

A Topology Paradigm for Metal-Organic Zeolites**

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Coordination polymers that afford controllable cavities and incorporate different guest molecules may provide structural prototypes for the design of porous host lattices for applications such as adsorption,^[1,2] ion exchange^[3] and heterogeneous catalysis.^[4] The elaboration of such materials is a considerable challenge, as only a few of the previously synthesized solids are stable to the loss of the initially accumulated guests and capable of taking up small organic molecules in the resulting molecular holes.^[1] New insights into the development of approaches for the engineering of metal-organic zeolites are possible on the basis of topological considerations.^[5] Attractive metal-organic-zeolite models of metal-organic frameworks may be predicted for novel “2D building blocks” of semiregular topology^[6] (Figure 1 b and c) that are expanded in a third direction by pillaring.^[7] In this case, initial plane tiling by a set of different polygons, instead of uniform square grids as in $[\text{Cu}(\text{bipy})_2\text{SiF}_6]$,^[2] generates closely packed molecular triangles (cf. molecular hexagons) with very open regions within the network. Thus, the free space appears to be concentrated, and the resulting framework of relatively low overall porosity, which is stable and robust, could maintain large cages for guest molecules. Realistic prototypes of such arrays are provided by the

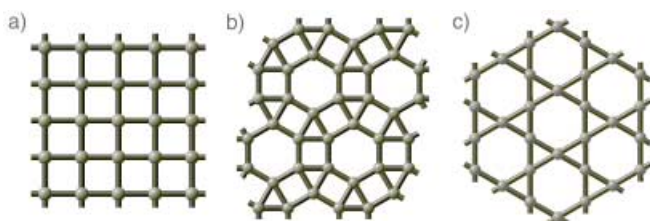


Figure 1. Four-connected plane nets of significance for chemical topology: a) regular 4^4 tiling, b),c) semiregular nets.

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structures of purely inorganic materials—tungsten bronzes.^[6b]

Herein, we report how the combination of the inherent functional features of organic and inorganic counterparts allows an especially effective implementation of this assembly scenario, and the generation of a target coordination network with unprecedented hexagonal tungsten bronze topology. Despite the fact that the angles at the net vertex (2×60 , $2 \times 120^\circ$) do not match the demands of a typical coordination environment around octahedrally coordinated transition-metal ions, the desired connectivity may be tuned by the conformational flexibility of the organic linker. First, the 3,3',5,5'-tetramethylsubstituted 4,4'-bipyrazolyl ligand (4,4'-bpz) acts as an angular linker.^[8] Its frame includes two planar pyrazolyl fragments, which have an angle of rotation around 60 – 80° and the resulting noncollinear orientation of two N–M vectors makes possible the assembly of the desired flat coordination net. Second, these coordination layers $[\text{M}(4,4'\text{-bpz})_2]_n$, formed by the octahedrally coordinated metal ions and two equivalents of the bridging 4,4'-bpz ligands, have a rich and versatile functionality for cross-linking into a 3D superstructure. Each four-coordinate point $\text{M}(\text{pyrazole})_4$ of the layer provides, in the two axial directions, six binding sites that include coordination positions at the metal atom, and four hydrogen bond donating NH groups of the coordinated pyrazole ligands. Thus, dense interconnection of the layers and generation of a rigid 3D network is feasible by the rational choice of an anionic counterpart to fit perfectly this set of binding sites.

The 3D structure of a new family of framework solids $[\text{M}(4,4'\text{-bpz})_2[\text{S}_2\text{O}_6]]_n$ **1** ($\text{M} = \text{Co}$ **1a**, Zn **1b**, Cd **1c**) is supported by cooperation of bridging functions of organic and inorganic linkers. The 2D $[\text{M}(4,4'\text{-bpz})_2]_n$ linkage exists as a triangular so-called Kagomé network^[9] (Figure 2) and dithionate anions are used as pillars. The present 2D metal-organic subunit is an isomer of “square grids” and represents a mode of plane tiling by a combination of molecular triangles and hexagons in 2:1 ratio, instead of a 4^4 regular tiling topology. The fragments $[\text{M}(4,4'\text{-bpz})_2]_6$ are distorted and adopt a roughly triangular shape that eliminates possible centers of inversion and the entire 3D structure is chiral. Dithionates are perfectly suited as pillars for the 1:4 metal-pyrazole coordination, as two oxygen atoms complete the octahedral environment of the metal atoms and the remaining four oxygen atoms form relatively strong $\text{NH}\cdots\text{O}$ hydrogen bonds with all available adjacent pyrazolyl groups (Scheme 1, Figure 3). This complementary set of donor/acceptor interactions, and effective shielding of the S_2O_6 linkers by eight methyl groups, presumably has an impact on the high thermal stability of the compounds, which remains unchanged in air up to 590 K.^[10] Noteworthy, simple inorganic dithionates themselves are much less stable and readily lose SO_2 upon heating.

Successive planes of $[\text{M}(4,4'\text{-bpz})_2]_n$ are stacked with an interlayer separation of approximately 7.97 Å, and the entire

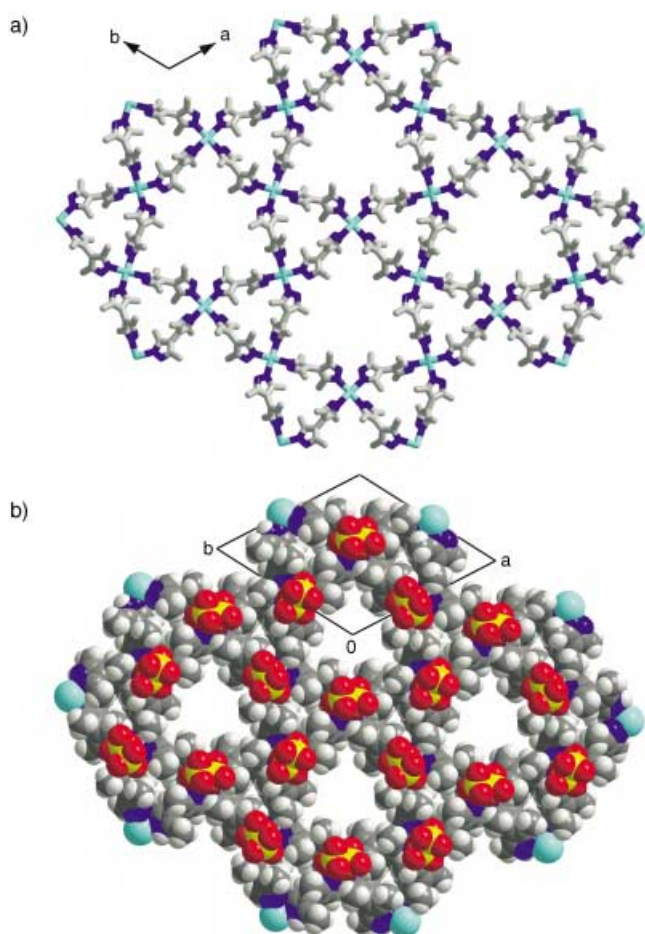
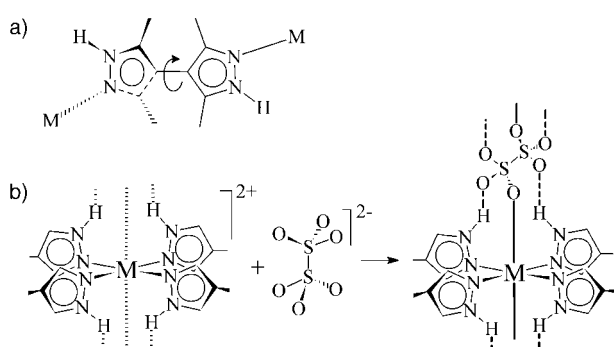


Figure 2. Structure of the 2D $[M(4,4'\text{-bpz})_2]_n$ ($M = \text{Co}, \text{Zn}, \text{Cd}$) network (a), and space-filling representation of the entire structure viewed down the c axis, which shows the cylindrical channels of about 8 Å size and how the bulky organic ligands shield the dithionate pillars (b).



Scheme 1. a) 3,3',5,5'-tetramethyl-4,4'-bipyrazolyl as an angular connector between two metal atoms; b) Illustration of how the functionality of the dithionate ion is complementary for 1:4 metal-pyrazole units.

structure has channels down the c axis. The total unpopulated area for **1a** is 737 Å³ per unit cell or about 29% of the crystal volume.^[11] The channels have inner dimensions of about 8 Å and are accessible for small guest molecules (Figure 2b). Indeed, the compounds are capable of the reversible adsorption of dichloromethane, as was found from vapor adsorption

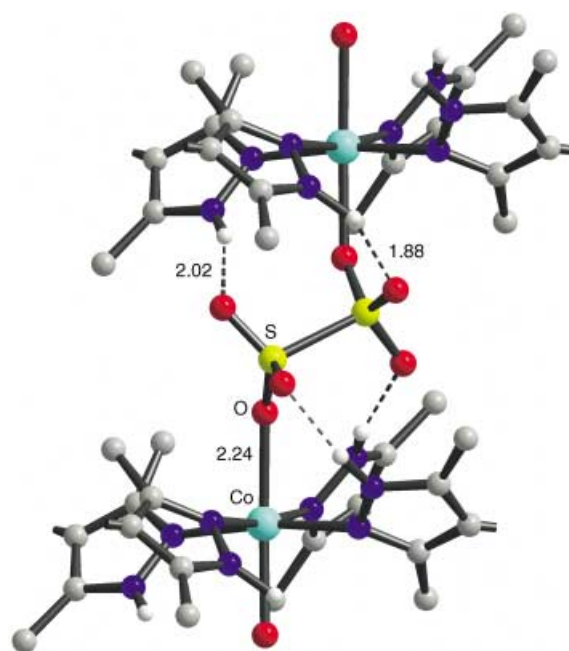


Figure 3. Function of dithionate group as a linker between metal-organic layers.

and by immersion calorimetry studies^[12] for **1a** ($M = \text{Co}$) and **1c** ($M = \text{Cd}$). The CH_2Cl_2 vapour adsorption isotherms showed reversible type I behavior and were analyzed in the framework of Dubinin's theory,^[13] which was developed for the filling of micropores in carbons and zeolites. A logarithmic plot of the Dubinin-Astakhov Equation (1):

$$N_a \text{ (mmol g}^{-1}\text{)} = N_{\text{ao}}^{-\text{(A/E)}^n}; \quad A \text{ (kJ mol}^{-1}\text{)} = RT \ln(ps/p) \quad (1)$$

leads to a single line for exponent $n = 4$. In the case of activated carbons and zeolites with relatively wide micropores, n is usually close to 2. A higher value, as in this case, corresponds to pores with higher adsorption energies.^[13] The overall fit leads to a characteristic energy $E = 10.3 \text{ kJ mol}^{-1}$, the limiting amount filling the micropores $N_{\text{ao}} = 2.53 \text{ mmol (215 mg) g}^{-1}$, and assuming a liquidlike state of the condensate, the apparent micropore volume W_0 is $0.16 \text{ cm}^3 \text{ g}^{-1}$ or $0.19 \text{ cm}^3 \text{ cm}^{-3}$. That is, comparable with the values obtained for zeolites; ranging from 0.18 for analcine to $0.47 \text{ cm}^3 \text{ cm}^{-3}$ for zeolite A. Immersion calorimetry experiments at 293 K suggest enthalpies $-\Delta_i H$ of -54 (**1a**) and -45 J g^{-1} (**1c**) versus the expected value of -33 J g^{-1} , calculated by using the adsorption data. This may be regarded as a satisfactory correlation and confirms a similar behavior of **1a** and **1c** towards CH_2Cl_2 .

In conclusion, our study introduces a novel 3D coordination architecture as an attractive prototype for the development of metal-organic zeolites. We believe that further expansion of the pillaring strategy into a family of semiregular plane nets could provide new structural types with alternating closely packed and very open regions. This approach would simplify the generation of robust solids with pores that are large enough for useful adsorption applications.

Experimental Section

Slow interdiffusion of the solutions of 0.086 g (0.26 mmol) $\text{CoS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ in 5 mL methanol and 0.100 g (0.52 mmol) 4,4'-bpz^[15] in 5 mL methanol and 5 mL chloroform afforded pink dithionate $[\text{Co}(4,4'\text{-bpz})_2(\text{S}_2\text{O}_6)] \cdot n\text{H}_2\text{O}$ ($n=2$) **1a**· $n\text{H}_2\text{O}$. Compound **1a** readily loses guest water in air within minutes, without collapse of the 3D structure to give $[\text{Co}(4,4'\text{-bpz})_2(\text{S}_2\text{O}_6)]$ **1a** (yield: 0.118 g, 75%). By using the same conditions zinc **1b** and cadmium **1c** complexes were crystallized as colorless blocks.

Crystallographic measurements were made at 153 K using a STOE Image Plate Diffraction System with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least-squares in the anisotropic approximation for all non hydrogen atoms by using SHELXS-86 and SHELXL-93.^[16] For **1a** the site of the guest water molecule was refined with partial occupancy, 0.5. All crystals were trigonal, space group $P321$ (No. 150), $Z=3$. Crystal data: **1a**, $\text{C}_{20}\text{H}_{28}\text{CoN}_8\text{O}_6\text{S}_2$, $M=599.55$, $a=b=19.329(1)$, $c=7.7651(4) \text{ \AA}$, $V=2512.5(3) \text{ \AA}^3$, $\rho_{\text{calcd}}=1.189 \text{ g cm}^{-3}$, $2\theta_{\text{max}}=52.0^\circ$, 2878 unique data, $R_1=0.036$, absolute structure parameter $x=-0.05(2)$; **1a**· H_2O , $\text{C}_{20}\text{H}_{30}\text{CoN}_8\text{O}_7\text{S}_2$, $M=617.57$, $a=b=19.311(3)$, $c=7.772(2) \text{ \AA}$, $V=2510.0(8) \text{ \AA}^3$, $\rho_{\text{calcd}}=1.226 \text{ g cm}^{-3}$, $2\theta_{\text{max}}=51.8^\circ$, 2624 unique data, $R_1=0.036$, $x=0.02(2)$. **1b**, $\text{C}_{20}\text{H}_{28}\text{N}_8\text{O}_6\text{S}_2\text{Zn}$, $M=603.98$, $a=b=19.298(4)$, $c=7.967(2) \text{ \AA}$, $V=2569.5(10) \text{ \AA}^3$, $\rho_{\text{calcd}}=1.171 \text{ g cm}^{-3}$, $2\theta_{\text{max}}=51.8^\circ$, 2025 unique data, $R_1=0.055$, $x=0.18(3)$. Cadmium complex **1c** is isomorphous: $a=b=19.877(1)$, $c=8.0067(6) \text{ \AA}$. CCDC 195428–195430 (**1a**, **1a**· H_2O , **1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The adsorption isotherms of CH_2Cl_2 were determined gravimetrically^[12] at 293, 308 and 318 K for **1a** and at 308 K for **1c**, in the range of relative pressures $10^{-4} < p/p_s^{-1} < 0.2$, following out-gassing at 383 K for 12–15 h (10^{-4} Torr). Immersion calorimetry experiments were carried out at 293 K on samples of 0.050–0.100 g by using a Tian-Calvet type calorimeter. The accuracy varies between 3 and 5%, depending on the absolute energy liberated in the process (usually 1 to 20 J) and on the amount of solid used. The enthalpy of immersion was calculated within the framework of Dubinin's theory.^[12,13]

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