···NO_3^- dimer (Figure 5) that leads to a quadrate unit (Figure 6). The adjacent quadrate units are interconnected through N−H···O hydrogen bonds formed between the pyridinium moiety of $\mathbf{L}^2\mathrm{H}^+$ and the nitrate anion to yield a two-dimensional molecular tape along the *b*-axis. Further, the tapes are interconnected through DMF molecules, which are entrapped in the clefts formed by the molecular tape, with the help of weak interactions such as C−F···π formed between the pentafluorophenyl moiety and the DMF molecule which leads to a two-dimensional planar sheet as shown in Figure 6. The solvent molecules act as connectors of the tapes to yield two-dimensional sheets. It is worth mentioning that the hydrogen bonding pattern and the crystal packing arrangements of the complex **4** resemble that of **1**. However, the fluorine substitutions on $\mathbf{L}^2$ do not have much influence on changing the hydrogen bonding pattern in the complex but a little on the molecular packing arrangement. The one-dimensional tapes in complex **4** are connected through the solvent molecules present in clefts, and similar types of molecular tapes in complex **1** are directly connected to each other through weak C−H···O hydrogen bonds formed between the tapes making use of the NO_3^- present in the ligand.

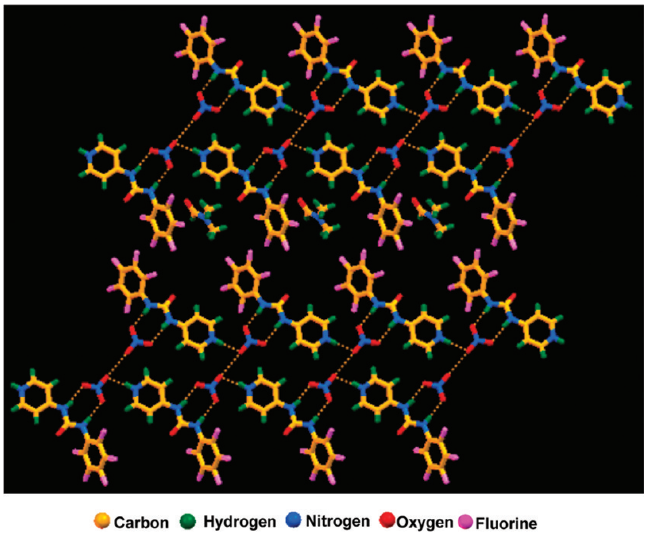


Figure 6. Two-dimensional sheets formed by the molecular tapes of $\mathbf{L}^2\mathrm{H}^+$ and NO_3 observed in complex **4**. Interactions of DMF molecules with the clefts are omitted for clarity.

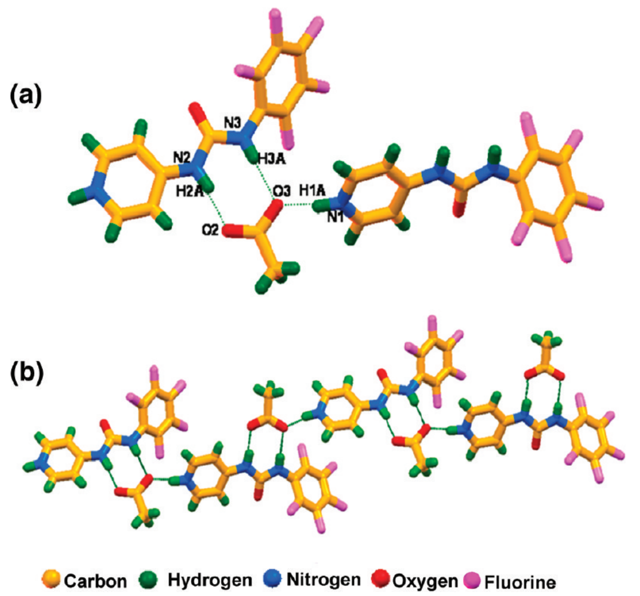


Figure 7. (a) Hydrogen bonding interactions of AcO^- ion with the protonated receptor units of $\mathbf{L}^2$ in complex **5**. (b) AcO^- assisted formation of a zigzag 1-D network in complex **5**.

*Binding of CH_3COO^- to $[H\mathbf{L}^2]^+$ in Complex **5**.* Complex **5** crystallized in *Pna*2_1 orthorhombic space group as colorless single crystals suitable for X-ray analysis by treating $\mathbf{L}^2$ with acetic acid in a solution of CH_3OH. The asymmetric unit of the complex contains one protonated unit of $\mathbf{L}^2\mathrm{H}^+$ and one CH_3COO^-. The structural analysis revealed that the acetate anion is bound with $\mathbf{L}^2\mathrm{H}^+$ via N−H···O interactions of the urea moiety (Figure 7). The detailed hydrogen bonding interactions and the bond parameters are as follows: N1−H1A···O3 (N1···O3 = 2.609(2) Å, ∠N1−H1A···O3 = 169.8(2)°), N2−H2A···O2 (N2···O2 = 2.681(2) Å, ∠N2−H2A···O2 = 167(2)) and N3−H3A···O3 (N3···O3 = 2.858(2) Å, ∠N3−H3A···O3 = 178(3)). A complete list of hydrogen

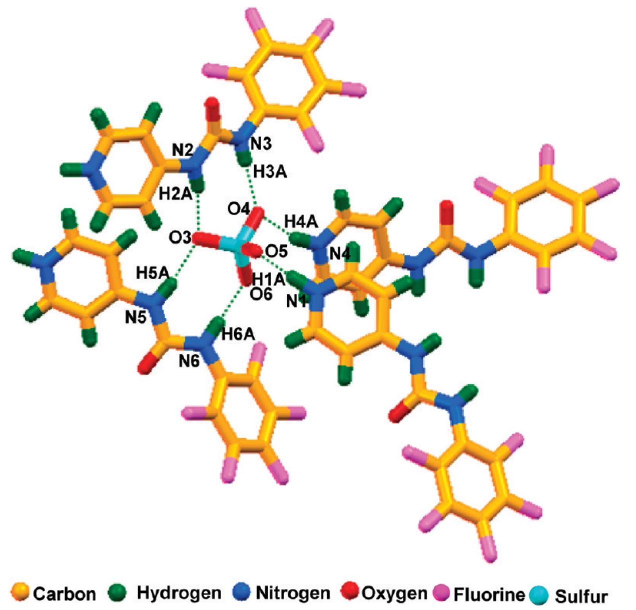


Figure 8. Hydrogen bonding interactions of SO_4^{2-} in complex **6**.

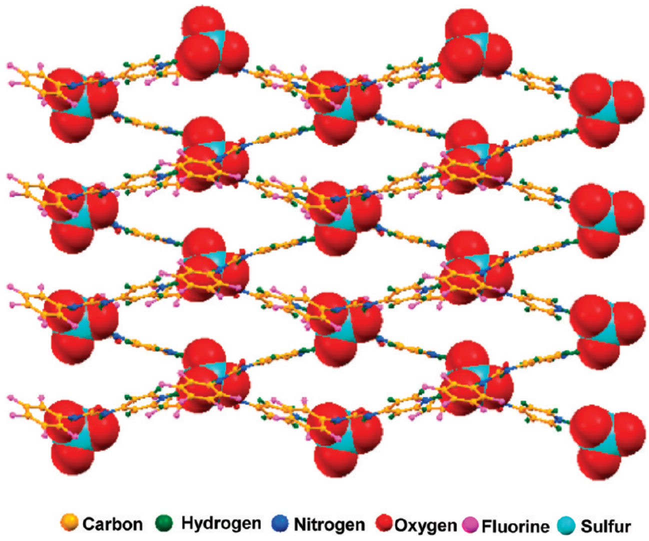


Figure 9. Packing diagram showing the three-dimensional network formed by SO_4^{2-} in complex **6**.

bonding interactions of complex **5** is given in Table 3. Such adjacent dimeric units are held together by N−H···O hydrogen bonds formed between the pyridinium moiety of $[HL^2]^+$ and acetate anion to form a one-dimensional zigzag chain (Figure 7b).

*Binding of SO_4^- to $[H\mathbf{L}^2]^+$ in Complex **6**.* The asymmetric unit of the complex **6** contains two protonated units of $[HL^2]^+$ and one sulfate (SO_4^{2-}) anion as revealed from its crystal structure. The structural analysis of the complex shows that one SO_4^{2-} anion is bound with four units of $\mathbf{L}^2H^+$ as shown in Figure 8. Among the four receptor units two are connected through $R_2^2(8)$ type N−H···O hydrogen bonds, formed between a urea moiety of the $\mathbf{L}^2H^+$ unit and SO_4^{2-} anion, while the other two units of $\mathbf{L}^2H^+$ are connected through N−H···O hydrogen bonds. Detailed hydrogen bonding interactions and bond parameters are as follows: N1−H1A···O5 (N1···O5 = 2.617(3) Å, ∠N1−H1A···O5 = 175(2)°), N2−H2A···O3 (N2···O3 = 2.897(3) Å, ∠N2−H2A···O3 = 170(3)°), N3−H3A···O4 (N3···O4 = 2.776(3) Å, ∠N3−H3A···O4 = 177(3)°), N3−H3A···O4 (N3···O4 = 2.776(3) Å, ∠N3−H3A···O4 = 177(3)°), N4−H4A···O4 (N4···O4 = 2.750(3) Å, ∠N4−H4A···O4 = 163(3)°), N5−H5A···O3 (N5···O3 = 2.912(3) Å, ∠N5−H5A···O3 = 166(3) °), N6−H6A···O6 (N6···O6 = 2.732(3) Å, ∠N6−H6A···O6 = 179(4) °). Other than these convention hydrogen bonding interactions, the coordinated sulfate is also involved in C−H···O interactions with the pyridinium units. A complete list of hydrogen bonding interactions along with bond parameters is given in Table 3. Further, this kind of adjacent spherical unit is connected through a similar type of N−H···O hydrogen bond, where the SO_4^{2-} anion is bound with the remaining urea moieties through $R_2^2(8)$ and two other pyridinium units forming a similar type of hydrogen bonding environment, to yield a three-dimensional network as shown in Figure 9. Thus, each spherical unit contains a SO_4^{2-} anion embedded around the four units of $\mathbf{L}^2H^+$ through the strong N−H···O hydrogen bonds.

CONCLUSION

In summary, we have shown the coordination of polyatomic anions of various geometries (planar, tetrahedral, and octahedral) with two new ureidopyridyl ligands in their protonated forms. Detailed structural analysis of these complexes clearly demonstrates that the anion binding occurs mostly via urea −NH, pyridinium −NH, and −CH hydrogen adjacent to the pyridinium moiety. In all cases, the primary binding of these polyatomic anion always occurs at the urea moiety, through the $R_2^2(8)$ recognition patterns formed by strong N−H···O hydrogen bonds. Thus, neither the substituents/topology of the receptor nor the geometry of the anions has influence on the primary binding motif of anions with receptors of this category.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** NMR spectra and crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Themed issue: Supramolecular chemistry of anionic species. *Chem. Soc. Rev.* **2010**, *39*, 3581−4008. (b) Bianchi, A.; Bowman-James, K., García-España, E., Eds. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997. (c) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry: Monographs in Supramolecular Chemistry*; RSC Publishing: Cambridge, U.K., 2006. (d) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516.

(2) (a) Mateus, P.; Bernier, N.; Delgado, R. *Coord. Chem. Rev.* **2010**, *254*, 1726–1747. (b) García-España, E.; Díaz, P.; Llinares, J. M.; Bianchi, A. *Coord. Chem. Rev.* **2006**, *250*, 2952–2986. (c) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678. (d) Arunachalam, M.; Ravikumar, I.; Ghosh, P. *J. Org. Chem.* **2008**, *73*, 9144–9147. (e) Lakshminarayanan, P. S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Inorg. Chem.* **2007**, *46*, 4769–4771.

(3) (a) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7882–7894. (b) Kang, S. O.; Hossain, M. A.; Bowman-James, K. *Coord. Chem. Rev.* **2006**, *250*, 3038–3052. (c) Arunachalam, M.; Ghosh, P. *Org. Lett.* **2010**, *12*, 328–331. (d) Arunachalam, M.; Ghosh, P. *Chem. Commun.* **2009**, 5389–5391. (e) Arunachalam, M.; Ghosh, P. *Inorg. Chem.* **2010**, *49*, 943–951. (f) Valiyaveettil, S.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 900–901. (g) Choi, K.; Hamilton, A. D. *J. Am. Chem. Soc.* **2001**, *123*, 2456–2457. (h) Liao, J.-H.; Chen, C.-T.; Fang, J. M. *Org. Lett.* **2002**, *42*, 561–564. (i) Kondo, S.-I.; Hiraoka, Y.; Kurumatani, N.; Yano, Y. *Chem. Commun.* **2005**, 1720–1722. (j) Beer, P. D.; Dickson, A. P.; Fletcher, N.; Goulden, A. J.; Grieve, A.; Hodacova, J.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1993**, 828–830. (k) Kuo, L.-J.; Liao, J.-H.; Chen, C.-T.; Huang, C.-H.; Chen, C. S.; Fang, J.-M. *Org. Lett.* **2003**, *5*, 1821–1824.

(4) (a) Steed, J. W. *Chem. Soc. Rev.* **2010**, *39*, 3686–3699. (b) Li, A.-F; Wang, J.-H; Wang, F.; Jiang, Y.-B. *Chem. Soc. Rev.* **2010**, *39*, 3729–3745. (c) Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem. Soc. Rev.* **2010**, *39*, 3889–3915.(d) Gale, P. A. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L.; Steed, J. W., Eds.; Marcel Dekker: New York, 2004; pp 31−41. (e) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77–99. (f) Lakshminarayanan, P. S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Chem. Commun.* **2007**, 5214–5216. (g) Ravikumar, I.; Lakshminarayanan, P. S.; Arunachalam, M.; Suresh, E.; Ghosh, P. *Dalton Trans.* **2009**, 4160–4168. (h) Ravikumar, I.; Ghosh, P. *Chem. Commun.* **2010**, *46*, 1082–1084.

(5) (a) Gale, P. A.; Sessler, J. L.; Camiolo, S. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L.; Steed, J. W., Ed.; Marcel Dekker: New York, 2004; pp 1176−1185. (b) Gale, P. A. *Chem. Commun.* **2008**, 4525–4540.

(6) (a) Gale, P. A. *Chem. Commun.* **2008**, 4525–4540. (b) Sessler, J. L.; Cho, D.-G.; Lynch, V. *J. Am. Chem. Soc.* **2006**, *128*, 16518–16519. (c) Gale, P. A.; Hiscock, J. R.; Jie, C. Z.; Hursthouse, M. B.; Light, M. E. *Chem. Sci.* **2010**, 215–220.

(7) (a) Anslyn, E. V.; Tohey, S. L. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L.; Steed, J. W., Eds.; Marcel Dekker: New York, 2004; pp 615−627. (b) Schmuck, C.; Dudaczek, J. *Tetrahedron Lett.* **2005**, *46*, 7101–7105. (c) Schug, K. A.; Lindner, W. *Chem. Rev.* **2005**, *105*, 67–113.

(8) (a) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383–2420. (b) Whitesides, G. M.; Mathias, J. P; Seto, C. T. *Science* **1992**, *254*, 1312–1314. (c) George, S.; Nangia, A.; Lam, C. K.; Mak, T. C. W.; Nicoud, J.-F. *Chem. Commun.* **2004**, 1202–1203. (d) Marivel, S.; Suresh, E.; Pedireddi, V. R. *Tetrahedron Lett.* **2008**, *49*, 3666–3671.

(9) (a) Russell, J. M.; Parker, A. D. M.; Radosavljevic-Evans, I.; Howard, J. A. K.; Steed, J. W. *Chem. Commun.* **2006**, 269–271. (b) Turner, D. R.; Smith, B.; Goeta, A. E.; Evans, I. R.; Tocher, D. A.; Howard, J. A. K.; Steed, J. W. *CrystEngComm* **2004**, *6*, 633–641. (c) Turner, D. R.; Smith, B.; Spencer, E. C.; Goeta, A. E.; Evans, I. R.; Tocher, D. A.; Howard, J. A. K.; Steed, J. W. *New J. Chem.* **2005**, *29*, 90–98. (d) Llyod, G. O.; Steed, J. W. *Soft Matter* **2011**, *7*, 75–84. (e) Rashdan, S.; Light, M. E.; Kilburn, J. D. *Chem. Commun.* **2006**, 4578–4580. (f) Wu, B.; Huang, X.; Xia, Y.; Yang, X.-J.; Janiak, J. *CrystEngComm* **2007**, *9*, 676–685. (g) Blondeau, P.; Lee, A. V. D.; Barboiu, M. *Inorg. Chem.* **2005**, *44*, 5649–5653. (h) Byrne, P.; Turner, D. T.; Llyod, G. O.; Clarke, N.; Steed, J. W. *Cryst. Growth Des.* **2008**, *8*, 3335–3344.

(10) Gale, P. A.; Light, M. E.; McNally, B.; Navakhun, K.; Sliwinski, K. E.; Smith, B. D. *Chem. Commun.* **2005**, 3773–3775.

(11) (a) Sheldrick, G. M. *SAINT and XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995. (b) *SADABS, Empirical Absorption Correction Program*; University of G€ottingen: Gottingen, Germany, 1997.

(12) Sheldrick, G. M. *SHELXTL Reference Manual*, Version 5.1; Bruker AXS: Madison, WI, 1997.

(13) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(14) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

(15) *Mercury 2.3*, Supplied with Cambridge Structural Database; CCDC: Cambridge, UK

(16) Nelyubina, Y. V.; Lyssenko, K. A.; Golovanov, D. G.; Antipin, M. Y. *CrystEngComm* **2007**, *9*, 991–996.