# Metal–organic frameworks exhibiting strong anion–π interactions†

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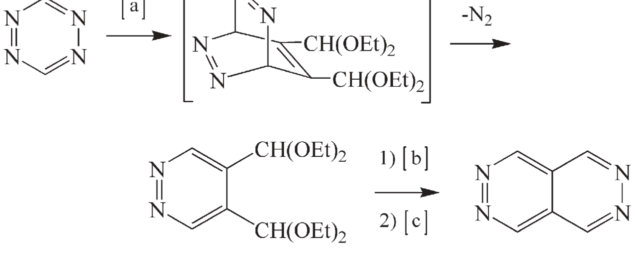
**Coordination frameworks of pyridazino[4,5-*d*]pyridazine reveal a pronounced ability for anion–π interactions.**

Coordination polymers offer a significant potential for applications in adsorption, guest and anion recognition and sensing.[1] Their structure commonly provides binding sites for such specific interactions as π–π stacking and XH···π hydrogen bonding.[2] The latter reflects the ability of the π-cloud to interact with positively polarized atoms. An electrostatic interaction between anionic species and electron deficient heterocycles, which parallels the above binding scheme, is also possible[3] and very recently the existence of anion–π interactions was proved in the solid state[3,4] and in solution.[5] This effect may be significant also for biomolecule/solution interfaces, as it occurs in protein structures.[6] In fact, such interactions could be especially relevant for host–guest chemistry of coordination polymers, particularly for functionalization of hydrophobic crystal cavities and for the design of geometrically rigid anion receptors.[7,8] However, typical electron deficient heterocycles such as 1,3,5-triazines and 1,2,4,5-tetrazines are very weak donors and they are hardly suitable for bridging metal ions and the generation of coordination frameworks.

As a system that combines efficient donor properties towards transition metal ions and a pronounced ability for anion–π interactions we have developed unsubstituted pyridazino[4,5-*d*]pyridazine, which was readily accessible by a novel one-pot synthesis involving inverse electron demand Diels–Alder cycloaddition (Scheme 1).‡ Unusual anion binding properties of the ligand may be clearly related to its electron-deficiency (LUMO energy −1.591 *vs.* −0.288 eV for the parent pyridazine),[9] influenced also by N-coordination to such Lewis acids as metal ions.



**Scheme 1** Synthesis of pyridazino[4,5-*d*]pyridazine. Reagents and conditions: [a] $(EtO)_2CHC{\equiv}CCH(OEt)_2$, dioxane, 90 °C, 20 h; [b] 4% HCl, 60 °C, 30 min; [c] $N_2H_4{\cdot}H_2O$, r.t., 1 h.

In metal complexes the bicyclic N-donor typically acts as a bitopic connector bridging pairs of metal ions at 9.0–9.2 Å, while its π-acidity results in very characteristic direct O(anion)···π interactions and hence in elimination of counter anions from the metal coordination environment. Unlike any of the hitherto reported structural precedents for anion–π binding, the condensed pyridazine has a symmetrical bicyclic structure and offers two equivalent sites for such interactions simultaneously. Thus, in the 1D chain-like polymer $[Zn(H_2O)_4(L)](NO_3)_2$ **1** § (Zn–N 2.085(1) Å) each of the π-systems supports equally effective interactions with non-coordinated nitrate anions as reflected by short O–C(N) contacts (mean 3.18 Å) and the situation of the oxygen atoms exactly above the centroids of the pyridazine rings (O···π 2.87 Å, angle of the O···π axis to the plane of the aromatic cycle $\varphi = 86.6°$) (Fig. 1). The same was observed also for $[Cu(H_2O)_2(L)_2]X_2{\cdot}nH_2O$ (**2**: X = $NO_3$, $n = 2$; **3**: X = $ClO_4$, $n = 4$) complexes. Their metal–organic portions adopt a 2D square grid structure and each of the square meshes houses a pair of the anions forming close O···π contacts (Fig. 1, b). The shortest ones were supported by the nitrate anions (2.83 Å, $\varphi = 88.5°$), while such interactions in **3** were somewhat weaker (3.05 Å, $\varphi = 84.9°$), in accordance with very low nucleophility of the perchlorate anions. To the best of our knowledge, compounds **1** and **2** display the shortest O···π separations found as yet in crystal structures. Comparable parameters (F···π 2.80–3.04 Å) were registered only for the extreme electron deficient tetrazine and the $AsF_6^-$ anion.[8,10] The only known precedent for such interaction of non-coordinated $NO_3^-$ anions (with 1,3,5-triazine cycle) revealed appreciably longer O···π distances (3.20 Å), while the results of an *ab initio* study (2.75 Å; $\varphi = 86.2°$)[11] exactly agree with the geometry of structures **1** and **2**.

Although the electron deficiency mitigates against coordination to many metal ions, the organic module may be readily integrated into a framework even as a N-tetradentate ligand, which offers special potential from the design perspective. First, this could be achieved for typical transition metal ions with the assistance of suitable inorganic bridges (*cf.* hydroxo). Second, the tetradentate function of the ligand may be disposed towards extremely soft acids (such as $Cu^+$ or $Ag^+$) favoring efficient back-bonding and coordination to unsaturated N atoms.

Both these approaches were suitably applicable to the generation of 3D frameworks. For copper(II) ions, this was achieved by using N-basic sulfamate anions $H_2NSO_3^-$ facilitating mild hydrolysis in aqueous solution and generating the hydroxopolymer $[Cu(\mu\text{-}OH)(L)](H_2NSO_3){\cdot}H_2O$ **4**. The ligand connects two pairs of adjacent metal ions from the infinite hydroxocopper(II) chains (Cu–O 1.95 Å); each channel of the resulting 3D framework has inner dimensions of 5 × 5 Å and hosts a chain of hydrogen bonded sulfamate ions (Fig. 2). The electron-deficient character of the ligand was reflected by relatively long Cu–N separations (2.10, 2.11

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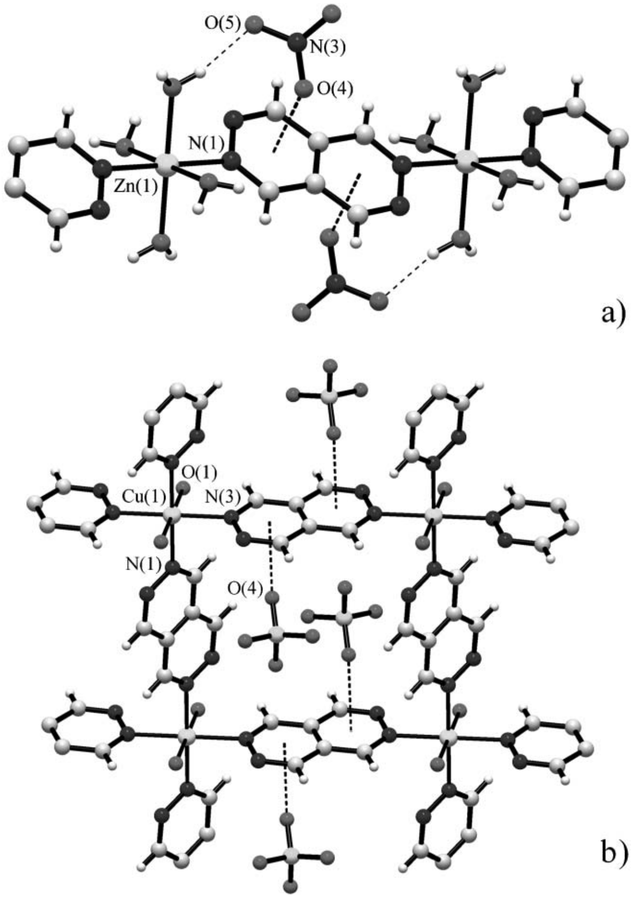


**Fig. 1** a) 1D chain in complex **1** showing characteristic O$\cdots\pi$ (2.875(2) Å) interactions with nitrate anions. b) Incorporation of $ClO_4^-$ anions inside a rectangular cage in structure **3** and their interaction with $\pi$-systems.

and 2.39, 2.52 Å) and the two most distal nitrogen atoms occupy axial positions in a typically distorted Cu(II) coordination octahedron. Actually the same framework structure was adopted by Ag(I) ions in $[Ag(\mu\text{-}H_2O)(L)](CH_3SO_3)\cdot H_2O$ **5**. The ligands connect pairs of the adjacent metal ions from 1D aquasilver(I) chains (all four Ag–N distances are in the range 2.46–2.52; Ag–O 2.60 Å) that are exactly similar to the hydroxocopper(II) chains in **4** (Scheme 2).

The uniform framework topology in **4** and **5** is new and it is related to the rare topological type "lvt" $\{4^2;8^4\}$,[12] with one extra bond (μ-oxo or μ-aqua bridge) for half of the nodes. The overall connectivity is a binodal four and six connected net, with the metal atoms representing the 6-c node and the organic tetradentates the planar 4-c node (total Schläfli symbol $\{3^2;6^2;7^2\}\{3^4;4^2;6^4;7^5\}$).

The structure of **4** reveals a very remarkable and unprecedented mode of anion–$\pi$ interaction that occurs between the fused pyridazine functions as a double receptor for oxygen and nitrogen sites of the anion. The dimensions of the sulfamate and pyridazino[4,5-*d*]pyridazine perfectly match each other (N–O 2.45 Å *vs.* distance between two ring centroids 2.44 Å) and this facilitates effective double binding (O$\cdots\pi$ + N$\cdots\pi$), in which the corresponding distances to the pyridazine centroids (3.14 and 3.10 Å) are similar to the ones observed for perchlorate (Fig. 3). It is worth noting that localization of the nitrogen atom lone pair is evident and it is directed towards the centre of the pyridazine cycle ($\angle$S–N$\cdots\pi$ 114°, H–N$\cdots\pi$ 94 and 114°) (Table 1).

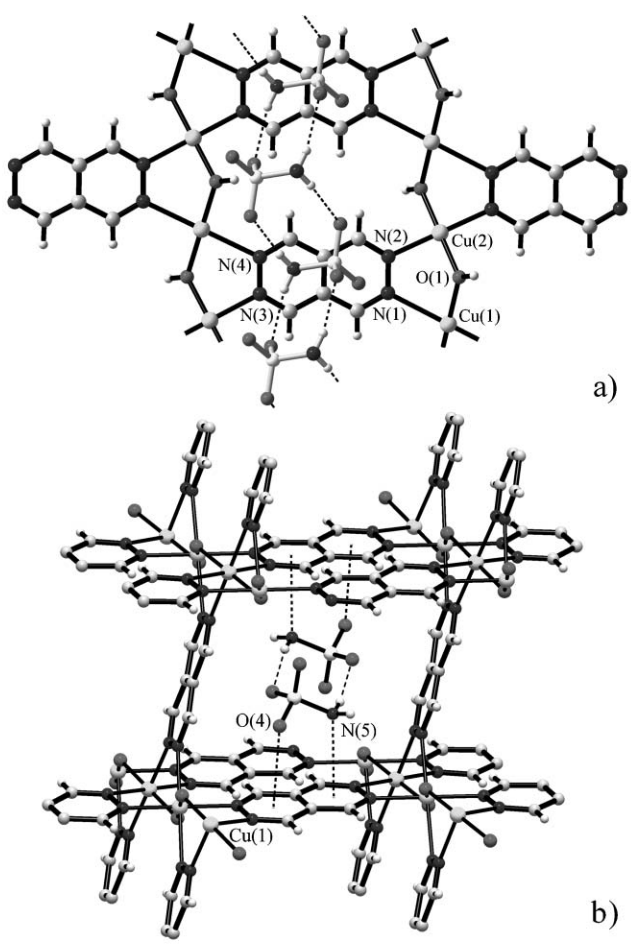
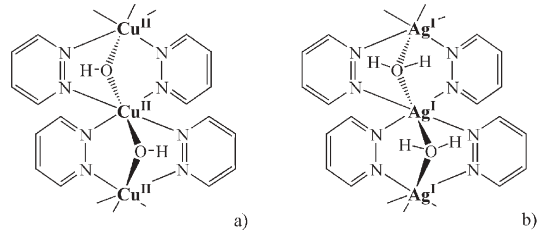


**Fig. 2** a) Fragment of the structure of **4** showing effective cooperation of hydroxo and pyridazine bridges and situation of the chain of hydrogen-bonded sulfamate anions. b) Immobilization of the anions inside the channels by O$\cdots\pi$ and N$\cdots\pi$ interactions.



**Scheme 2** Chemically different but topologically equivalent motifs involving infinite hydroxocopper(II) (a) and aquasilver(I) (b) chains.

This illustrates the possibility for even multiple O(N)$\cdots\pi$ interactions with aromatic polycycles and development of metal–organic arrays with multicenter aromatic receptors for anions. The unusual ligand–sulfamate double binding may be directly compared with the behaviour of methanesulfonate anions in the closely related structure **5**. Such analogy was also suggestive of the lone pair (N)$\cdots\pi$ attraction since the parameters for the sulfonate–$\pi$ interactions in both structures (**5**: O$\cdots\pi$ 3.09 Å) are very similar. The $NH_2/CH_3$ functionalities were clearly responsible for the orientations of the anions towards the aromatic planes (Fig. 3) and in the case of $CH_3SO_3^-$ the $CH_3\cdots\pi$ interaction is rather repulsive (C$\cdots\pi$ 3.97 Å). Such effective lone pair$\cdots\pi$ bonding itself has very

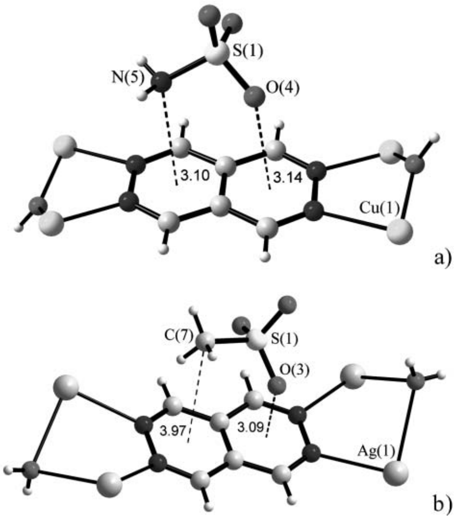


**Fig. 3** Modes of the anion–π interactions in the structures of **4** (a, $H_2NSO_3^-$) and **5** (b, $CH_3SO_3^-$): Accessibility of the lone pair influences double π,π-binding of sulfamate.

**Table 1** Geometry of the anion–π interaction in structures **4** and **5**

| Anion involved | Site | X···C(N) range/° | X···centroid distance/Å | X···plane distance/Å | $\varphi^a$/° |
|---|---|---|---|---|---|
| $H_2NSO_3^-$ | O | 3.26–3.60 | 3.140(2) | 3.109(3) | 81.9 |
| | N | 3.09–3.64 | 3.101(2) | 3.013(3) | 76.3 |
| $H_3CSO_3^-$ | O | 3.09–3.65 | 3.093(2) | 3.011(2) | 76.8 |
| | C | 3.89–4.49 | 3.971(3) | 3.861(3) | 76.5 |

[a] Angle of the X···π axis to the plane of the aromatic cycle.

little precedent in the literature; in particular it was involved as a stabilizing factor for sugar–nucleobase intramolecular interactions.[13]

In conclusion, the ability of the pyridazine compounds for anion–π interactions provides an attractive structural prototype and a unique π-bifunctional building block for novel polymeric and molecular anion receptors. The system reported herein is important for solid-state modelling of 4 + 1 cycloaddition reactions, similar to those that occur between tetrazines and isocyanides.[14] Our results demonstrate also a useful methodology for annelation of pyridazine cycles and provide the easiest chemical access to the pyridazino[4,5-*d*]pyridazine frame.[15]

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## Notes and references

‡ Pyridazino[4,5-*d*]pyridazine. A solution of 5.83 g (71 mmol) 1,2,4,5-tetrazine and 15.30 g (66 mmol) acetylenedialdehyde tetraethyl acetal in 80 mL of dry dioxane was stirred at 90 °C for 20 h and then evaporated *in vacuo*. The dark residue was dissolved in 100 mL of 4% HCl and stirred at 60 °C for 30 min, after which 10 mL of $N_2H_4 \cdot H_2O$ was added and stirring was continued for an additional hour. The black solution was extracted with 30 × 200 mL chloroform and the extracts were evaporated to dryness. The solid was sublimed (180 °C, 0.2 Torr) and then crystallized from methanol yielding pure product (4.54 g, 52%) as faintly yellow needles.

Coordination compounds were prepared from aqueous solutions of the components. In a typical synthesis, a solution of 0.031 g (0.1 mmol) of $Cu(H_2NSO_3)_2 \cdot 3H_2O$ and 0.016 g (0.12 mmol) of the ligand in 3 mL water was slowly evaporated over a period of 7–8 d yielding green prisms of $[Cu(OH)(L)](H_2NSO_3) \cdot H_2O$ **4** (0.023 g, 70%).

§ Crystallographic measurements were made at 220 K using a Stoe IPDS diffractometer (Mo-Kα, $\lambda$ = 0.71073 Å).

*Crystal data*: for $[Zn(H_2O)_4(L)](NO_3)_2$ **1**: $C_6H_{12}N_6O_{10}Zn$, $M$ = 393.59, triclinic, space group $P\bar{1}$, $a$ = 6.3661(7), $b$ = 7.5923(9), $c$ = 8.0357(9) Å, $\alpha$ = 103.58(1), $\beta$ = 103.12(1), $\gamma$ = 109.69(1)°, $V$ = 334.98(7) Å$^3$, $Z$ = 1, $\mu$(Mo-Kα) = 1.904 mm$^{-1}$, $D_{calc}$ = 1.951 g cm$^{-3}$, 1771 unique reflections, $R1$ = 0.025, $wR2$ = 0.067.

For $[Cu(H_2O)_2(L)_2](NO_3)_2 \cdot 2H_2O$ **2**: $C_{12}H_{16}CuN_{10}O_{10}$, $M$ = 523.89, monoclinic, space group $Cc$, $a$ = 13.1173(9), $b$ = 13.2215(9), $c$ = 12.0518(8) Å, $\beta$ = 113.404(2)°, $V$ = 1918.2(2) Å$^3$, $Z$ = 4, $\mu$(Mo-Kα) = 1.220 mm$^{-1}$, $D_{calc}$ = 1.814 g cm$^{-3}$, 3769 unique reflections, $R1$ = 0.041, $wR2$ = 0.112.

For $[Cu(H_2O)_2(L)_2](ClO_4)_2 \cdot 4H_2O$ **3**: $C_{12}H_{20}Cl_2CuN_8O_{14}$, $M$ = 634.80, triclinic, space group $P\bar{1}$, $a$ = 7.3893(8), $b$ = 9.0008(9), $c$ = 9.0474(9) Å, $\alpha$ = 92.65(1), $\beta$ = 107.18(1), $\gamma$ = 95.60(1)°, $V$ = 570.4(1) Å$^3$, $Z$ = 1, $\mu$(Mo-Kα) = 1.280 mm$^{-1}$, $D_{calc}$ = 1.848 g cm$^{-3}$, 2691 unique reflections, $R1$ = 0.028, $wR2$ = 0.078.

For $[Cu(OH)(L)](H_2NSO_3) \cdot H_2O$ **4**: $C_6H_9CuN_5O_5S$, $M$ = 326.78, monoclinic, space group $P2_1/c$, $a$ = 6.7875(7), $b$ = 10.5615(9), $c$ = 14.212(1) Å, $\beta$ = 97.57(1)°, $V$ = 1009.9(2) Å$^3$, $Z$ = 4, $\mu$(Mo-Kα) = 2.395 mm$^{-1}$, $D_{calc}$ = 2.149 g cm$^{-3}$, 2365 unique reflections, $R1$ = 0.036, $wR2$ = 0.096.

For $[Ag(H_2O)(L)](CH_3SO_3) \cdot H_2O$ **5**: $C_7H_{11}AgN_4O_5S$, $M$ = 371.13, orthorhombic, space group $P2_12_12_1$, $a$ = 7.4389(5), $b$ = 10.572(1), $c$ = 14.777(1) Å, $V$ = 1162.2(2) Å$^3$, $Z$ = 4, $\mu$(Mo-Kα) = 1.934 mm$^{-1}$, $D_{calc}$ = 2.121 cm$^{-3}$, 2762 unique reflections, $R1$ = 0.020, $wR2$ = 0.042.

CCDC 619868–619871 and 622647. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612660j

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