Supplemental Information

Variable length ligands: a new class of bridging ligands for supramolecular chemistry and crystal engineering

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S1: Ligand Synthesis

The unsubstituted diaza-crown was prepared using the method reported by Dietrich *et al*.[1] The ligand *N,N′*-bis(4-pyridyl-methyl)diaza-18-crown-6 (bpmdc) was prepared as reported by Tsukube *et al*.[2] The general ligand synthesis involved the reaction of diaza-18-crown-6 with a halogen functionalised pendant arms. The reaction was carried out under basic conditions (triethylamine) using ethanol as the solvent. Purification was achieved through solvent extraction methods or through chromatography. Characterisation was carried out using ^{1}H NMR, mass spectrometry and infra-red spectroscopy.

S2: Inorganic Synthesis (A.(Ø) – H.(2H_2O))

Two standard methods for obtaining X-ray quality crystalline products were employed: i) direct mixing of all reagents with the reaction allowed to stand for a period of time, and ii) slow diffusion of separate ligands and metal solvent layers through a neat solvent layer. Various solvent systems were employed throughout the investigation depending on the solubility and behaviour of starting materials and products.

[Co(bpmdc)Cl_2]·(MeOH) (**A.(Ø)**): 25 mg (56 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 2 ml of ethanol was mixed with 12 mg (48 μmol) of $CoCl_2.6H_2O$ in 2 ml of ethanol. The mixture was allowed to slowly evaporate over 1-2 days after which time blue X-ray quality crystals were obtained. Yield: 18 mg (55 %). Anal. Calcd for $C_{25}H_{40}N_4O_5Cl_2Co$: C, 49.51; H, 6.65; N, 9.24. Found: C, 47.19; H, 6.02; N, 9.01. IR (ATR, cm^{-1}): 3423s, 2861m, 1654sh, 1618s, 1460sh, 1426m, 1384s, 1122s, 1030w, 929w.

[$Fe(NCS)_2$(bpmdcH(H_2O))$_2$](ClO_4)$_2$·MeOH (**B.(H^+/H_2O)**): Onto a solution of 20 mg (45 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 4 ml of chloroform was layered a solution containing 3.9 mg (23 μmol) of $Fe(NCS)_2$ in 4 ml of methanol. The reaction was allowed to diffuse over several days. After this time diethyl ether was diffused into the solution. Small dark orange X-ray quality crystals formed after 5 days. Yield 8.2 mg (33 %). IR (ATR, cm^{-1}): 3426m, 2920m, 2060s, 1615m, 1460sh, 1424m, 1066s, 1018sh, 821w.

[Ag(bpmdcAg)](CF_3SO_3)$_2$ (**C.(Ag^+)**): 20 mg (45 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 10 ml of ethanol was mixed with 25 mg (97 μmol) of silver(I) triflate in 5 ml ethanol. The solution was stirred for 20 min and then ether was allowed to slowly diffused. Pale yellow X-ray quality crystals were obtained after 3 days. Yield: 22 mg (50 %). Anal. Calcd for $C_{26}H_{36}N_4O_{10}F_6S_2Ag_2$: C, 32.58; H, 3.79; N, 5.85. Found: C, 32.68; H, 3.95; N, 5.85. IR (ATR, cm^{-1}): 2852m, 1617m, 1461w, 1433w, 1275sh, 1243s, 1222sh, 1152s, 1088s, 1024s, 980sh, 824m.

[$Fe(NCS)_4$(bpmdcH_2)]·2(MeOH) (**D.(2H^+)**): 23 mg (67 μmol) of $Fe(BF_4).6H_2O$ and 34 mg (135 μmol) of $Ba(NCS)_2$ were combined in 4 ml of dry methanol and added to 30 mg (67 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 4 ml of dry methanol. The mixture was allowed to stand for 5 days and yielded 36 mg (70 %) of large dark orange X-ray quality crystals. Anal. Calcd for $C_{30}H_{46}N8O_6S_4Fe$: C, 45.11; H, 5.80; N, 14.03. Found: C, 44.63; H, 5.42; N, 13.81. IR (ATR, cm^{-1}): 2893m, 2616m, 2107sh, 2061s, 1612m, 1424m, 1108s, 734m.

[$Fe(NCS)_2$(bpmdcBa($NCS)_2$(H_2O))]·2($CHCl_3$) (**E.(Ba^{2+})**): To a solution of 20 mg (45 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 4 ml of chloroform/ethanol (1:1) was added an excess of $Ba(NCS)_2$ in ethanol. To this mixture 3.9 mg (23 μmol) of $Fe(NCS)_2$ was added and the mixture stirred for 5 min. After this time the solution was filtered and allowed to stand for 2 weeks. Yield: 8 mg (22 %). Insufficient product was obtained for further analysis.

[Co(bpmdc$CaCl_2$)(H_2O)$_2$$Cl_2$] (**F.($Ca^{2+}$)**): 22 mg (49 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 7 ml of ethanol/ water (1:1) was added to an excess of $CaCl_2$ in 2 ml of water. To this mixture 14 mg (56 μmol) of $CoCl_2.6H_2O$ in 2 ml of ethanol/water (1:1) was added and stirred. The mixture was allowed to crystallise over 4 days and yielded pink/orange X-ray quality crystals. Yield: 10 mg (29 %). Insufficient product was obtained for further analysis.

[Co(bpmdcK)(H_2O)$_2$$Cl_2$]Cl·2($H_2O$) (**G.($K^+$)**): 25 mg (56 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 7 ml of ethanol was mixed with 25 mg (335 μmol) of KCl in 1 ml of water. To this mixture 14 mg (56 μmol) of $CoCl_2.6H_2O$ in 2

ml of ethanol/water (1:1) was added. The mixture was allowed to slowly evaporate over 3 days after which time orange/pink X-ray quality crystals were obtained. Yield: 20 mg (52 %). Anal. Calcd for $C_{24}H_{44}N_4O_8CoKCl_3$: C, 39.98; H, 6.15; N, 7.77. Found: C, 39.19; H, 6.23; N, 7.46. IR (ATR, cm^{-1}): 3422s, 2885w, 1654m, 1611w, 1560m, 1425m, 1384m, 1357w, 1092m, 1071w, 1022w, 932m, 625m.

$[Co(NCS)_2(H_2O)_2(bpmdc)]$ (**H.($2H_2O$)**): A solution containing 8 mg (45 μmol) of $Co(NCS)_2$ was prepared by adding 7.4 mg of NaNCS to 16.7 mg of $Co(ClO_4)_2.6H_2O$ in 4 ml of ethanol. To this solution 40 mg (90 μmol) of *N,N′*-bis(4-pyridylmethyl)diaza-18-crown-6 in 10 ml of anhydrous ethanol was mixed added and stirred. The precipitate that formed was dissolved with a few drops of DMF. The mixture was allowed to slowly evaporate and small, pale orange, X-ray quality crystals formed after 2 weeks. Yield: 38 mg (34 %). IR (ATR, cm^{-1}): 3384br, 2953sh, 2873m, 2823w, 2073s, 1653m, 1608m 1556w, 1451w, 1417w, 1342w, 1135sh, 1100m, 924w.

S3: Single Crystal X-ray Diffraction

[Co(bpmdc)Cl_2]·(MeOH) (**A.(Ø)**): Solved and refined in the monoclinic space group $P2_1/c$ at 150 K. The structure consists of 1-D chains that are constructed by the linkage of Co^{II} centres by bdpmc units through the pyridyl nitrogens. The distorted tetrahedral coordination geometry around the Co^{II} centre is completed by two chloride anions, with the asymmetric unit shown in Figure S-1. Two crystallographically inequivalent ligands are present within the asymmetric unit, however, only half of each ligand is unique, with the other half being generated through symmetry. Selected bond lengths and angles are summarised in Table S-1.

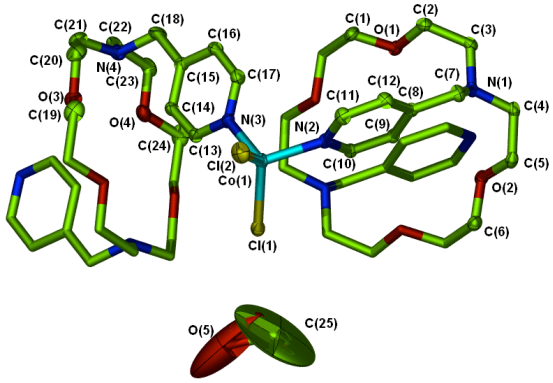


Figure S-1 – Asymmetric unit of **A.(Ø)** (thermal ellipsoids 50 %). Hydrogen atoms have been omitted for clarity.

Table S-1 – Summary of selected bond lengths (Å) and angles (°) in **A.(Ø)**.

Co(1)-N(2)	2.033(2)	Cl(1)-Co(1)-N(2)	108.14(6)
Co(1)-N(3)	2.026(2)	Cl(1)-Co(1)-N(3)	106.57(7)
Co(1)-Cl(1)	2.2310(8)	Cl(2)-Co(1)-N(2)	105.36(6)
Co(1)-Cl(2)	2.2445(8)	Cl(2)-Co(1)-N(3)	111.76(7)
Cl(1)-Co(1)-Cl(2)	118.55(3)	N(2)-Co(1)-N(3)	105.72(8)

Intra-ligand hydrogen bonds exists between the C(9) bound hydrogen of the pyridyl ring and O(1) and O(2) of the diaza-crown (C-H…O = 3.205(3) and 3.368(3) Å, respectively). A similar interaction is present in the other ligand but only to one oxygen atom, between C(14) and O(3) (C-H…O = 3.094(3) Å). Symmetrical equivalents of these interactions are generated through inversion centres situated at the centre of each diaza-crown. These interactions result in both the ligands adopting a compact 'S' configuration with ligand lengths of 7.714(3) and 8.442(3) Å. The solvent methanol present within the crystal lattice has no significant interactions with the 1-D chains. A summary of the hydrogen bond lengths (donor atom-acceptor atom) and bond angles are shown in Table S-2.

Table S-2 - Hydrogen bond lengths (Å) and angles (°) present in **A.(Ø)**.

C(9)-H(9)…O(1)	3.205(3)	C(9)-H(9)…O(1)	87.5(2)
C(9)-H(9)…O(2)	3.268(3)	C(9)-H(9)…O(2)	144.4(2)
C(14)-H(14)…O(3)	3.094(3)	C(14)-H(14)…O(3)	105.9(3)

The 1-D chains adopt a zig-zag configuration and are aligned along the *b*-axis with no significant inter-chain interactions found, Figure S-2. The chains pack in an AB type fashion such that alternating layers are translated along the *b*-axis, Figure S-2.

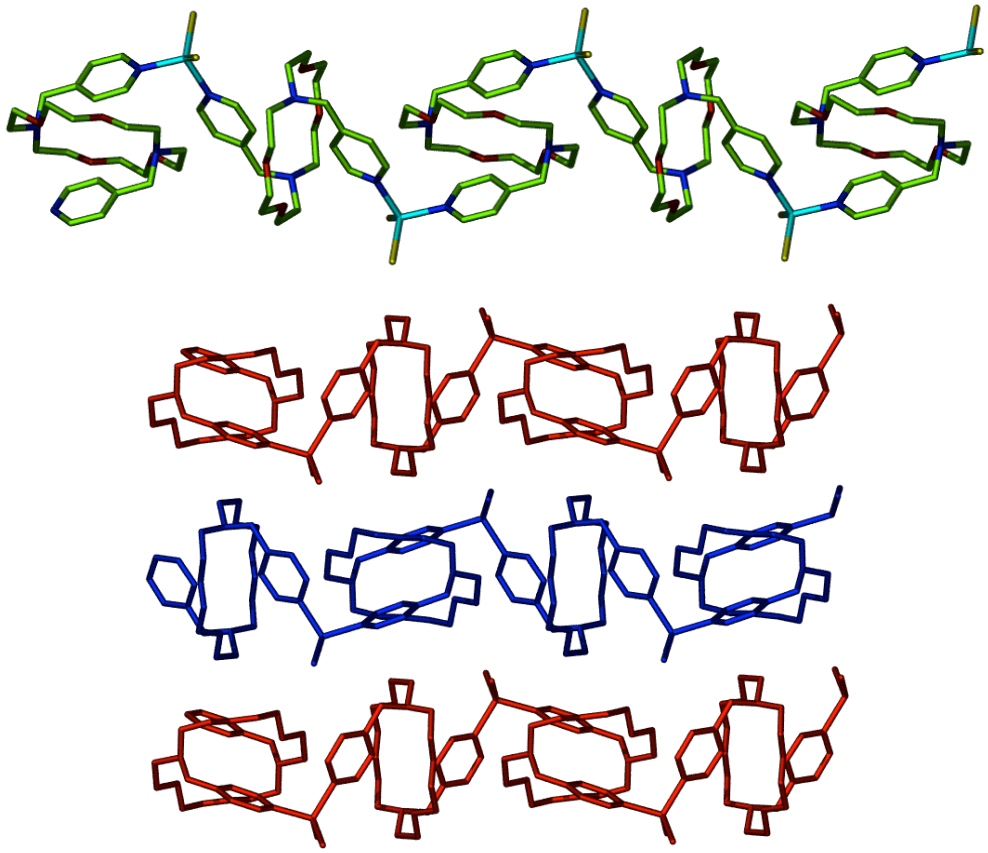


Figure S-2 – Top: The 1-D chains of **A.(Ø)**. Bottom: Representation of the AB type packing present in **A.(Ø)**. The view is looking down the *c* axis.

[Fe(NCS)$_2$(bpmdcH(H$_2$O))$_2$](ClO$_4$)$_2$·MeOH (**B.(H$^+$/H$_2$O)**): The structure of **B.(H$^+$/H$_2$O)** was solved and refined in the monoclinic space group *C*2/*c* at 150 K. The asymmetric unit consists of one Fe^{II} cation coordinated to a NCS$^-$ anion and one bpmdc ligand. There is an uncoordinated ClO$_4^-$ and methanol within the lattice. The asymmetric unit of **B.(H$^+$/H$_2$O)** is shown in Figure S-3. Selected bond lengths and angles are summarised in Table S-3.

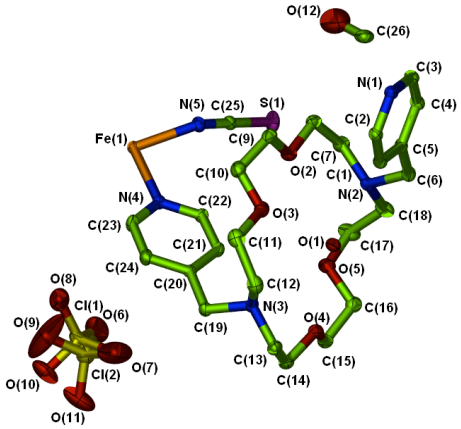


Figure S-3 – Asymmetric unit of **B.(H$^+$/H$_2$O)** (50 % thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table S-3 - Summary of selected bond lengths (Å) and angles (°) in **B.(H^+/H_2O)**.

Fe(1)-N(1)	2.212(2)	N(1)-Fe(1)-N(4)	88.4(1)
Fe(1)-N(4)	2.195(2)	N(1)-Fe(1)-N(4)	90.9(1)
Fe(1)-N(5)	2.128(2)	N(4)-Fe(1)-N(5)	91.95(7)

One amine nitrogen within the diaza-crown ether is protonated and hydrogen bonds to a water molecule located at the centre of the diaza-crown. This water molecule in turn hydrogen bonds to two diaza-crown oxygen atoms, Figure S-4. The charge carried by the protonated amine is balanced by the ClO_4^- anion. The resultant ligand length is 8.886(7) Å. A summary of the hydrogen bond lengths (donor atom-acceptor atom) and bond angles are shown in Table S-4.

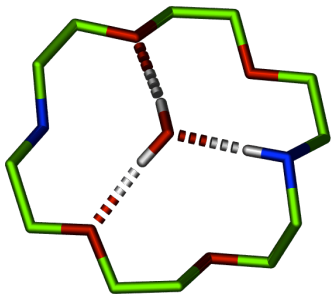


Figure S-4 – Hydrogen bonding present with the structure of **B.(H^+/H_2O)**.

Table S-4 - Hydrogen bond lengths (Å) and angles (°) present in **B.(H^+/H_2O)**.

N(2)-H(N2)…O(1)	2.778(2)	N(2)-H(N2)…O(1)	159.1(3)
O(1)-H(O1)…O(3)	2.867(2)	O(1)-H(O1)…O(3)	173.4(3)
O(1)-H(O1)…O(4)	2.826(2)	O(1)-H(O1)…O(4)	170.2(3)

The Fe^{II} cation exists in a distorted octahedral coordination geometry and is coordinated to two NCS^- anions and four bpmdc ligands via the pyridyl nitrogen atoms. This gives rise to a 2-D undulating (4,4) sheet as shown in Figure S-5. These (4,4) sheets pack in an AB type arrangement through a two-fold rotation along the 110 direction with a small degree of interdigitation, Figure S-6.

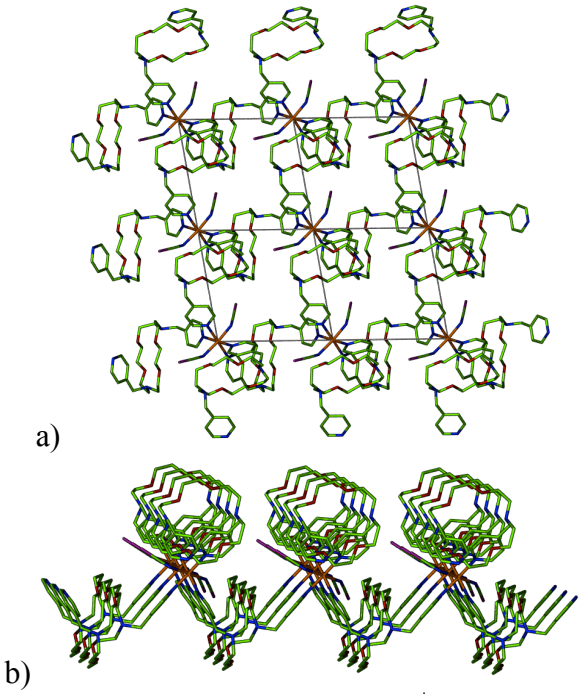


Figure S-5 – (a) The 2-D (4,4) sheet present in **B.(H^+/H_2O)**. View is down the *c* axis. (b) The undulating nature of the (4,4) sheet viewed down the 110 direction.

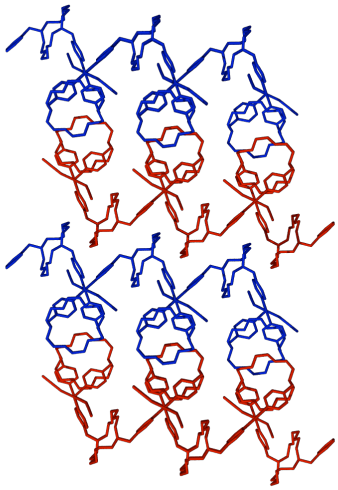


Figure S-6 – The AB type packing in **B.(H^+/H_2O)** showing the interdigitation. View is down the 110 direction.

[Ag(bpmdcAg)](CF_3SO_3)$_2$ (**C.(Ag^+)**): Solved and refined in the trigonal space group *R*-3*c* at 150 K. The structure showed two Ag^I metal ions present in two different coordination environments. The asymmetric unit is shown in Figure S-7. One Ag^I atom, Ag(1), is situated within the diaza-crown and coordinated to two amine nitrogens. Long range interactions exist between the oxygen atoms of the diaza-crown and Ag(1). The other Ag^I atom, Ag(2), is coordinated to two ligands via the pyridyl nitrogens. Both these Ag^I atoms have an approximately linear coordination geometry, however, Ag(2) has a long range interaction with an oxygen from two triflate anions, 2.813(4) Å, which results in a pseudo-square planar geometry. The resultant ligand length is 9.695(5) Å. Selected bond lengths and angles are summarised in Table S-5. The triflate anion is disordered over two positions with relative occupancies of 76:24

resulting in some bond lengths and angles needing to be restrained in order for the model refinement to be stable. The Ag(1)-bpmdc moiety and Ag(2) form 1-D undulating chains, Figure S-8. These chains, which orientate 120° to each other are shown in Figure S-9.

NOTE: based on elemental analysis (see Section S2) one ethanol molecule is associated with the complex, however in the crystal structure determination only diffuse electron density was observed within the void volume. Thus the ethanol molecule is included in the chemical formula but not the structure. The data was run through the SQUEEZE routine within PLATON[3] to remove the unmodelled diffuse electron density from the solvent molecule.

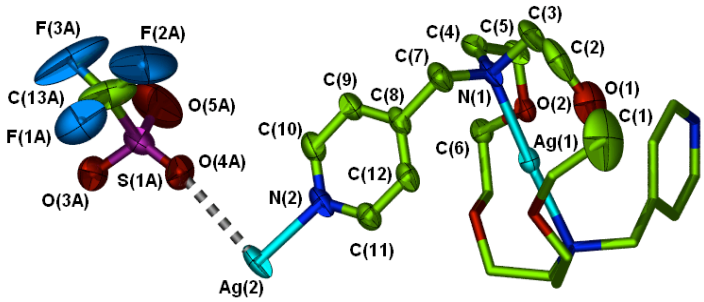


Figure S-7 – Asymmetric unit of **C.(Ag$^+$)** (50 % thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Only one triflate anion is shown.

Table S-5 - Summary of selected bond lengths (Å) and angles (°) in **C.(Ag$^+$)**.

Ag(1)-N(1)	2.308(4)	Ag(2)…O(3B)	2.813(4)
Ag(1)…O(1)	2.836(4)	Ag(2)…O(4A)	2.839(7)
Ag(1)…O(2)	2.625(4)	N(2)-Ag(2)…O(3B)	93.0(4)
N(1)-Ag(1)-N(1)	172.48(19)	N(2)-Ag(2)…O(4A)	88.9(4)
Ag(2)-N(2)	2.140(4)		

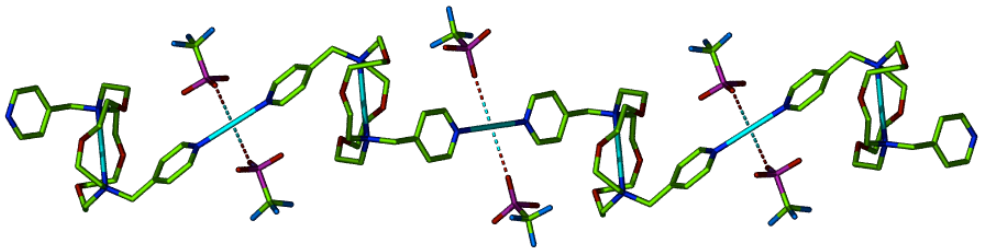


Figure S8 – 1-D undulating chains of **C.(Ag$^+$)**.

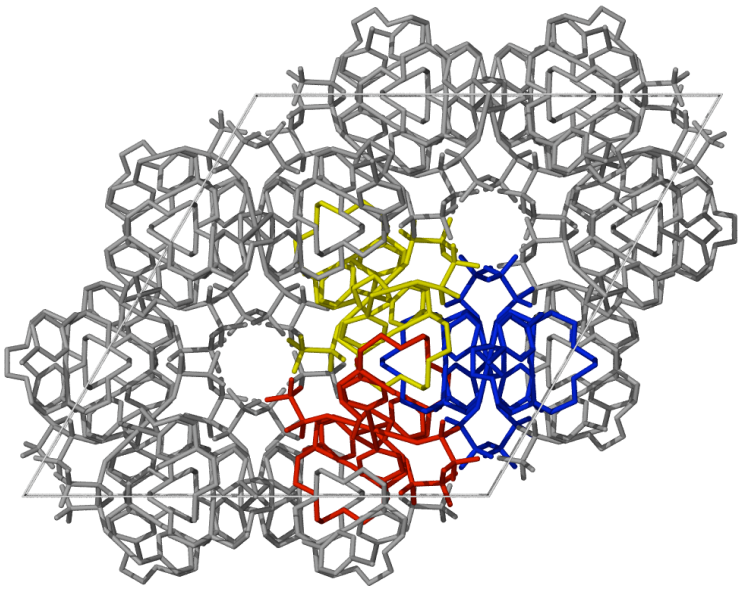


Figure S9 – Crystal packing of **C.(Ag$^+$)** viewed down the *c* axis showing the ABC type packing. The yellow, blue and red chains highlighted show the three orientations of the chains.

[Fe(NCS)$_4$(bpmdcH$_2$)]·2(MeOH) (**D.(2H$^+$)**): Solved and refined in the triclinic space group *P*-1 at 150 K. The structure of **D.(2H$^+$)** consists of a 1-D coordination polymer comprised of a distorted octahedral Fe^{II} metal ion with four NCS$^-$ ligands coordinated equatorially and two bpmdc ligands coordinated through the pyridyl nitrogen in the axial positions. Only two NCS$^-$ anions and half the ligand are crystallographically unique. The diaza-crown ether remains uncoordinated, however, both tertiary amines are protonated. A methanol molecule completes the asymmetric unit which is shown in Figure S-10. The resultant ligand length is 12.726(5) Å. Selected bond lengths and angles are summarised in Table S-6. The 1-D chains form hydrogen bonded (4,4) sheets via hydrogen bonds between the sulphur atoms of two *trans* coordinated NCS$^-$ anions and the protonated diaza-crown amines. A further hydrogen bond exists between the methanol hydroxyl group and the sulphur atoms of the remaining two NCS$^-$ anions, Figure S-11. This hydrogen bonding motif gives rise to AB type packing arrangement, Figure S-12. A summary of the hydrogen bond lengths and angles is given in Table S-7.

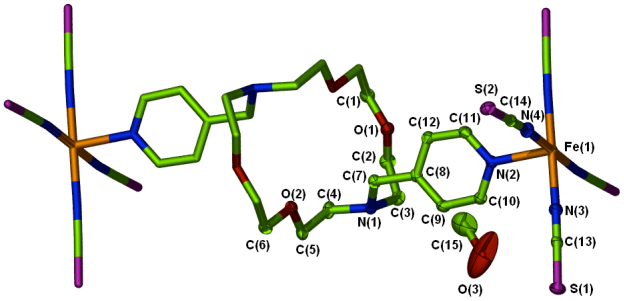


Figure S-10 – Asymmetric unit of **D.(2H$^+$)** (50 % thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table S-6 - Summary of selected bond lengths (Å) and angles (°) in **D.(2H$^+$)**.

Fe(1)-N(2)	2.223(2)	N(2)-Fe(1)-N(3)	89.5(1)
Fe(1)-N(3)	2.144(2)	N(2)-Fe(1)-N(4)	89.6(1)
Fe(1)-N(4)	2.137(2)	N(3)-Fe(1)-N(4)	88.3(1)

Table S-7 - Hydrogen bond lengths (Å) and angles (°) present in **D.(2H$^+$)**.

O(3)-H(3)…S(1)	3.373(4)	O(3)-H(3)…S(1)	165.8(1)
N(1)-H(1)…S(2)	3.227(2)	N(1)-H(1)…S(2)	175.3(1)
C(7)-H(7A)…O(1)	2.887(3)	C(7)-H(7A)…O(1)	112.3(2)
C(7)-H(7B)…O(2)	3.000(3)	C(7)-H(7B)…O(2)	118.9(2)

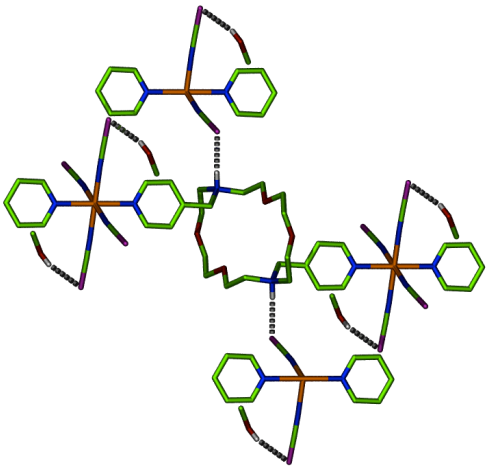


Figure S-11 – Diagram of the hydrogen bonding between chains present in **D.(2H$^+$)**.

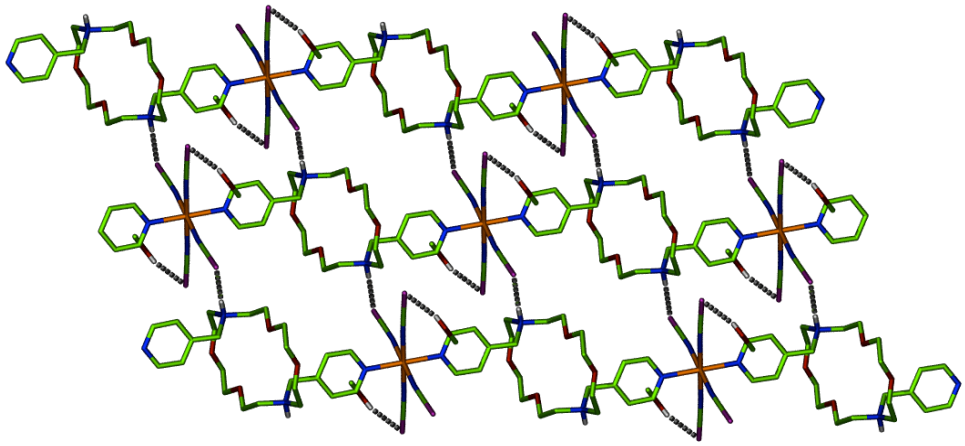


Figure S-12 – The AB type packing present in **D.(2H$^+$)**. View is down the 110 direction.

[Fe(NCS)$_2$(bpmdcBa(NCS)$_2$(H$_2$O))$_2$]·2(CHCl$_3$) (**E.(Ba^{2+})**): Solved and refined in the orthorhombic space group *Cmca* at 150 K. The structure consists of (4,4) sheets comprised of Fe^{II}(NCS)$_2$ metal centres linked via the bpmdc ligand containing a coordinated Ba^{II} cation. The Ba^{II} cation is coordinated to all six hetero-atoms within the diaza-crown ether along with a water molecule and two NCS$^-$ anions. The bpmdc ligand adopts a saddle-like conformation with the Ba^{II} cation sitting above the plane of the diaza-crown oxygen atoms and in line with the diaza-crown nitrogen atoms. The Ba^{II} bound water molecule is situated below the diaza-crown, while the two NCS$^-$

anions lie above this plane. There is one unique Fe^{II} and Ba^{II} centre, only half of one ligand is unique and a solvent chloroform molecule is present in the lattice. The resultant ligand length is 13.932(6) Å. The asymmetric unit is shown in Figure S-13 and selected bond lengths and angles are summarised in Table S-8. The (4,4) sheet adopts an undulating zig-zag motif with large diamond shaped windows. These (4,4) sheets stack on top of each other in an AB fashion, Figure S-14.

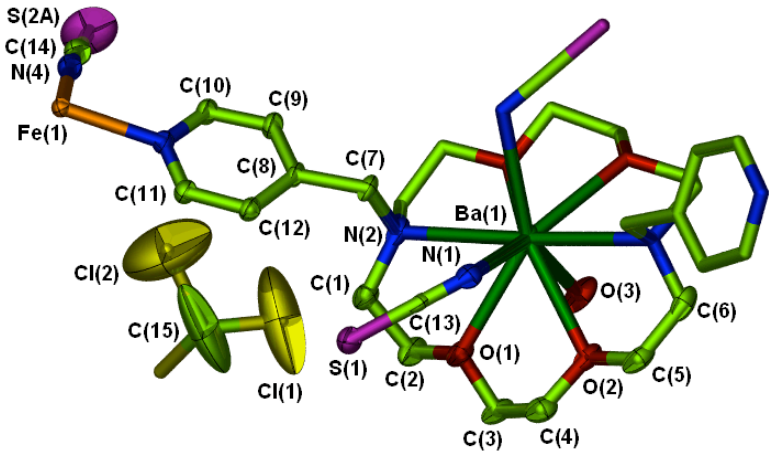


Figure S-13 – Asymmetric unit of **E.(Ba^{2+})** (50 % thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table S-8 - Summary of selected bond lengths (Å) and angles (°) and hydrogen bonds and angles in **E.(Ba^{2+})**.

Fe(1)-N(3)	2.229(6)	Ba(1)-O(2)	2.785(5)
Fe(1)-N(4)	2.101(6)	Ba(1)-O(3)	2.734(8)
Ba(1)-N(1)	2.889(6)	N(3)-Fe(1)-N(4)	90.6(2)
Ba(1)-N(2)	2.923(6)	O(3)-H(3)…N(1)	2.960(4)
Ba(1)-O(1)	2.773(6)	O(3)-H(3)…N(1)	173.8(3)

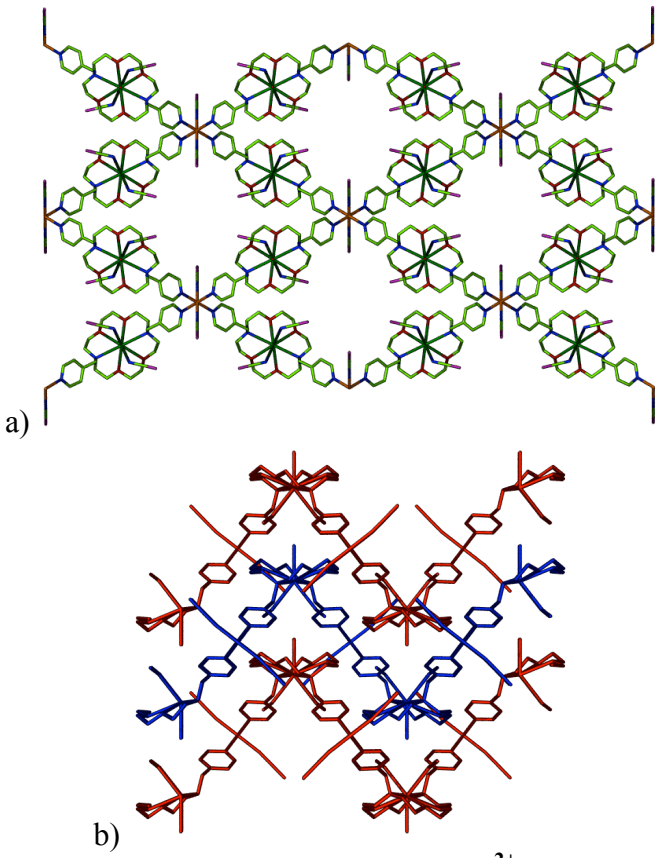


Figure S-14 – (a) Diagram of the (4,4) sheet in **E.(Ba^{2+})**. View is down the *b* axis. (b) AB packing arrangement of the (4,4) sheets in **E.(Ba^{2+})**. View is down the *a* axis. In addition, the packing between (4,4) sheets is such that the Ba^{II} coordinated water molecule in one sheet hydrogen bonds (2.960(4) Å) to the two nitrogen atoms of the NCS^- anions coordinated the Ba^{II} cation above it, resulting in the Ba^{II} diaza-crown moiety stacking as shown it Figure S-15.

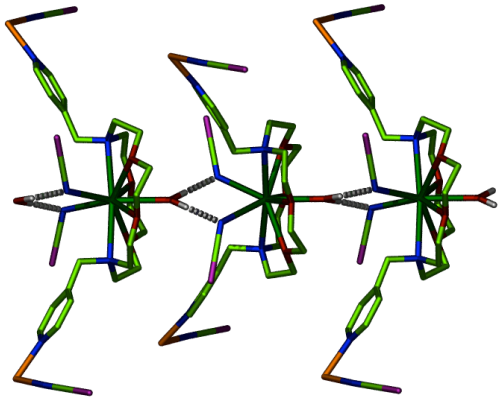


Figure S-15 – Illustration of the stacking formed through hydrogen bonding in **E.(Ba^{2+})**.

[Co(bpmdcCaCl$_2$)(H$_2$O)$_2$Cl$_2$] (**F.(Ca^{2+})**): Solved and refined in the orthorhombic space group *Pbca* at 150 K. The structure consists of 1-D chains that are constructed by the linkage of Co^{II} metal centres by bpmdc ligands. The asymmetric unit is shown in Figure S-16. The distorted octahedral coordination geometry around the Co^{II} metal centre contains two bpmdc, coordinated through the pyridyl nitrogens, two water

molecules, and two chloride anions, with each species coordinated in a *trans* orientation. A calcium cation is coordinated to all six hetero-atoms within the diaza-crown along with two chlorine anions above the plane of the crown. As a result of this calcium coordination the diaza-crown adopts a saddle conformation. Only half the bpmdc ligand and one Co^{II} metal centre are unique with the other half of the ligand being generated through symmetry. The resultant ligand length is 14.457(8) Å. Selected bond lengths and angles are summarised in Table S-9. The undulating 1-D chains align along the *ac* plane with alternating chains rotated 87.2° around the *b* axis, Figure S-17.

NOTE: Diffuse electron density was observed within the void volumes of this compound however refinement of these peaks arising from solvent molecules was not successful. As elemental analysis of the bulk material was not possible here to determine the solvent content, the data was run through the SQUEEZE routine within PLATON[3] to remove the unmodelled diffuse electron density. As such the final solution contains a large volume of void space.

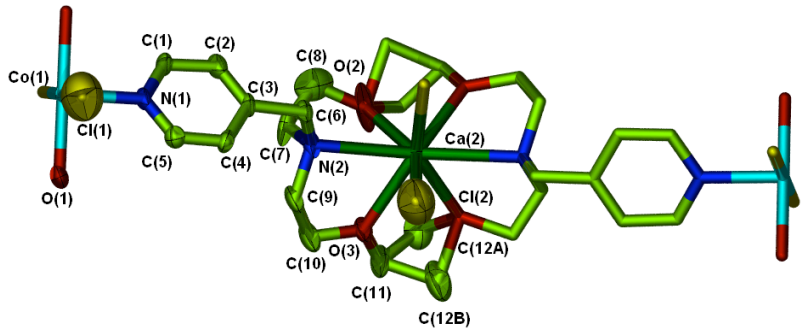


Figure S-16 – The asymmetric unit of **F.(Ca^{2+})** (50 % thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table S-9 - Summary of selected bond lengths (Å) and angles (°) in **F.(Ca^{2+})**.

Co(1)-Cl(1)	2.116(4)	N(1)-Co(1)-O(1)	88.7(2)
Co(1)-O(1)	2.110(4)	Ca(2)-Cl(2)	2.366(3)
Co(1)-N(1)	2.154(3)	Ca(2)-N(2)	2.747(3)
Cl(1)-Co(1)-O(1)	88.8(2)	Ca(2)-O(2)	2.434(4)
Cl(1)-Co(1)-N(1)	88.6(2)	Ca(2)-O(3)	2.454(3)

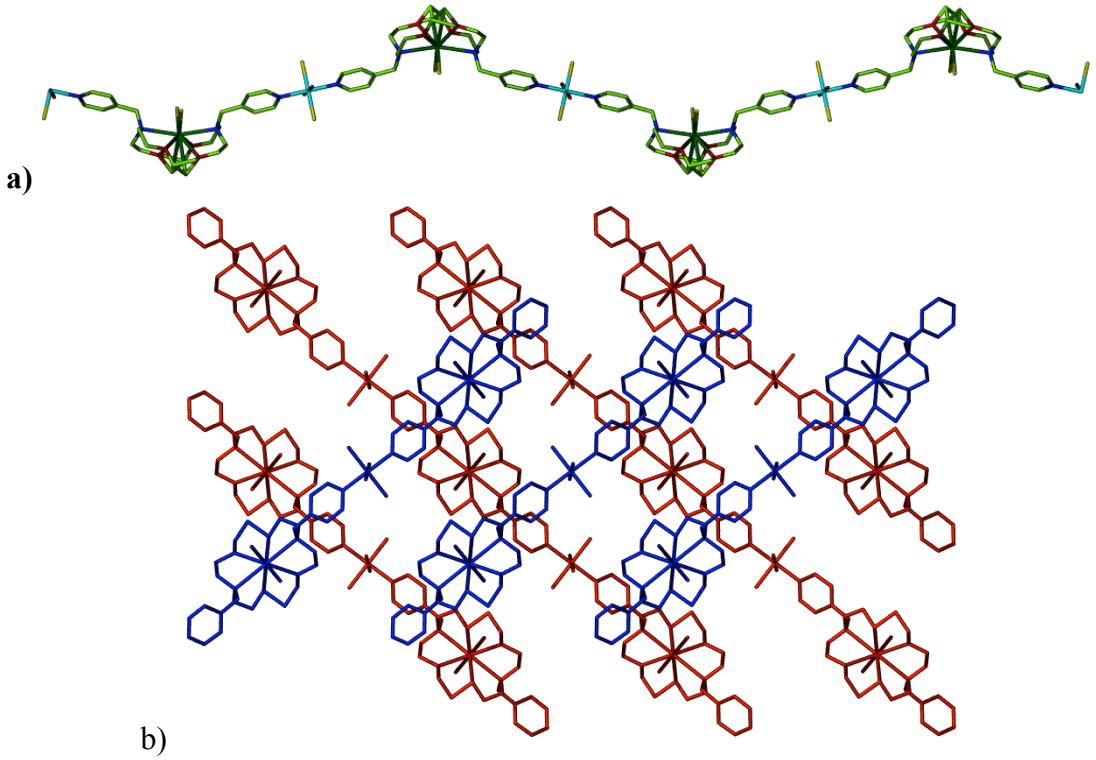


Figure S-17 – (a) 1-D undulating chains of **F.(Ca^{2+})**. (b) Packing of two layers of 1-D chains of **F.(Ca^{2+})** showing the rotation between layers. View is down the *b* axis.

[Co(bpmdcK)(H_2O)$_2$$Cl_2$]Cl·2($H_2O$) (**G.($K^+$)**): Solved and refined in the triclinic space group *P*-1 at 150 K. The structure consists of 1-D chains that are constructed by the linkage of Co^{II} centres by bpmdc units bound through the pyridyl nitrogens. Two water molecules and two chloride anions, both in the *trans* configuration, complete the distorted octahedral coordination geometry and the asymmetric unit is shown in Figure S-18. There is an uncoordinated chloride anion (refined at half occupancy) and a water molecule residing within the lattice. The oxygen atom of the water molecule is disordered over two positions. Only half of one bpmdc ligand is crystallographically unique with a potassium cation situated within the centre of the diaza-crown and coordinated to all six hetero-atoms within the diaza-crown ether.

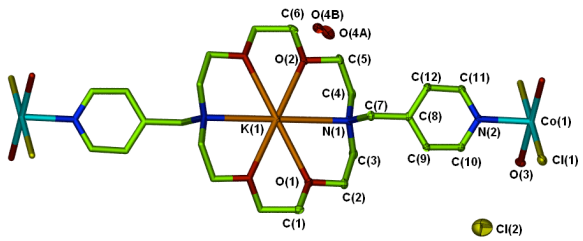


Figure S-18 – Crystal structure of **G.(K^+)**. Thermal ellipsoids are at 50 % and labeled atoms represent the asymmetric unit. Hydrogen atoms have been omitted for clarity.

The potassium also interacts axially to two cobalt bound chlorine anions from adjoining chains. This results in the potassium adopting a distorted hexagonal bipyramidal coordination geometry. This interaction gives rise to a pseudo 2-D, (4,4) sheet, Figure S-19. The resultant ligand length is 15.957(5) Å. Selected bond lengths and angles are summarised in Table S-10.

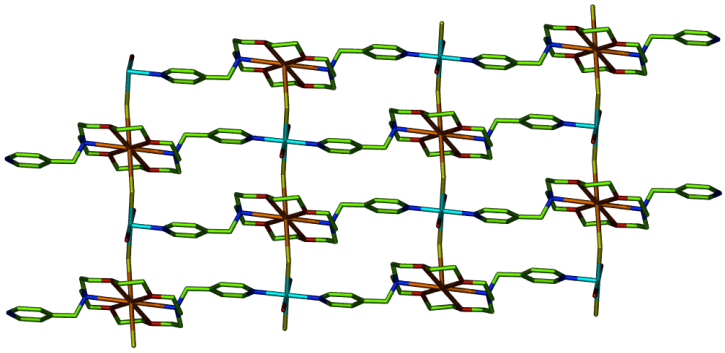


Figure S-19 – Diagram showing the (4,4) sheet arrangement of **G.(K^+)**. View is down the *c* axis.

Table S-10 – Summary of selected bond lengths (Å) and angles (°) in **G.(K^+)**.

Co(1)-Cl(1)	2.4442(6)	N(2)-Co(1)-O(3)	90.54(8)
Co(1)-N(2)	2.158(2)	K(1)-Cl(1)	3.1046(6)
Co(1)-O(3)	2.098(2)	K(1)-O(1)	2.822(2)
Cl(1)-Co(1)-O(3)	90.84(5)	K(1)-O(2)	2.808(2)
Cl(1)-Co(1)-N(2)	89.54(6)	K(1)-N(1)	2.964(2)

An extensive hydrogen-bonding network is present between all chlorine anions and water molecules along with the O(2) atom of the diaza-crown ether. These interactions give rise to the 3-D hydrogen bonded network shown in Figure S-20. A summary of the hydrogen bond lengths (donor atom-acceptor atom) and bond angles are shown in Table S-11.

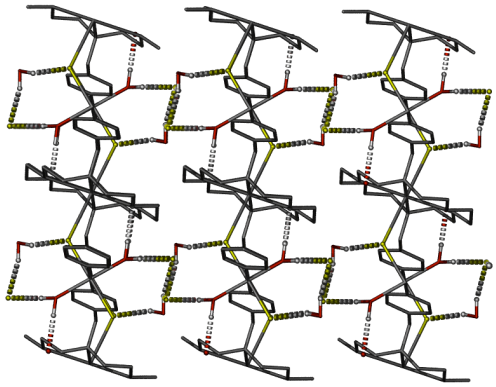


Figure S-20 – A diagram of the hydrogen bonded network present within **G.(K^+)**. View is down the 101 direction.

Table S-11 - Hydrogen bond lengths (Å) and angles (°) present in **G.(K^+)**.

O(3)-H(O3A)…O(2)	2.826(3)	O(3)-H(O3A)…O(2)	169(4)
O(3)-H(O3B)…Cl(2)	3.041(2)	O(3)-H(O3B)…Cl(2)	170(4)
O(4A)-H(O4A)…Cl(1)	3.219(3)	O(4A)-H(O4A)…Cl(1)	159.5(2)
O(4A)-H(O4B)…Cl(2)	3.162(2)	O(4A)-H(O4B)…Cl(2)	146.0(2)

[Co(NCS)$_2$(H$_2$O)$_2$(bpmdc)] (**H.(2H$_2$O)**): Solved and refined in the monoclinic space group $P2_1/n$ at 150 K. The structure contains a 1-D coordination polymer consisting of a slightly distorted octahedral Co^{II} cation coordinated to two water molecules, two thiocyanate anions and two pyridyl groups, each of which are coordinated in the *trans* conformation. The asymmetric unit is shown in Figure S-21. The resultant ligand length is 16.566(8) Å. Selected bond lengths and angles are summarised in Table S-12.

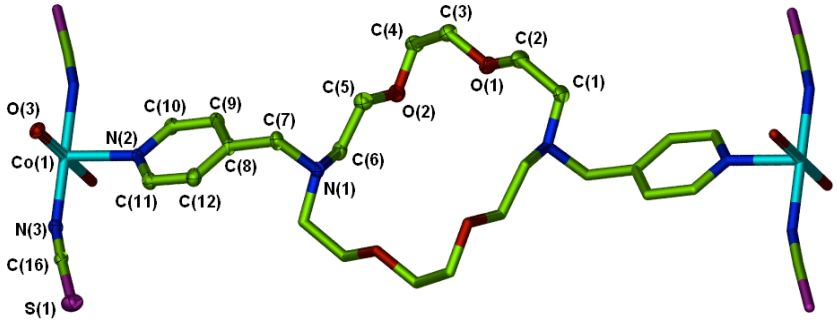


Figure S-21 - Crystal structure of **H.(2H$_2$O)**. Thermal ellipsoids are at 50 % and show the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table S-12 - Summary of selected bond lengths (Å) and angles (°) in **H.(2H$_2$O)**.

Co(1)-O(3)	2.111(2)	O(3)-Co(1)-N(2)	89.61(9)
Co(1)-N(2)	2.181(2)	O(3)-Co(1)-N(3)	87.45(10)
Co(1)-N(3)	2.095(3)	N(2)-Co(1)-N(3)	89.21(9)

Hydrogen bonding exists between the coordinated water molecule and one nitrogen and one oxygen of the diaza-crown of an adjacent chain to give rise to a trellis-like network. A summary of the hydrogen bond lengths (donor atom-acceptor atom) and bond angles are shown in Table S-13. The 1-D chains align parallel to the *bc* plane with alternating chains rotated 29.1° around the *a* axis to give AB type packing, Figure S-22 and S-23.

Table S-13 - Hydrogen bond lengths (Å) and angles (°) present in **H.(2H$_2$O)**.

O(3)-H(3AO)…N(1)	2.879(3)	O(3)-H(3AO)…N(1)	166(5)
O(3)-H(3BO)…O(2)	2.928(3)	O(3)-H(3BO)…O(2)	174(4)

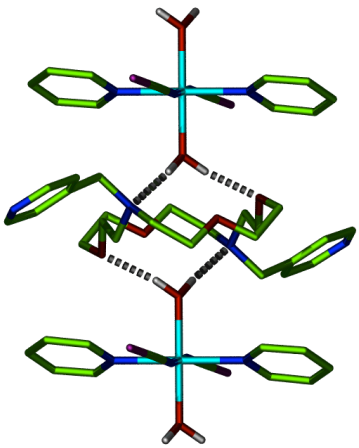
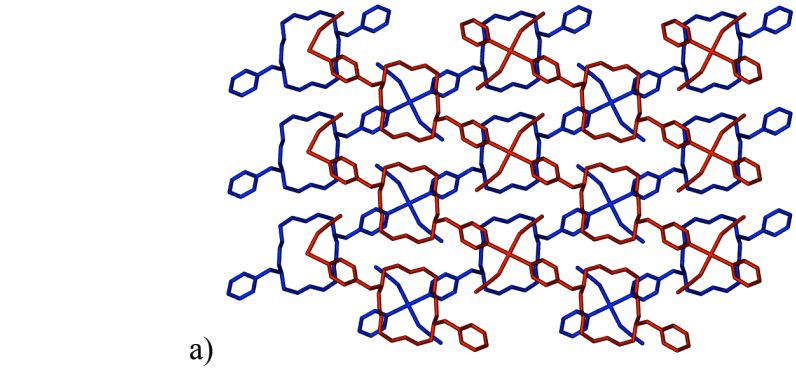
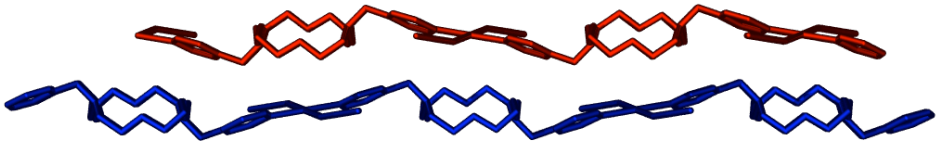


Figure S-22 – Diagram of the hydrogen bonding between chains present in **H.(2H$_2$O)**.



a)



b)

Figure S-23 – Schematic diagram of the packing present in **H.(2H$_2$O)**. (a) View down the *a* axis. (b) View down the *c* axis.

References

1. B. Dietrich, J.-M. Lehn, J. P. Sauvage and J. Blanzat, *Tetrahedron*, 1973, 29, 1629-1645.
2. H. Tsukube, K. Yamashita, T. Iwachido and M. Zenki, *J. Org. Chem.*, 1991, 56, 268-272.
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