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Anion binding of a bis(pyridylcarbamate) receptor bearing a diethylene glycol spacer

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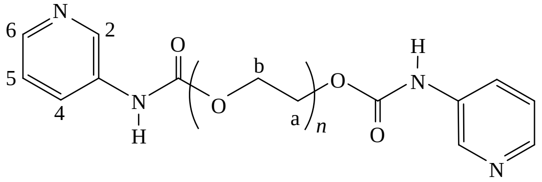
A flexible bis(pyridylcarbamate) receptor, 3-pyridyl-carbamic-acid-oxydi-1,2-ethanediylester (L^2) and the anion complexes (**1**–**3**) of the doubly protonated ligand ($[L^2H_2]^{2+}$) with ClO_4^-, SO_4^{2-} and Cl^- are reported. The binding modes of $[L^2H_2]^{2+}$ with the anions in **1**–**3** in the solid state are established by X-ray single crystal diffraction. Compounds **1** and **3** feature intriguing anionic polymer fashions. In compound **1**, two zigzag perchlorate–water chains are encapsulated in the 1D channel constructed by 2+2 ($2[L^2H_2]^{2+} + 2ClO_4^-$) hydrogen-bonded macrocycles, while in **3** the chloride ions are trapped on the wall of the hydrogen-bonded 1D channel formed by two U-shaped ligands. For compound **2**, the packing diagram displays a corrugated layer structure, with the sulphate ions and the water molecules located between the layers. Receptor L^2 crystallises with perchlorate from the acid mixture $HClO_4$, H_2SO_4 and HCl.

Keywords: anion receptor; bis(pyridylcarbamate); hydrogen-bonded macrocycle

Introduction

The design of anion receptors is of much interest due to the important roles anions play in a variety of areas (*1*). Many synthetic anion receptors based on hydrogen-bonding interactions of appropriate functionalities (e.g. NH group) have been prepared over the last two decades (*2*). However, it is noticed that self-association of the receptor may occur during the anion complexation, which can reduce the available hydrogen bond donor sites for anions. For example, *N*,*N*′-disubstituted ureas tend to be self-bound via hydrogen bonding with the graphic set R_2^1 (6) to form a 1D tape (*3*). Hence, it should be taken into consideration in the design for anion receptors to ensure that the hydrogen-bonding donors are fully utilised to coordinate to anions.

We have been interested in anion binding by a series of urea-based pyridyl ligands (*4*). To avoid self-association of the receptors, recently, we have also synthesised a bis(pyridylcarbamate) receptor with an ethylene glycol linker, 3-pyridinyl-carbamic-acid-1,2-ethanediylester (L^1, Chart 1), and found that it had a high affinity for anions without any self-interactions (*5*). Herein, we report a more flexible bis(pyridylcarbamate) analogue with a longer diethylene glycol linker, 3-pyridinyl-carbamic-acid-oxydi-1,2-ethanediylester (L^2, Chart 1), and three adducts (**1**–**3**) of the doubly protonated ligand ($[L^2H_2]^{2+}$) with tetrahedral anions (SO_4^{2-} and ClO_4^-) and the spherical anion Cl^-. As with ligand L^1, there is no self-association for the new receptor L^2 in the acid adducts and all the N^+H (pyridinium) and NH groups are involved in the direct or indirect coordination with anions as expected.



L^n

Chart 1. Structure of L^n.

Results and discussion

The ligand 3-pyridinyl-carbamic-acid-oxydi-1,2-ethanediylester (L^2) was synthesised by a similar method as reported for its analogue L^1 (*5*), except that diethylene glycol was used instead of ethylene glycol. The white powder of ligand L^2 is soluble in methanol, ethanol, acetonitrile, acetone, DMF and DMSO. Compounds **1**–**3** were obtained by the reaction of L^2 with the corresponding diluted acids $HClO_4$, H_2SO_4 and HCl, respectively, in an ethanol–water solution. The compounds are soluble in methanol, hot ethanol, DMF and DMSO.

Crystal structure

*$L^2 \cdot 2HClO_4 \cdot H_2O$ (**1**)*

Compound **1** crystallises in the triclinic space group *P*-1. The asymmetric unit contains a fully protonated ligand ($[L^2H_2]^{2+}$ cation), two perchlorate anions and one crystalline water molecule. The protonated ligand adopts a GAAG conformation with torsion angles of 67.36,

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Table 1. Hydrogen bond parameters (Å, °) for $L^2 \cdot 2HClO_4 \cdot H_2O$ (**1**).

D—H···A	D—H	H···A	D···A	∠D—H···A
N1—H1B···O8	0.86	2.15	2.836(8)	137.0
N1—H1B···O12	0.86	2.30	2.961(8)	133.3
N2—H2B···O14[a]	0.86	2.18	3.012(8)	162.0
N3—H3B···O14[a]	0.86	2.19	3.039(7)	169.5
N4—H4A···O13[b]	0.86	2.09	2.801(7)	139.2
O14—H14C···O9[c]	0.852(10)	2.09(4)	2.858(7)	150(8)
O14—H14B···O3	0.851(10)	1.958(19)	2.801(7)	170(8)

Notes: Symmetry codes: (a) $x+1, y, z$, (b) $-x, 1-y, 1-z$ and (c) $x-1, y, z$.

−163.92, 160.74 and −65.37° for the diethylene glycol spacer, resulting in a twisted molecule with a U shape. Here, the A (*anti*) and G (*gauche*) conformations are given when the O—C—C—O or C—C—O—C torsion angle (θ) is in the range $180 \geq \theta > 90°$ and $0 \leq \theta \leq 90°$, respectively (*6*). Moreover, regardless of the types of anions and solvents, the ligand molecule in compounds **2** and **3** also adopt a similar GAAG conformation and retain the U shape, which is advantageous for ligand L^2 to envelop anions. On the other hand, according to the relative orientation of the C═O group and the pyridyl nitrogen atom, the ligand in **1** assumes the *anti–syn* conformation, which facilitates the formation of the 2+2 macrocycle containing two protonated $[L^2H_2]^{2+}$ cations and two perchlorate anions (*vide infra*). The two pyridyl rings of ligand L^2 have a dihedral angle of 32.77° with a centroid–centroid distance of 8.46 Å.

There is an intriguing hydrogen-bonded network in **1** (the hydrogen bond parameters are summarised in Table 1). The two independent ClO_4^- anions have significantly different coordination environments. The first one, $Cl(1)O_4^-$, accepts two N^+—H···O ($N1^+$—H1B···O12 and $N4^+$—H4A···O13) hydrogen bonds from two pyridinium N^+—H fragments of two ligand molecules. Thus, two U-shaped ligands are bridged by two perchlorate ions to form a 2+2 hydrogen-bonded macrocycle (Figure 1(a)). To the best of our knowledge, such a 2+2 hydrogen-bonded macrocycle with perchlorate has not been reported, although the 2+2 cycles with halide bridges are common (*7*). To the other perchlorate anion $[Cl(2)O_4^-]$, only one pyridinium $N1^+$—H is involved in the hydrogen bonding ($N1^+$—H1B···O8). However, it forms an additional hydrogen bond with the crystalline water molecule (Figure 1(b)). It should be noted that the water molecule serves not only as hydrogen bond donors forming two O_w—H···O contacts with $[Cl(2)O_4^-]$ (O14—H14C···O9) and the central oxygen atom (O14—H14B···O3) of the diethylene glycol unit, respectively, but also as a hydrogen bond acceptor forming two N—H···O_w (N2—H2B···O14 and N3—H3B···O14) contacts with two amide NH groups from one ligand molecule in a cooperative fashion (Figure 1(b)).

More interestingly, a zigzag chain is formed along the *a*-axis by alternating $[Cl(2)O_4^-]$ ions and H_2O molecules through hydrogen bonds (O14—H14C···O9) and short O···O contacts (O6···O14, 3.02 Å) (Figure 1(c)) (*8*). The zigzag chain is significantly different from the double-stranded chain, with alternating perchlorate ions and water molecules formed by a protonated monopyridylurea (*4c*), and is also different from the hydrogen-bridged helical perchlorate chain found in the perchloric acid

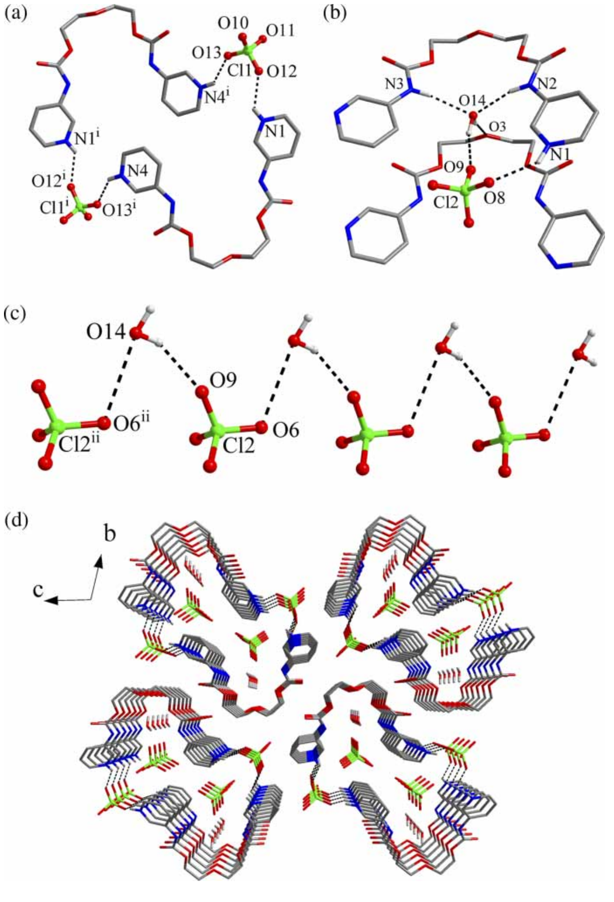

Figure 1. (a) The 2+2 macrocycle in **1** constructed by two protonated L^2 molecules and two perchlorate anions $[Cl(1)O_4^-]$ through four N^+—H···O hydrogen bonds. (b) Hydrogen-bonding interactions around $[Cl(2)O_4^-]$ and the water molecule. (c) The zigzag chain formed by alternating $[Cl(2)O_4^-]$ anions and H_2O molecules. (d) Packing diagram showing the 1D channels and the encapsulated anion–water chains. (i) $-x, 1-y, 1-z$ and (ii) $x-1, y, z$.

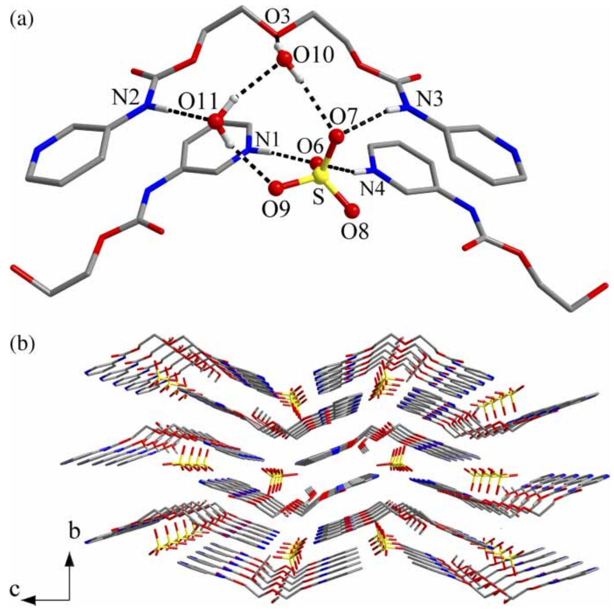

Figure 2. (a) Hydrogen bonds around the SO_4^{2-} ion in **2**. (b) Packing diagram showing the corrugated layer structure with SO_4^{2-} and H_2O molecules between the layers.

adduct of L^1 (*5*). The 2+2 hydrogen-bonded macrocycles (Figure 1(a)) stack on top of each other in a parallel manner along the *a*-axis to form a 1D channel, which is parallel to the perchlorate–water chain. According to a calculation performed with PLATON (*9*), these incipient voids occupy 13.3% of the unit cell volume of **1** (152.2 Å^3 out of the 1144.9 Å^3 unit cell volume), which are large enough to include two of such zigzag perchlorate–water chains (Figure 1(d)).

*$L^2\cdot H_2SO_4\cdot 2H_2O$ (**2**)*

The sulphate compound **2** crystallises in the monoclinic space group *P*2/*c*. There are one fully protonated ligand ($[L^2H_2]^{2+}$ cation), one sulphate anion and two crystalline water molecules in the asymmetric unit. The protonated ligand in compound **2** also adopts a GAAG conformation with torsion angles of 70.20, 156.82, −170.87 and −68.92° for the diethylene glycol linker. The C=O bond and the corresponding pyridyl N atom are in the *syn–syn* orientation, which is different from that in **1**. The two pyridyl rings of L^2 in compound **2** display a dihedral angle of 37.37° with a distance of 12.66 Å, longer than that in **1**.

In compound **2**, a sulphate ion is held within the two arms of a U-shaped ligand through one direct hydrogen-bond N3—H3A···O7 from a carbamate NH donor. The two crystalline water molecules bridge the sulphate ion to the ligand through hydrogen-bonding interactions with the other carbamate NH donor and the central oxygen atom of the diethylene glycol spacer (O10—H10C···O7, O10—H10D···O3, O11—H11A···O9, N2—H2A···O11) (Figure 2(a)). Furthermore, the sulphate anion is hydrogen-bonded by two pyridinium (N^+H) moieties from two other ligands ($N1^+$—H1A···O6 and $N4^+$—H4···O6). Thus, the sulphate ion is bound by a total of five (one N—H···O, two N^+—H···O and two O_w—H···O; Figure 2(a)) hydrogen bonds. This is different from the [—sulphate—$(H_2O)_2$—]$_n$ chain which shows four O_w—H···O bonds around the sulphate ion held within the shorter ligand L^1 (*5*). In the sulphate complex of the monopyridylurea ligand, however, the sulphate ion is surrounded by six hydrogen bonds with two urea groups (four NH donors) and two pyridinium donors (*4c*). One water···water contact is present (O11—H11B···O10) in compound **2**, and the two water molecules are both hydrogen bond donor and acceptor in a cooperative fashion as in **1**. The hydrogen bond parameters for **2** are summarised in Table 2. The hydrogen-bonded supramolecular 3D network of **2** shows a corrugated layer structure viewed along the *a*-axis, with the sulphate anions and water molecules located between the layers (Figure 2(b)).

*$L^2\cdot 2HCl$ (**3**)*

Compound **3** crystallises in the monoclinic space group *P*2$_1$/*c*. Its asymmetric unit contains two fully protonated

Table 2. Hydrogen bond parameters (Å, °) for $L^2\cdot H_2SO_4\cdot 2H_2O$ (**2**).

D—H···A	D—H	H···A	D···A	∠D—H···A
N1—H1A···O6[a]	0.86	1.76	2.6141(18)	172.1
N2—H2A···O11[b]	0.86	1.89	2.748(2)	177.7
N3—H3A···O7[b]	0.86	1.97	2.7890(17)	158.3
N4—H4···O6[c]	0.86	1.82	2.6587(18)	164.2
O10—H10C···O7	0.74(3)	2.04(3)	2.779(2)	175(3)
O10—H10D···O3[d]	0.91(6)	2.13(6)	3.010(2)	163(4)
O11—H11A···O9	0.81(3)	1.99(3)	2.785(3)	165(4)
O11—H11B···O10	0.84(3)	1.95(3)	2.773(3)	166(3)
C2—H2···O1[b]	0.93	2.58	3.278(2)	132.0
C14—H14···O5[b]	0.93	2.53	3.243(2)	133.4

Notes: Symmetry codes: (a) 2 − *x*, 1 − *y*, 2 − *z*, (b) *x*, *y* − 1, *z*, (c) 1 − *x*, 1 − *y*, 2 − *z* and (d) *x*, *y* + 1, *z*.

ligands ($[L^2H_2]^{2+}$ cation) and four chloride ions. Both of the two protonated ligands adopt the GAAG conformation with almost same torsion angles of −78.30, −176.69, 151.43, 72.22° and −73.08, −149.27, 176.37, 76.80° for the diethylene glycol bridges, respectively. In contrast to the *anti–syn* conformation in **1** and *syn–syn* arrangement in **2**, the orientation of the carbonyl relative to the pyridyl N atom in the protonated ligand is *anti–anti* in compound **3**, which makes possible the formation of the hydrogen-bonded 1D channel (*vide infra*).

Unlike compounds **1** and **2**, there is no solvent molecule in **3**, and the protonated ligand molecule is involved in hydrogen bonding with four chloride ions through the N—H and N^+—H groups. For the four crystallographically non-equivalent chloride ions, each of them is surrounded by three ligand molecules via four hydrogen bonds (one N^+—H···Cl, one N—H···Cl and two C_{py}—H···Cl bonds; Figure 3(a)). With the aid of these interactions, the two crystallographically non-equivalent ligand molecules and the chloride ions form a hydrogen-bonded rectangular 1D channel (cross-section of ca. 3.3 × 13.0 Å) along the *a*-axis with the chloride ions located on the wall (Figure 3(b)). This is similar to the channel in compound **1**, with the $[Cl(1)O_4^-]$ ions as part of the wall (while the other perchlorate ion is included within the channel). However, the void in the channel of compound **2** is too small to accommodate any guest molecules. A 3D supramolecular network is achieved by the packing of such infinite 1D channels in a parallel fashion via intermolecular C—H···O═C hydrogen bonds (C8—H8B···O6 and C24—H24···O1) (Figure 3(c)) (*10*). The hydrogen bond parameters for **3** fall in the normal range (*11*) and are summarised in Table 3.

Anion selectivity

The reaction of ligand L^2 with individual inorganic acids $HClO_4$, H_2SO_4 and HCl yielded the corresponding adducts **1**–**3**. Although some other acids, such as HNO_3, HBr and CF_3COOH, were also used to react with L^2, no products have been isolated so far. Nonetheless, the selectivity of L^2 for the anions was examined by the following experiment. Ligand L^2 (1 equiv.) was dissolved in an aqueous solution containing 2 equiv. of $HClO_4$ and HCl and 1 equiv. of H_2SO_4, respectively. Under the same conditions as in the preparation of complexes **1**–**3**, colourless crystals were obtained after several days. Powder X-ray diffraction (PXRD) of the product showed identical diffraction patterns to the perchlorate complex **1** (Figure 4), indicating that the doubly protonated ligand L^2 can extract the perchlorate ion from the mixed acids following the Hofmeister series (*12*). This is similar to the case of a monopyridylureas (*4c*), but is different from the anion selectivity of L^1 which crystallised with sulphate from the mixed acids (*5*). A detailed structural investigation for the acid adducts showed that, in the three cases of anion

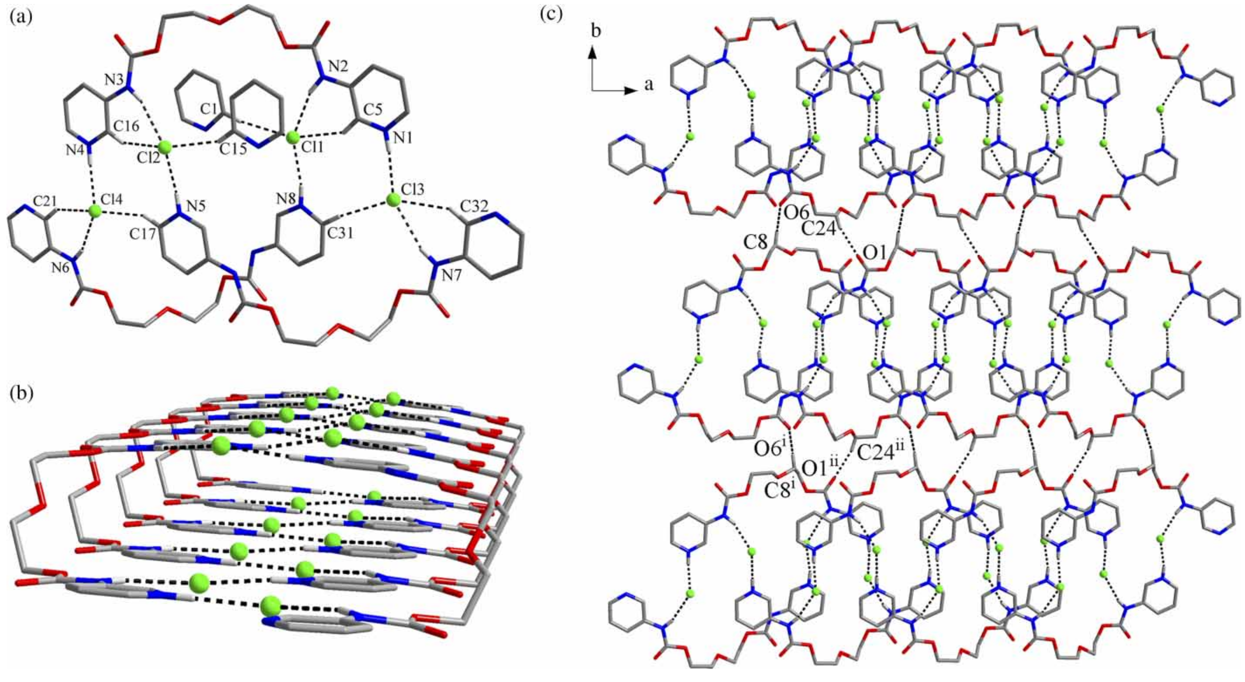

Figure 3. (a) Hydrogen bonds around the four Cl^- ions in **3**. (b) Hydrogen-bonded 1D channel along the *a*-axis (the C_{py}—H···Cl bonds are omitted). (c) Packing diagrams showing the parallelly arranged 1D channels viewed along the *c*-axis. (i) $-x-1$, $y-0.5$, $0.5-z$ and (ii) $-x$, $y-0.5$, $0.5-z$.

Table 3. Hydrogen bond parameters (Å, °) for L^2·2HCl (**3**).

D—H···A	D—H	H···A	D···A	∠D—H···A
N1—H1B···Cl3	0.86	2.19	3.033(2)	168.3
N2—H2B···Cl1	0.86	2.36	3.1922(18)	162.0
N3—H3B···Cl2	0.86	2.44	3.2672(19)	160.6
N4—H4A···Cl4[a]	0.86	2.18	3.035(2)	174.4
N5—H5B···Cl2[a]	0.86	2.19	3.039(2)	170.7
N6—H6A···Cl4[a]	0.86	2.40	3.2252(18)	161.8
N7—H7C···Cl3[a]	0.86	2.38	3.2179(18)	164.0
N8—H8C···Cl1	0.86	2.18	3.021(2)	165.5
C1—H1A···Cl1[b]	0.93	2.59	3.508(3)	168.8
C5—H5A···Cl1	0.93	2.63	3.446(2)	146.7
C15—H15A···Cl2[a]	0.93	2.56	3.408(3)	151.9
C16—H16A···Cl2	0.93	2.55	3.388(2)	149.6
C17—H17A···Cl4[c]	0.93	2.52	3.377(3)	153.3
C21—H21A···Cl4[a]	0.93	2.56	3.388(2)	148.3
C31—H31A···Cl3	0.93	2.60	3.515(3)	166.7
C32—H32A···Cl3[a]	0.93	2.60	3.429(2)	148.0
C8—H8B···O6[d]	0.97	2.56	3.359(3)	139.6
C24—H24B···O1[e]	0.97	2.47	3.409(3)	164.3

Notes: Symmetry codes: (a) $x - 1, y, z$, (b) $x + 1, y, z$, (c) $x - 2, y, z$, (d) $-x, y + 0.5, 0.5 - z$ and (e) $1 - x, y - 0.5, 0.5 - z$.

separation, the preferred anion (sulphate by L^1 (*5*) and perchlorate by L^2 (this work) and the monopyridylurea (*4c*)) not only forms strong hydrogen bonds with the NH and N^+H groups of the receptor similar to other anions, but also takes part in the formation of intriguing anion–water polymers, such as the zigzag perchlorate–water chain in compound **1** (in this work), the infinite $[\text{—sulphate—}(H_2O)_2\text{—}]_n$ chain for L^1 and the double-stranded chain with alternating perchlorate ion and water molecule for the monopyridylurea. The selectivity may thus be attributed to the formation of these water–anion chains via strong O—H···O hydrogen bonds, which endow the complexes' higher lattice energies.

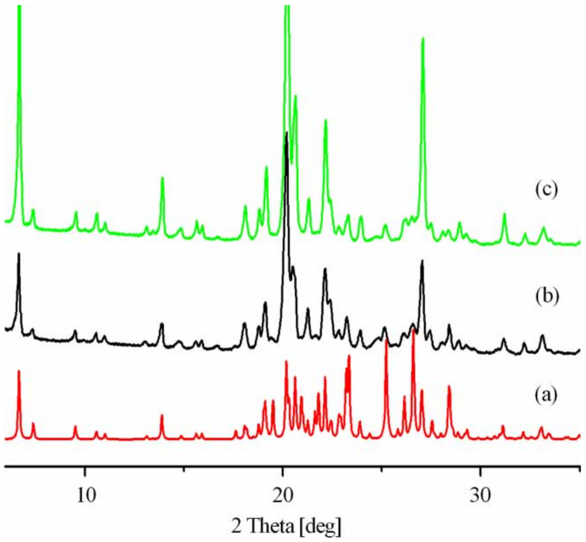

Figure 4. PXRD patterns. (a) Simulated for **1**. (b) Compound **1**. (c) Product from the reaction of L^2 with $HClO_4$, H_2SO_4 and HCl, showing identical diffraction patterns to those of **1**.

Thermal analysis

The thermal stability of adducts **1**–**3** was studied by TGA analysis. For compound **1**, the release of the crystalline water molecule was observed from room temperature to 102°C (observed weight loss 3.11%, calculated 3.19%). For **2**, the loss of the crystalline water molecules occurred from room temperature to 149°C (observed weight loss 7.23%, calculated 7.50%). The three compounds exhibit considerable stabilities, decomposing at 242, 164 and 211°C, respectively, which are similar to the acid adducts of L^1 (*5*).

Conclusions

We have designed a bis(pyridylcarbamate) receptor (L^2) with the diethylene glycol linker and studied its anion binding properties. Structural analyses of three acid adducts of L^2 demonstrate that there is no self-association for the new ligand. The perchlorate compound **1** and chloride compound **3** feature interesting 1D tubular structures. There are two zigzag anion–water chains encapsulated in the channel formed by ligand molecules and perchlorate ions in **1**, but no guests are included in the channel of compound **3**. Ligand L^2 shows a preference for the perchlorate ion according to the Hofmeister sequence.

Experimental section

General

All chemicals and solvents were commercially available and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed on a

VarioEL instrument from Elementar Analysensysteme GmbH. IR spectra were measured with an HP5890II GC/NEXUS870. PXRD data were recorded with an X'Pert PRO instrument. TG analysis was carried out with a Pyris diamond instrument (Perkin-Elmer) under N_2 atmosphere with a heating rate of 10°C/min.

Synthesis of L^2

Ligand L^2 was synthesised by a similar method reported previously (*5*) as a white powder. Yield: 81%. Mp 141–142°C. Anal. Calcd for $C_{16}H_{18}N_4O_5$ (346.3): C, 55.49; H, 5.24; N, 16.18. Found: C, 55.27; H, 5.06; N, 15.93. ESI-MS: *m/z* 347.6 $[M+H]^+$. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.68 (t, 4H, $J = 4.4$ Hz, CH_2a); 4.22 (t, 4H, $J = 4.4$ Hz, CH_2b); 7.28 (dd, 2H, $J_1 = 4.8$ Hz, $J_2 = 8.0$ Hz, Py-H5); 7.86 (d, 2H, $J = 8.0$ Hz, Py-H4); 8.18 (d, 2H, $J = 4.4$ Hz, Py-H6); 8.61 (d, 2H, $J = 2.4$ Hz, Py-H2); 9.94 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): 63.8, 68.5, 123.6, 125.1, 135.8, 140.1, 143.5, 153.6. IR (KBr, ν, cm^{-1}): 3246 (NH), 2957, 2900, 1729 (C=O), 1618, 1559, 1486, 1419, 1234, 1083, 799, 764, 702.

Synthesis of the acid complexes

The complexes of ligand L^2 with H^+/anion (**1–3**) were obtained by the reaction of L^2 with the corresponding diluted acids $HClO_4$, H_2SO_4 and HCl in ethanol–water solution. In a typical experiment, L^2 (15 mg, 43.3 mmol) was dissolved in an excess of diluted acid (1 mol/L) to give a clear solution. Colourless block crystals were obtained by slow diffusion of ethanol into the clear solution for several days.

*$L^2 \cdot 2HClO_4 \cdot H_2O$ (**1**)*

Yield: 47%. Mp 172–173°C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.71 (t, 4H, $J = 4.4$ Hz, CH_2a); 4.28 (t, 4H, $J = 4.4$ Hz, CH_2b); 7.92 (dd, 2H, $J_1 = 5.2$ Hz, $J_2 = 8.8$ Hz, Py-H5); 8.33 (d, 2H, $J = 8.0$ Hz, Py-H4); 8.52 (d, 2H, $J = 5.2$ Hz, Py-H6); 8.92 (s, 2H, Py-H2); 10.70 (s, 2H, NH). Anal. Calcd for $C_{16}H_{22}N_4O_{14}Cl_2$ (565.3): C, 34.00; H, 3.92; N, 9.91. Found: C, 34.41; H, 3.74; N, 10.10. IR (KBr, ν, cm^{-1}): 3553 (H_2O, OH), 3250 (NH), 2962, 2886, 1730 (C=O), 1616, 1552, 1465, 1242, 1091 (Cl—O), 798, 675, 621.

*$L^2 \cdot H_2SO_4 \cdot 2H_2O$ (**2**)*

Yield: 59%. Mp 107–109°C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.69 (t, 4H, $J = 4.4$ Hz, CH_2a); 4.24 (t, 4H, $J = 4.4$ Hz, CH_2b); 7.63 (dd, 2H, $J_1 = 5.2$ Hz, $J_2 = 8.0$ Hz, Py-H5); 8.11 (d, 2H, $J = 8.0$ Hz, Py-H4); 8.36 (d, 2H, $J = 5.2$ Hz, Py-H6); 8.77 (d, 2H, $J = 1.6$ Hz, Py-H2); 10.39 (s, 2H, NH). Anal. Calcd for $C_{16}H_{24}N_4O_{11}S$ (480.5): C, 40.00; H, 5.04; N, 11.66. Found: C, 40.10; H, 4.55; N, 11.85. IR (KBr, ν, cm^{-1}): 3498 (H_2O, OH), 3354 (NH), 2964, 2918, 1723 (C=O), 1572, 1461, 1399, 1243, 1126 (S—O), 820, 770, 593.

Table 4. Crystallographic data and refinement details for **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{16}H_{22}N_4O_{14}Cl_2$	$C_{16}H_{24}N_4O_{11}S$	$C_{16}H_{20}N_4O_5Cl_2$
M_r	565.28	480.45	419.26
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*2/*c*	*P*2$_1$/*c*
a (Å)	5.0350(10)	19.1475(15)	8.9508(18)
b (Å)	13.635(3)	7.6071(6)	32.709(7)
c (Å)	17.256(4)	14.3925(11)	13.405(3)
α (°)	104.42(3)	90.00	90.00
β (°)	91.94(3)	99.1940(10)	97.17(3)
γ (°)	92.64(3)	90.00	90.00
V (Å^3)	1144.9(4)	2069.4(3)	3893.8(14)
Z	2	4	8
D_{calcd} (g cm^{-3})	1.640	1.542	1.430
F (000)	584	1008	1744
μ (mm^{-1})	0.365	0.226	0.368
Crystal size (mm^3)	0.37 × 0.30 × 0.21	0.44 × 0.33 × 0.27	0.38 × 0.30 × 0.26
θ range (°)	1.71–26.15	1.08–27.91	1.25–28.65
Reflections collected	6104	12,574	25,739
Independent reflections	4355	4890	9644
Parameters	331	305	487
GOF (F^2)	0.991	0.994	0.981
R (int)	0.0560	0.0217	0.0415
$R1$; $wR2$ [$I > 2\sigma(I)$]	0.1058; 0.2689	0.0389; 0.1229	0.0488; 0.1020
$R1$; $wR2$ (all data)	0.1593; 0.3011	0.0545; 0.1406	0.1141; 0.1255

L^2·2HCl (**3**)

Yield: 39%. Mp 169–171°C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.74 (t, 4H, $J = 4.4$ Hz, CH$_2$a); 4.31 (t, 4H, $J = 4.4$ Hz, CH$_2$b); 7.92 (dd, 2H, $J_1 = 5.6$ Hz, $J_2 = 8.8$ Hz, Py-H5); 8.41 (dd, 2H, $J_1 = 1.2$ Hz, $J_2 = 8.8$ Hz, Py-H4); 8.53 (d, 2H, $J = 5.6$ Hz, Py-H6); 8.94 (d, 2H, $J = 2.0$ Hz, Py-H2); 10.82 (s, 2H, NH). Anal. Calcd for $C_{16}H_{20}N_4O_5Cl_2$ (419.3): C, 45.84; H, 4.81; N, 13.36. Found: C, 46.29; H, 4.65; N, 13.54. IR (KBr, ν, cm^{-1}): 3238 (NH), 2977, 2906, 1738 (C═O), 1619, 1559, 1476, 1226, 1074, 805, 767, 676.

X-ray crystallography

Data collection was performed on a Bruker-AXS SMART CCD area detector diffractometer at 293 K using ω-rotation scans with a scan width of 0.3° and Mo Kα radiation ($\lambda = 0.71073$ Å). Multi-scan corrections were applied using SADABS (*13*). Structure solutions and refinements were performed with the SHELXL-97 package (*14*). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the program SHELXL-97. The hydrogen atoms were included in idealised geometric positions with thermal parameters equivalent to 1.2 times those of carbon and nitrogen atoms. Hydrogen atoms on the two water oxygen atoms in compounds **1** and **2** were located from the difference Fourier map and then refined with restraints [O—H = 0.85(1) Å], with U(H) fixed at 0.08 Å^2. The crystal parameters and experimental details of the data collection are summarised in Table 4. The CCDC number is 746249–746251.

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