# Modular construction of 3D coordination frameworks incorporating SiF$_6$$^{2-}$ links: Accessing a significance of [M(pyrazole)$_4${SiF$_6$}] synthon

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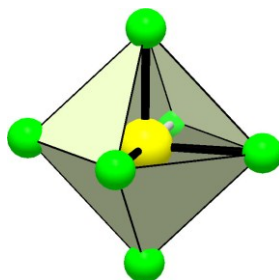
SUPPORTING INFORMATION

Refinement of [Cd(*Me₄bpz*)₂{NCS}₂]·⅔CH₂Cl₂ (1)

All non-hydrogen atoms corresponding to the metal-organic framework were refined anisotropically (Figure S1). CH (methyl) and NH hydrogen atoms were added geometrically, with $U_{iso} = 1.5U_{eq}$ of the parent C (N) atom.

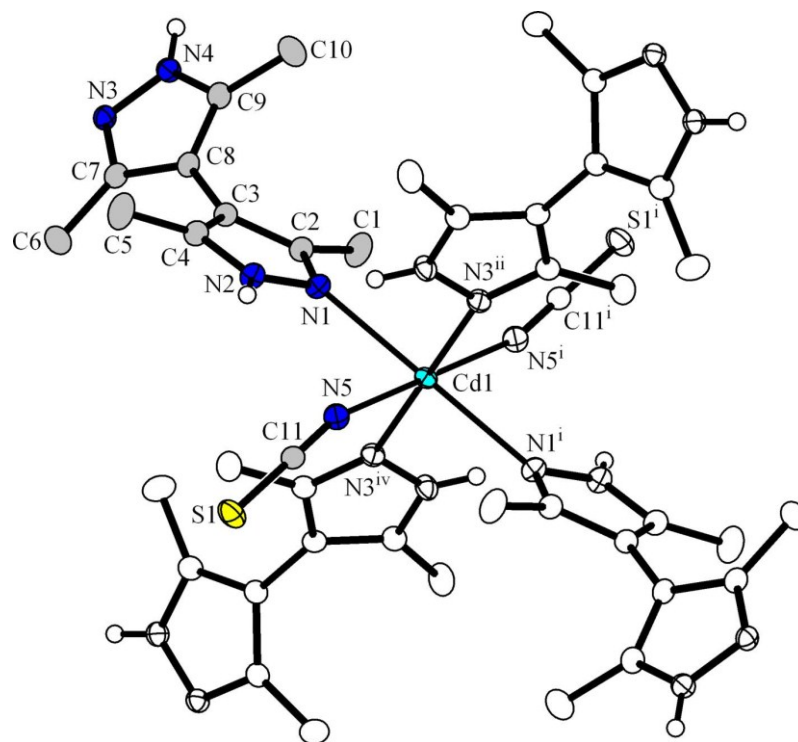**Figure S1.** Atom labeling scheme in structure **1** (40% probability ellipsoids) (Symmetry codes: (i) 1−*x*, -*y*, -*z*; (ii) ⅔-*x*+*y*, ⅓-*x*, -⅔+*z*; (iv) ⅓+*x*-*y*, -⅓+*x*, ⅔-*z*). Unique part of the structure is marked in color.

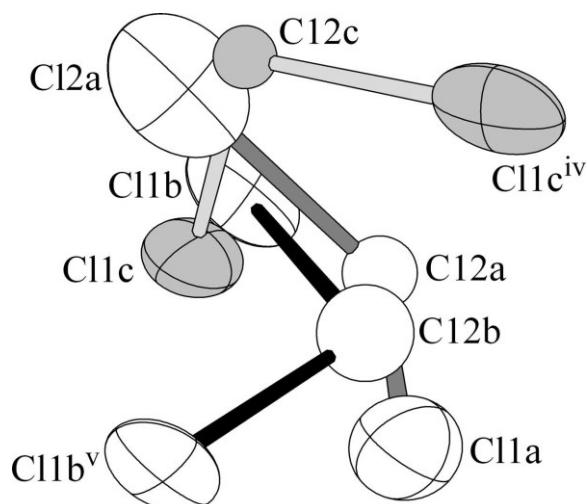**Figure S2.** Refined disordering models for the solvate dichloromethane molecules (25% probability thermal ellipsoids). Symmetry codes: (iv) 1-*y*, *x*-*y*, *z*; (v) 1-*x*+*y*, 1-*x*, *z*.

In the solvent region, a set of electron density peaks indicated disorder of CH_2Cl_2 guest across a three-fold axis. At the same time, the guest molecule adopts three orientations, for two of which the carbon atoms reside in special positions. Thus, the partial occupancy factor for the major component of the disorder (Cl1a-C12a-Cl2a) was 0.1667 (half of the occupancy defined by disorder across 3-axis) and the second part was provided by two half-molecules (Cl1b-C12b-Cl1b^v and Cl1c-C12c-Cl1c^{iv}, symmetry codes: (iv) 1-y, x-y, z; (v) 1-x+y, 1-x, z) (Figure S2). In each the case, the geometry of the disorder components was restrained: C-Cl = 1.760±0.008 Å and Cl···Cl = 2.883±0.008 Å. Only heavy chlorine atoms were refined anisotropically for the sake of overall convergence, while carbon atoms were left isotropic and the H atoms were not added to this disordered portion.

Refinement of [Cd$_2$(*Me$_4$bpz*)$_4${SiF$_6$}{NCS}$_2$]·6CHCl$_3$ (2)

Si1 atom of the hexafluorosilicate resides on a center of inversion. The refinement for the framework portion was essentially standard. CH (methyl) and NH hydrogen atoms were added geometrically, with U_{iso} = 1.5U_{eq} of the parent C (N) atom. There are three independed solvate chloroform molecules, one of which was refined freely and anisotropically [C22-Cl = 1.709(12)-1.729(10) Å]. Two other solvent molecules are disordered over two closely separated positions. The molecule referenced by carbon atom C23 adopts two orientations (partial contribution factors 0.5) with the common atom Cl4. Therefore, the occupancy factors were 0.5 for C23, Cl5, C6, C23A, Cl5A, C6A and 1.0 for Cl4. It was possible to refine this molecule anisotropically and without restraints in geometry [C-Cl = 1.63(2)-1.76(3) Å]. At the same time, the molecule referenced by C24 is unequally disordered over two positions with partial contributions 0.65 (C24) and 0.35 (0.35). It was left isotropic [U_{iso} (Cl) = 0.14-0.27 Å^2], two contributions of the disordered carbon atom were assigned with an equal isotropic thermal parameter (EADP) and the restraints for the C-Cl bond lengths [1.73(1) Å] were applied in order to improve the stability of the refinement. In each case, the partial contributions were rifened with PART –n and the hydrogen atoms added with corresponding partial occupancies.
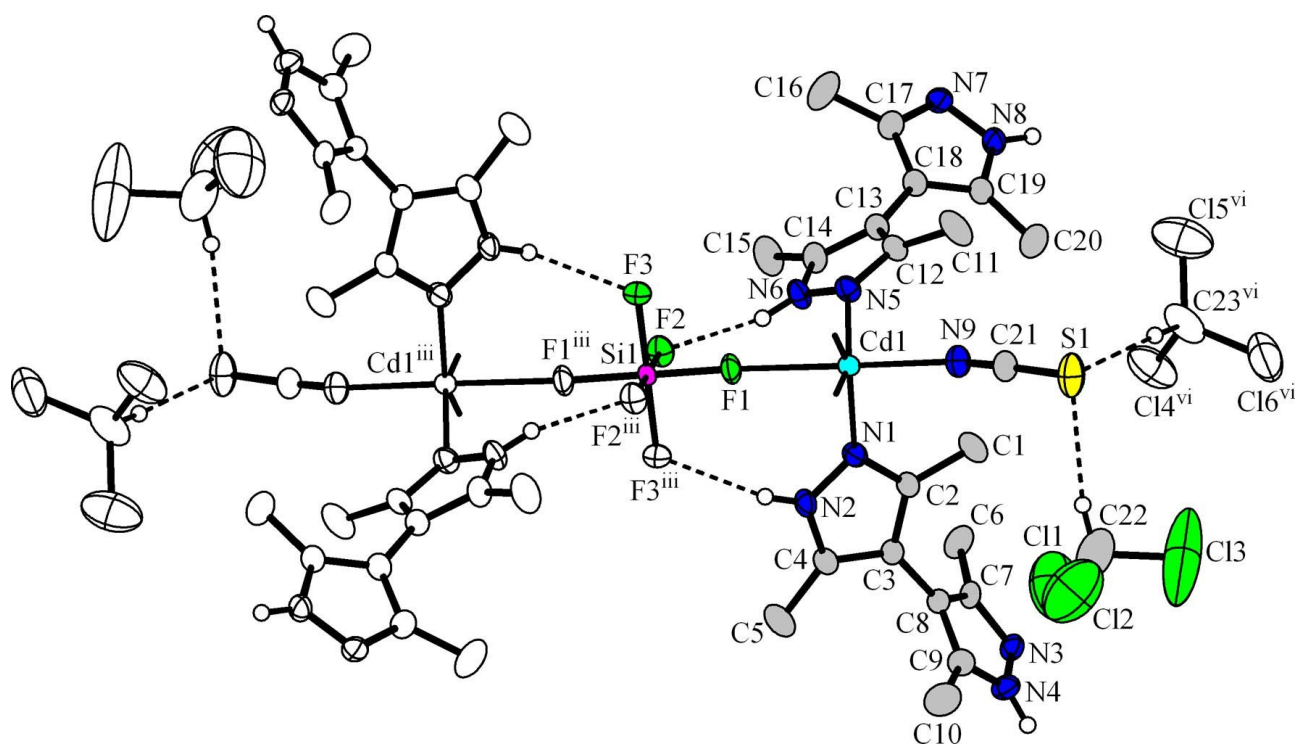
Figure S3. Atom labeling scheme in structure **2** (40% probability ellipsoids) (Symmetry codes: (iii) –*x*, -*y*, 1-*z*; (vi) -0.5+*x*, *y*, 0.5-*z*) showing "half" of the $[Cd_2(\mu\text{-}SiF_6)(Me_4bpz)_4(NCS)_2]$ cage. Note the positioning of the solvate chloroform molecules forming weak CH···S hydrogen bonds with N-coordinated thiocyanates (for details, see Table S1). Unique part of the structure is marked in color.
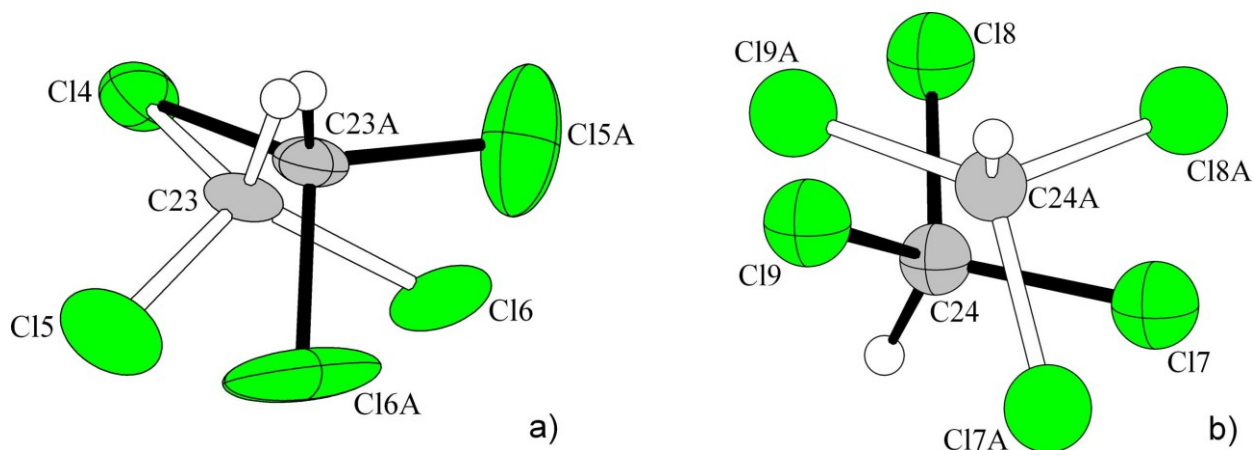

Figure S4. Refined disordering models for the solvate chloroform molecules referenced by carbon atoms (a) C23 (30% probability thermal ellipsoids) and (b) C24 (isotropic refinement). C23···C23A = 0.65 Å; C24···C24A = 1.00 Å.

Table S1.

Geometry of $Cl_3CH\cdots S$ hydrogen bonding in structure **2**

Donor (D)	H-atom	Acceptor (A)	D-H/ Å	H$\cdots$A/ Å	D$\cdots$A/ Å	$\angle$DH$\cdots$A/ °
C22	H22	S1	0.99	2.68	3.642(11)	165
C23	H23	S1 (0.5+x, y, 0.5-z)	0.99	2.57	3.55(2)	174
C23A	H23A	S1 (0.5+x, y, 0.5-z)	0.99	2.52	3.44(2)	155

Refinement of $[Cd_2(Me_4bpz)_4\{SiF_6\}\{NCS\}_2]\cdot 2CH_2Cl_2$ (3)

Crystals of the compound are twinned by merohedry (low symmetry tetragonal (4/m) cell emulates high symmetry tetragonal lattice (4/mmm). Solution in space group P4$_2$/mbc led to badly disordered model and the subsequent refinement eventually led to divergence ($R1 > 0.20$). Well refinable model was found in space group $P4_2/m$, with equal contributions of twin components (twin law {0 1 0 1 0 0 0 0 -1}).

The refinement for the framework portion was essentially standard. CH (methyl) and NH hydrogen atoms were added geometrically, with $U_{iso} = 1.5U_{eq}$ of the parent C (N) atom.

Three unique solvent molecules (one molecule in general position and two half-molecules lying across mirror planes) were located. Their atoms possess large parameters for the thermal motion, indicating possible disorder. We were not successful to resolve it. These molecules were included in calculations with fixed geometry [C-Cl = 1.750±0.008 and Cl$\cdots$Cl = 2.880±0.008 Å]; they were left isotropic. It was impossible to locate additional solvent molecules, although *checkcif* routine indicates remaining solvent accessible voids in the structure.

Refinement of $[Cd(Me_4bpz)_2\{SiF_6\}]\cdot 6H_2O$ (4)

The crystals were twinned. They emulate orthorhombic-C lattice by pseudomerohedry (a common case of monoclinic cell with β≈90°), giving $R_{int} = 0.049$ and $|E\cdot E^{-1}| = 0.678$. Solution in the orthorhombic-C space groups (for example, *Cmcm*) was possible leading to the poorly refinable models (R1 ≥ 0.15), which involve disorder of either SiF$_6{}^{2-}$ or *Me$_4$bpz* moieties, and systematically $F_o{}^2 \gg F_c{}^2$. Therefore, the data frames were integrated for the monoclinic cell (β = 90.047(8)°) and the structure successfully solved and refined as twin in monoclinic space group

$C2/c$. The twin law was {-1 0 0 0 -1 0 0 0 1} and the refined parameter BASF = 0.49734 was indicative for the equal contributions from the twin domains.

Atoms of the framework were freely refined anisotropically and CH (methyl) and NH hydrogen atoms were added geometrically, with $U_{iso} = 1.5U_{eq}$ of the parent C (N) atoms. The solvate water molecules are disordred over two positions (separated at 1.0-1.5 Å). In this way, two indepeded molecules are equally disordered by symmetry (O3 and O4) and were refined with partial contribution factors of 0.5. Two other molecules were unequally disordered and in both cases the partial occupancies of 0.65 and 0.35 were suggested by the refinement of thermal parameters (U_{iso} = 0.14-0.17 Å^2). All disordered water molecules were refined isotropically and the OH hydrogen atoms were not added.

Refinement of [Cd(Me_4bpz)$_2${SiF$_6$}]·1.5CH$_2$Cl$_2$ (5)

Note: The non-standard monoclinic-*I* setting was selected accordingly to the latest IUCr recommendations (See A.D. Mighel, Acta Cryst. (2003). B59, 300-302).

Atoms of the framework were freely refined anisotropically and CH (methyl) and NH hydrogen atoms were added geometrically, with $U_{iso} = 1.5U_{eq}$ of the parent C (N) atoms. Molecule of the solvent is equally disordered across a center of inversion (Figure S5), however, a significant residual electron density in this region was indicative for contribution from a second minor orientation of this molecule. Therefore, the partial occupancies for the major component of the disorder were 0.5 (related by inversion) and 0.25 for C11A, Cl1A, Cl2A (these atoms were left isotropic). The major component was refined anisotropically. A set of geometry restraints was applied to the disordered portion: C-Cl distances were restrained at 1.74(1) Å and intramolecular contacts Cl···Cl at 2.88(1) Å.
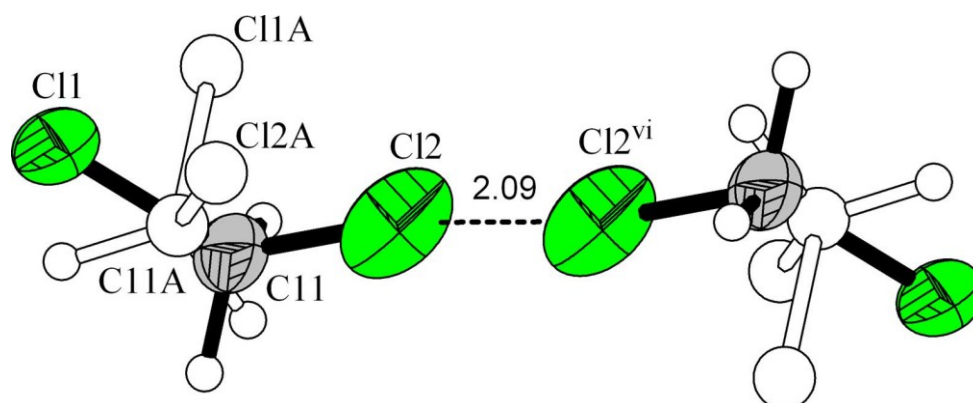

Figure S5. Refined disordering models for the solvate dichloromethane molecules in structure 5 (30% probability thermal ellipsoids). Symmetry code: (vi) 1-*x*, 2-*y*, -*z*.
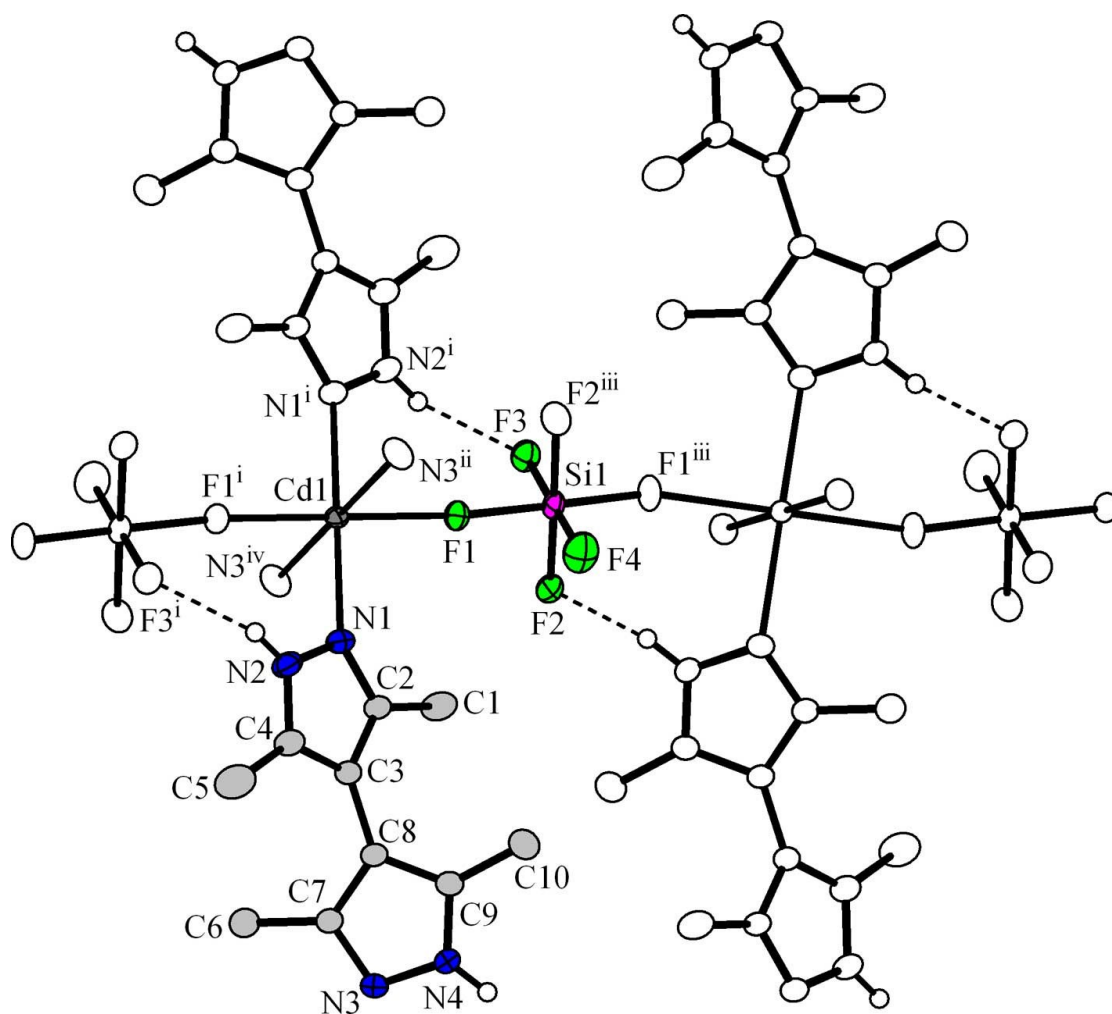
Figure S6. Atom labeling scheme in structure **5** (Symmetry codes: (i) –*x*, 1-*y*, -*z*; (ii) *x*, 1.5-*y*, -0.5+*z*; (iii) 0.5-*x*, *y*, -*z*; (iv) –*x*, -0.5+*y*, 0.5-*z*). Unique part of the structure is marked in color and the probability ellipsoids are drawn at 50% level.