Metal-organic frameworks exhibiting strong anion-π interactions

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1. Synthesis

Pyridazino[4,5-d]pyridazine.

This condensed heterocycle was prepared (G. Adembri, F. De Sio, R. Nesi and M. Scotton, Chem. Commun., 1967, 1006) by a laborious procedure, which involves: oxidation of phthalazine to pyridazine-4,5 dicarboxylic acid; esterification to diethyl pyridazine-4,5 dicarboxylate; low-temperature reduction with LiAlH₄ to corresponding dialdehyde and its reaction with hydrazine. This method was poorly reproducible in our laboratory and therefore we have elaborated a new simple one-pot procedure, with using of readily accessible starting materials.
1,2,4,5-Tetrazine was prepared by the method of Sauer (Eur. J. Org. Chem., 1998, 2885) and acetylene dialdehyde tetraethylacetal (colorless solid, m.p. 18°C) was synthesized in a standard way, reacting ethylmagnesium bromide with acetylene gas and HC(OEt)₃. 4+2 Cycloaddition that occurs between the components is an “inverse electron demand Diels-Alder reaction”, in which tetrazine acts as an electron deficient azadiene. Therefore the utilization of the dialdehyde in the form of acetal (electron rich acetylene) was essential for success of the synthesis.

A solution of 5.83 g (71 mmol) 1,2,4,5-tetrazine and 15.30 g (66 mmol) acetylenedialdehyde tetraacetal in 80 ml dry dioxane was stirred at 90°C for 20 h. The reaction proceeds smoothly with extensive evolution of nitrogen and crimson-red color of tetrazine was mostly disappeared after 14-16 h. The solvent together with the excess of tetrazine were distilled off from the resulting brown mixture in vacuo. The dark oily residue was dissolved in 100 mL of 10% HCl and stirred at 60°C for 30 min (hydrolysis of the acetal), after which the solution was cooled to r.t., 10 mL N₂H₄·H₂O was added and stirring was continued for an additional hour. The black solution was extracted with 30 × 200 mL chloroform (total volume 6 L) and the extracts were evaporated to dryness. The yellow-brown solid was sublimed (180°C, 0.2 Torr) and then crystallized from methanol yielding pure product (4.54 g, 52%) as faintly yellow needles. The compound is soluble in water.

Preparation of [Cu(H₂O)₂(L)₂](ClO₄)₂·4H₂O 3

A solution of 0.037 g (0.1 mmol) of Cu(ClO₄)₂·6H₂O and 0.026 g (0.02 mmol) of pyridazino[4,5-d]pyridazine in 3 mL water was allowed to stand at r.t. for 10 d. After evaporation of the solution to 1/2 of the initial volume, the complex crystallizes in the form of large blue-green blocks. The yield was 0.050 g (80%).

Anal. (Carlo Erba Str.): C₁₂H₂₀Cl₂CuN₈O₁₄, Calcd., %: C, 22.70; H, 3.18; N, 17.66. Found, %: C, 22.58; H, 3.07; N, 17.81.

Compounds [Cu(H₂O)₂(L)₂](NO₃)₂·2H₂O 2 (green-blue prisms), [Zn(H₂O)₄(L)](NO₃)₂ 1 (faintly yellow blocks) and [Ag(H₂O)(L)](CH₃SO₃)·H₂O 5 (yellow needles) were prepared similarly starting with Zn(NO₃)₂·6H₂O, Cu(NO₃)₂·2.5H₂O and AgCH₃SO₃.
Preparation of \([\text{Cu}(\text{OH})(\text{L})](\text{H}_2\text{NSO}_3)\cdot\text{H}_2\text{O}\) 4

A solution of 0.031 g (0.1 mmol) of Cu(\(\text{H}_2\text{NSO}_3\))2·3H2O and 0.016 g (0.12 mmol) of the ligand in 3 mL water was slowly evaporated at r.t. in a vacuum desiccator over concentrated H2SO4 for the period of 7-8 d yielding green prisms of \([\text{Cu}(\text{OH})(\text{L})](\text{H}_2\text{NSO}_3)\cdot\text{H}_2\text{O}\) 4 (0.023 g, 70%).

Anal. (Carlo Erba Str.): C6H9CuN5O5S, Calcd., %: C, 22.05; H, 2.78; N, 21.44. Found, %: C, 21.94; H, 2.66; N, 21.60.

2. Crystallography

The intensity data were collected at 220 K on a Stoe Image Plate Diffraction System [1] using MoK\(\alpha\) graphite monochromated radiation (\(\lambda = 0.71073\) Å): \(\phi\) oscillation scans 0–200°, step \(\Delta\phi = 1.0°\). The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-87 [2] and SHELXL-97 [3]. In structures 1, 3, 4 and 5 all hydrogen atoms were located in a difference map and treated as riding, with U\(_{\text{iso}}\)(H) = 1.2 U\(_{\text{eq}}\) (C) or 1.5 U\(_{\text{eq}}\) (O, N).

Structure 2 can be solved in centrosymmetric space group \(C2/c\). In this case, each of two unique nitrate anions was disordered over two closely separated positions related by a symmetry and the subsequent refinement led to poor convergence at \(R1 = 0.12\). However, refinement in space group \(Cc\) proceeded smoothly and it did not lead to such type disorder of the counter anions. One of two solvate water molecules was equally disordered over two positions and both components of the disorder were refined anisotropically. Hydrogen atoms for CH groups and coordinated water molecules were located and treated as above, H atoms of solvate water molecules were not included.

Graphical representation of the crystal structures was made using program Diamond [4].

Figure S1. Atom labeling scheme for structure \([\text{Zn(H}_2\text{O})_4(\text{L})](\text{NO}_3)_2\) 1. Thermal ellipsoids are at 50% probability level and hydrogen atoms are represented as small circles of arbitrary radii. Unique part of the structure is shaded grey and with bold lines. The Zn atoms and centroids of the ligands occupy centres of inversion. Symmetry codes used to generate equivalent atoms: a) \(-x, -y, -z\); b) \(1-x, -y, 1-z\).

Figure S2. Atom labeling scheme for structure \([\text{Cu(H}_2\text{O})_2(\text{L})_2](\text{NO}_3)_2\cdot2\text{H}_2\text{O}\) 2. The hydrogen atoms are represented as small circles of arbitrary radii. Unique part of the structure is shaded grey. Symmetry codes used to generate equivalent atoms: a) \(x, 1-y, -0.5+z\); b) \(x, 2-y, -0.5+z\).
Figure S3. Atom labeling scheme for structure [Cu(H₂O)₂(L)₂][ClO₄]₂·4H₂O. Thermal ellipsoids are at 50% probability level and hydrogen atoms are represented as small circles of arbitrary radii. Unique part of the structure is shaded grey and with bold lines. The copper atoms occupy centres of inversion. Symmetry codes used to generate equivalent atoms: a) \(-x, -y, -z\); b) \(-x, -y, -1-z\); c) \(-x, 1-y, -z\).

Figure S4. Space filling presentation of structure [Cu(H₂O)₂(L)₂][ClO₄]₂·4H₂O showing location of the perchlorate anions inside the channels of the framework.
**Figure S5.** Hydrogen bonding between perchlorate anions and solvate water molecules in structure \([\text{Cu}(\text{H}_2\text{O})_2(\text{L})_2](\text{ClO}_4)_2\cdot4\text{H}_2\text{O}\) 3. Compare with a typical 2:2 cyclic \(\text{ClO}_4^-/\text{water}\) bonding (for example, K.V. Domasevitch and I. Boldog, *Acta Crystallogr., Sect. C*, 2005, 61, o373-o376).

**Figure S6.** Atom labeling scheme for structure \([\text{Cu(OH)}(\text{L})](\text{H}_2\text{NSO}_3)\cdot\text{H}_2\text{O}\) 4. Thermal ellipsoids are at 50% probability level and hydrogen atoms are represented as small circles of arbitrary radii. Unique part of the structure is shaded grey and with bold lines. Both unique copper atoms occupy centres of inversion. Symmetry codes used to generate equivalent atoms: a) \(x, 0.5–y, 0.5+z\); b) \(-1-x, 0.5+y, 0.5–z\); c) \(-1-x, 1-y, 1-z\); d) \(-x, 1-y, 1-z\); e) \(-x, 0.5+y, 0.5-z\).
**Figure S7.** Hydrogen bonding in structure [Cu(OH)(L)](H$_2$NSO$_3$)·H$_2$O 4: sulfamate anions and water molecules form infinite hydrogen bonded chain, which is located inside channel of the 3D coordination framework and held by OH---O hydrogen bonding with bridging hydroxo ligands. Symmetry codes used to generate equivalent atoms: c) 1-x, 1+y, 1-z; f) 2-x, 1-y, 1-z.

Hydrogen bonding in the structure [Cu(OH)(L)](H$_2$NSO$_3$)·H$_2$O 4

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**Figure S8.** Atom labeling scheme for structure \([\text{Ag(H}_2\text{O})(\text{L})](\text{CH}_3\text{SO}_3)\cdot\text{H}_2\text{O}\) 5. Thermal ellipsoids are at 40% probability level and hydrogen atoms are represented as small circles of arbitrary radii. Unique part of the structure is shaded grey and with bold lines.

**Figure S9.** Polymeric aquasilver(I) motif in structure \([\text{Ag(H}_2\text{O})(\text{L})](\text{CH}_3\text{SO}_3)\cdot\text{H}_2\text{O}\) 5. Compare with the hydroxocopper(II) subconnectivity in structure 4.
**Figure S10.** Perspective view of 3D framework in structure \([\text{Ag(H}_2\text{O})(\text{L})](\text{CH}_3\text{SO}_3)\cdot\text{H}_2\text{O}\ 5\), with non-coordinated methanesulfonate anions and water molecules located in the channels.

**Figure S11.** Hydrogen bonding involving coordinated and non-coordinated water molecules and sulfonate anions in structure \([\text{Ag(H}_2\text{O})(\text{L})](\text{CH}_3\text{SO}_3)\cdot\text{H}_2\text{O}\ 5\).