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## Modular construction of 3D coordination frameworks incorporating $\text{SiF}_6^{2-}$ links: Accessing the significance of $[\text{M(pyrazole)}_4\{\text{SiF}_6\}]$ synthon<sup>†</sup>

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Rational combination of  $\text{Cd}^{2+}$  cations, bitopic pyrazole ligands, bridging  $\text{SiF}_6^{2-}$  and terminal  $\text{NCS}^-$  anions provide generation of 3D frameworks and precise control over connectedness of the net nodes: two-fold interpenetrated 4-connected  $\text{NbO}$ -like net (**nbo**) in  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2] \cdot \frac{2}{3}\text{CH}_2\text{Cl}_2$  (**1**), uninodal 5-connected **noz** framework in  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2] \cdot 6\text{CHCl}_3$  (**2**), novel 5-connected binodal topology (with a point symbol of  $\{4^2 \cdot 5 \cdot 6^2 \cdot 7\}$   $\{4^2 \cdot 5^6 \cdot 6^2\}$ ) in  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2] \cdot 2\text{CH}_2\text{Cl}_2$  (**3**) and 6-connected  $\alpha$ -Po cubic nets (**pcu**) in  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}] \cdot 6\text{H}_2\text{O}$  (**4**) and  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}] \cdot 1.5\text{CH}_2\text{Cl}_2$  (**5**) ( $\text{Me}_4\text{bpz} = 3,3',5,5'-\text{tetramethyl-4,4'-bipyrazole}$ ). Hexafluorosilicate anions act as bridges between Cd ions yielding further linkage of 4-connected  $[\text{Cd}(\text{Me}_4\text{bpz})_2]$  subtopologies. Characteristic and specific interaction between  $\text{SiF}_6^{2-}$  and the metal-organic portion is conditioned by a synergy of coordination and multiple strong  $\text{NH}\cdots\text{F}$  bonds, which suggests perfect compatibility of the bipyrazole and  $\text{SiF}_6^{2-}$  linkers for the construction of 3D structures, either by pillaring of 2D layers or cross-linking of 3D frameworks. Two observed motifs, 1D  $[\text{M(pyrazole)}_4\{\mu\text{-SiF}_6\}]_n$  (in **4** and **5**) and discrete  $\{[\text{M(NCS)}(\text{pyrazole})_4]\}_2\{\mu\text{-SiF}_6\}$  (in **2** and **3**) are discussed as special supramolecular synthons for the framework solids. An improved large-scale and cost-effective procedure for the synthesis of the organic ligand  $\text{Me}_4\text{bpz}$  is also described.

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## Introduction

Hexafluorosilicate offers a number of special possibilities for supramolecular synthesis of framework solids. Unlike charge-diffuse monoanions,  $\text{SiF}_6^{2-}$  displays significant nucleophilicity and pronounced ability for hydrogen bonding, often being a crucial factor for hybrid organic-inorganic crystal lattices.<sup>1–6</sup> Its inherent symmetry and functionality perfectly complements demands imposed by octahedral metal ions coordinating a set of four equatorial ligands, *cf.*  $\text{M}(\text{Py})_4^{2+}$ , and therefore such the combination is especially beneficial for the construction of 3D structures by cross-linking coordination layers formed by metal ions and common N-donor bridging ligands, *cf.*  $\{\text{M(bipy)}_2^{2+}\}_n$ . In particular, the framework structures of  $[\text{M(bipy)}_2\{\text{SiF}_6\}]$  ( $\text{M} = \text{Zn}, \text{Cu}$ ) were of paramount significance for developing common approaches of supramolecular chemistry and crystal engineering,<sup>3</sup> while receiving new rapidly

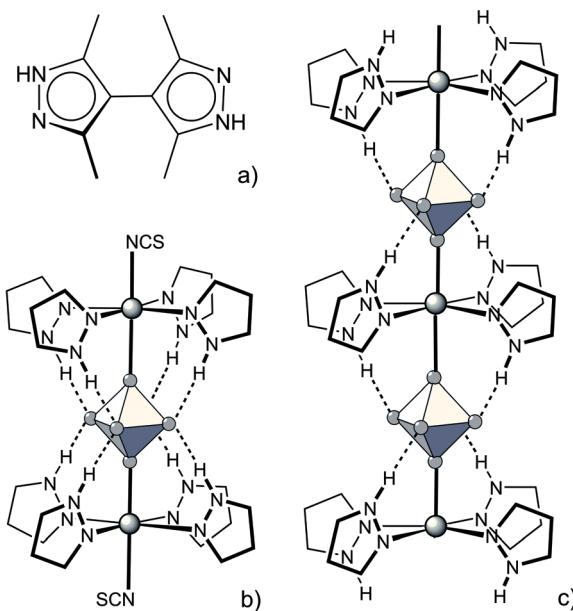
growing interest as prototypical host lattices for selective sorption of carbon dioxide.<sup>4</sup> A series of hexafluorosilicate frameworks prepared utilizing either smaller (pyrazine)<sup>5</sup> or extended (incorporating ethylene-, acetylene-, phenylene-, naphthylene-diyl and other spacers)<sup>4,6</sup> analogs of bipyridine reveals effective tuning of the micropore size, while preserving the characteristic motif in the form of  $\{\text{SiF}_6^{2-}\}$ -pillared square grid networks. The highly probable assembly of such characteristic  $[\text{M(Py)}_4\{\text{SiF}_6\}]$  entities, which could be viewed as supramolecular synthons, is defined by concerted interaction of the components, *via* coordination bonding and a set of weak  $\text{CH}\cdots\text{F}$  hydrogen bonds. Recently, a special significance of  $\text{SiF}_6^{2-}$  building blocks was seen for selective sorption stimulated studies for the closely related  $\text{GeF}_6^{2-}$ ,  $\text{SnF}_6^{2-}$  and  $\text{TiF}_6^{2-}$  compounds.<sup>7</sup>

An even more energetically favorable structure of the synthon could be feasible while exploiting synergy of coordination bonds and conventional strong  $\text{NH}\cdots\text{F}$  interactions. In this view, a valuable combination of the donor and acceptor functionalities, which is perfectly suited for accommodation of  $\text{SiF}_6^{2-}$ , could be recognized in the structure of  $[\text{M(pyrazole)}_4]^{2+}$  scaffolds.<sup>8</sup> The latter combines axial coordination positions at the metal ion and a set of four sterically accessible NH-donors, predetermining a very efficient multi-center

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**Scheme 1** (a) Bitopic conformationally flexible Me<sub>4</sub>bpz linker examined in the present study; (b) Discrete and (c) 1D polymeric motifs supported by SiF<sub>6</sub><sup>2-</sup> (represented as octahedra) and metal-pyrazole portion. Note the concerted action of coordination and hydrogen bonding and how the interconversion of the motifs may be controlled by the terminal NCS<sup>-</sup>.

interaction with the shape- and charge-complementary SiF<sub>6</sub><sup>2-</sup> substrate. Therefore, exploitation of SiF<sub>6</sub><sup>2-</sup> (and the related octahedral hexafluoroanions) as pillaring blocks for the construction of functional 3D frameworks could be most efficient when combined with pyrazole ligands. In the present work we illustrate the utility of such an approach with the prototypical bitopic ligand 3,3',5,5'-tetramethyl-4,4'-bipyrazole (Me<sub>4</sub>bpz) (Scheme 1). This structurally simple and chemically accessible organic linker has found wide and versatile applications for construction of coordination frameworks,<sup>9,10</sup> including covalent pyrazolate frameworks,<sup>11</sup> and hydrogen-bonded structures.<sup>12</sup> Conformational flexibility of the tecton predetermines structural diversity and rich supramolecular isomerism of the M<sup>2+</sup>-Me<sub>4</sub>bpz coordination systems, which is a particularly important factor for the adaptability of the tecton towards metric and functional demands coming from the inorganic component of the structure.

## Experimental section

### Synthesis

3,3',5,5'-Tetramethyl-4,4'-bipyrazole (Me<sub>4</sub>bpz) was prepared in yields up to 95% by reaction of 3,4-diacetyl-2,5-hexanedione (tetraacetylene) with hydrazine hydrate in methanol<sup>9d</sup> or water and recrystallization of the product from aqueous methanol yields semihydrate Me<sub>4</sub>bpz·0.5H<sub>2</sub>O as large colorless prisms.<sup>12a</sup> Preparation of tetraacetylene by coupling of sodium acetylacetone, Na(Acac), in ether suspension (41–59%) is described in *Organic Syntheses*.<sup>13</sup> This method, however, was insufficient for the large-scale syntheses leading

to poor yields of the product. Considering possible industrial applications of bipyrazolate frameworks as gas adsorbents,<sup>11</sup> we have elaborated an improved procedure for coupling of 1,3-diketones in DMF solution. The present method provides constant and reproducible yields (78–84%, for the 0.5–500 g batch scales of Na(Acac)·2H<sub>2</sub>O) and very simple isolation of the product.

### Preparation of 3,4-diacetyl-2,5-hexanedione

Solution of 47.0 g (0.185 mol) iodine in 200 mL DMF was added dropwise for 1 h at 5–10 °C to an intensively stirred solution of 60.0 g (0.38 mol) of Na(Acac)·2H<sub>2</sub>O<sup>13</sup> in 300 mL DMF. One or two additional 50 mL portions of DMF were added towards the end of the reaction in the case of necessity, to decrease the viscosity of the NaI·2DMF slurry. The resulting brown reaction solution was poured into 2 L of ice water and the mixture was stirred for 15 min. The precipitate was filtered, washed with water and recrystallized from 2-propanol (3.7 g per 100 mL) yielding pure colorless tetraketone (28.4 g, 78%). M.p. 193 °C. When the anhydrous Na(Acac) was used as a starting material, the yield was 60%.

### Preparation of coordination compounds

[Cd<sub>2</sub>(Me<sub>4</sub>bpz)<sub>4</sub>{SiF<sub>6</sub>}·{NCS}<sub>2</sub>]·nSolv (2: Solv = CHCl<sub>3</sub>, n = 6; 3: Solv = CH<sub>2</sub>Cl<sub>2</sub>, n = 2). A solution of 23.5 mg (0.065 mmol) of CdSiF<sub>6</sub>·6H<sub>2</sub>O and 14.8 mg (0.065 mmol) of Cd(NCS)<sub>2</sub> in 3 mL of methanol was layered over a solution of 49.8 mg (0.25 mmol) of Me<sub>4</sub>bpz·0.5H<sub>2</sub>O in 1 mL of methanol and 4 mL of dichloromethane. The CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> mixture (1:1 v/v, 6 mL) was introduced as an intermediate layer. Slow interdiffusion of the solutions for a period of 20 d yields 45 mg (55%) of colorless crystalline product 3. Complex 2 was prepared similarly (yield 70%) using methanol and chloroform solutions. The compounds are unstable in air and readily lose the solvent of crystallization within minutes.

[Cd(Me<sub>4</sub>bpz)<sub>2</sub>{SiF<sub>6</sub>}]<sub>2</sub>·6H<sub>2</sub>O (4). A mixture of 25.3 mg (0.070 mmol) of CdSiF<sub>6</sub>·6H<sub>2</sub>O, 27.9 mg (0.140 mmol) of Me<sub>4</sub>bpz·0.5H<sub>2</sub>O, and 4 mL of water was stirred for 30 min in a Teflon vessel and then it was heated at 140 °C for 70 h. Slow cooling to r.t. over period of 48 h (cooling rate 2.5 °C h<sup>-1</sup>) affords pure product as colorless prisms (yield: 31.2 mg, 60%). Anal. for 4 C<sub>20</sub>H<sub>40</sub>CdF<sub>6</sub>N<sub>8</sub>O<sub>6</sub>Si. Calc. (%): C, 32.32; H, 5.43; N, 15.08. Found: C, 32.47; H, 5.38; N, 15.21%. According to the TGA data, loss of water molecules occurs in the temperature range 180–270 °C (14.3%, calc. 14.53%) followed by further decomposition above 280 °C.

[Cd(Me<sub>4</sub>bpz)<sub>2</sub>{SiF<sub>6</sub>}]<sub>2</sub>·1.5CH<sub>2</sub>Cl<sub>2</sub> (5). A solution of 27.2 mg (0.075 mmol) of CdSiF<sub>6</sub>·6H<sub>2</sub>O in 3 mL of methanol was layered over a solution of 29.9 mg (0.150 mmol) of Me<sub>4</sub>bpz·0.5H<sub>2</sub>O in 5 mL of 1:2 v/v CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> mixture, with the intermediate layer constituted by 5 mL of 2:1 v/v CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> mixture. Small colorless prisms of the product grew on the walls of the tube as the solutions

**Table 1** Crystal data for  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_3^2\text{CH}_2\text{Cl}_2$  (**1**),  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot6\text{CHCl}_3$  (**2**),  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot2\text{CH}_2\text{Cl}_2$  (**3**)  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}] \cdot 6\text{H}_2\text{O}$  (**4**) and  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}] \cdot 1.5\text{CH}_2\text{Cl}_2$  (**5**)

| Formula   | <b>1</b>  | <b>2</b>  | <b>3</b>   | <b>4</b>  | <b>5</b>  |
|---|---|---|--|---|---|
| <i>M</i>  | $\text{C}_{22}\text{H}_{28}\text{CdN}_{10}\text{S}_2 \cdot \frac{2}{3}\text{CH}_2\text{Cl}_2$ | $\text{C}_{48}\text{H}_{62}\text{Cd}_2\text{Cl}_{18}\text{F}_6\text{N}_{18}\text{S}_2\text{Si}$ | $\text{C}_{44}\text{H}_{60}\text{Cd}_2\text{Cl}_4\text{F}_6\text{N}_{18}\text{S}_2\text{Si}$ | $\text{C}_{20}\text{H}_{40}\text{CdF}_6\text{N}_8\text{O}_6\text{Si}$ | $\text{C}_{20}\text{H}_{28}\text{CdF}_6\text{N}_8\text{Si} \cdot 1.5\text{CH}_2\text{Cl}_2$ |
| Crystal system                                      | Trigonal  | Orthorhombic  | Tetragonal   | Monoclinic  | Monoclinic  |
| Space group   | <i>R</i> $\bar{3}$  | <i>Pbca</i>   | <i>P4<sub>2</sub>/m</i>  | <i>C2/c</i>   | <i>I2/a</i>   |
| <i>Z</i>  | 9   | 4   | 8  | 4   | 4   |
| <i>a</i> / $\text{\AA}$                             | 25.791(2)   | 14.4685(12)   | 19.5220(8)   | 13.6869(10)   | 15.8930(12)   |
| <i>b</i> / $\text{\AA}$                             | 25.791(2)   | 22.858(3)   | 19.5220(8)   | 15.5383(9)  | 11.8892(11)   |
| <i>c</i> / $\text{\AA}$                             | 11.1284(13)   | 23.048(3)   | 33.791(3)  | 15.8770(12)   | 16.7929(12)   |
| $\beta$ /°  |   |   |  | 90.047(8)   | 91.161(3)   |
| <i>U</i> / $\text{\AA}^3$                           | 6410.5(11)  | 7622.5(15)  | 12878.0(16)  | 3376.6(4)   | 3172.5(4)   |
| $\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$             | 1.070   | 1.322   | 0.972  | 0.759   | 1.041   |
| <i>D</i> <sub>calc</sub> /g $\text{cm}^{-3}$        | 1.552   | 1.708   | 1.459  | 1.462   | 1.596   |
| $2\theta_{\max}$ /°                                 | 55.7  | 54.2  | 49.8   | 53.5  | 55.7  |
| Measd/Unique reflns                                 | 13066/3332  | 42980/8386  | 38193/11058  | 12133/3490  | 9366/3741   |
| <i>R</i> <sub>int</sub>                             | 0.027   | 0.031   | 0.048  | 0.047   | 0.012   |
| Parameters refined                                  | 213   | 460   | 705  | 194   | 209   |
| <i>R</i> 1, <i>wR</i> 2 ( <i>I</i> > $2\sigma(I)$ ) | 0.035, 0.079  | 0.058, 0.156  | 0.056, 0.149   | 0.031, 0.079  | 0.029, 0.073  |
| <i>R</i> 1, <i>wR</i> 2 (all data)                  | 0.040, 0.081  | 0.069, 0.162  | 0.065, 0.154   | 0.034, 0.080  | 0.031, 0.074  |
| Goof on <i>F</i> <sup>2</sup>                       | 1.136   | 1.046   | 0.994  | 1.019   | 1.098   |
| Max, min peak/e $\text{\AA}^{-3}$                   | 0.58, -1.87   | 1.13, -1.20   | 1.54, -0.67  | 0.70, -0.59   | 1.08, -0.78   |

interdiffused for the period of 15–20 d. Complex  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_3^2\text{CH}_2\text{Cl}_2$  (**1**) was prepared in a similar fashion, starting with  $\text{Cd}(\text{NCS})_2$  (yield: 55%).

### X-ray crystallography

Crystallographic measurements were made at 213 K using a Siemens SMART CCD diffractometer and a Stoe Imaging Plate Diffraction System (for **4**) with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{\AA}$ ) (Table 1). The structures were refined by full-matrix least-squares in the anisotropic approximation using SHELX-97.<sup>14</sup> CH and NH hydrogen atoms were added geometrically. In **2**, two of three unique  $\text{CHCl}_3$  molecules were disordered over two positions. One of them was refined anisotropically with equal contributions of the disorder components, while the second one (contributions 0.65 and 0.35) was left isotropic. The hydrogen atoms were not added to the disordered molecules. Refinement of the disorder in the region of guest molecules was relevant for all structures **1**–**5**.

Crystals of **3** and **4** were twinned. In the first case, low symmetry tetragonal (*4/m*) cell emulates high symmetry tetragonal lattice (*4/mmm*) by merohedry. Solution in space group *P4<sub>2</sub>/mbc* led to a badly disordered model and the subsequent refinement eventually led to divergence ( $R1 > 0.20$ ). A well refinable model was found in space group *P4<sub>2</sub>/m*, with equal contributions of twin components. For monoclinic crystals of **4**, pseudomerohedral twinning ( $\beta \approx 90^\circ$ ) results in emulation of orthorhombic cell. The twinning was indicated by almost total disorder for the tested orthorhombic models, systematically  $F_o^2 \gg F_c^2$  and suspiciously low  $|E^2 - 1|$  at  $\sim 0.67$ . Solution was found in monoclinic space group *C2/c* and the structure was refined with equal contributions of the twin components.

Graphical visualization of the structures was made using the program Diamond 2.1e,<sup>15</sup> and the topological analysis was performed using TOPOS 4.0.<sup>16</sup>

### Results and discussion

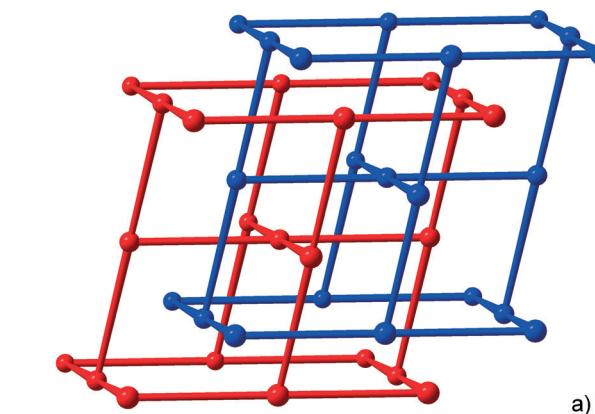
Unlike the symmetrical pyridine-N donors providing identity of two axial sides at the  $\text{MN}_4$  plane, two kinds of special supramolecular synthons may be anticipated for pyrazole systems, depending on configuration of the NH-sites (Scheme 1): catamer  $[\text{M}(\text{pzH})_4\{\text{SiF}_6\}]_n$  (which is equivalent to  $[\text{M}(\text{Py})_4\{\text{SiF}_6\}]_n$  catamers,  $\text{M/SiF}_6 = 1:1$ ) and a peculiar discrete cage-like pattern  $[\{\text{M}(\text{pzH})_4\}_2\{\text{SiF}_6\}]$  with  $\text{M/SiF}_6 = 2:1$  ratio and two additional terminal anionic groups ensuring charge compensation. Such partial fragmentation of the catamer decreases the connectedness of the framework, still retaining  $\text{SiF}_6^{2-}$  links, down to five. This suggests different possibilities for the stepwise cross-linking of the coordination layers (or 3D nets) supported by bifunctional pyrazole  $\text{Me}_4\text{bpz}$ , with facile interconversion of four-, five- and six-connected frameworks, influenced by the actual  $\text{M/SiF}_6$  ratios:  $[\text{M}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2] \rightarrow [\{\text{M}(\text{Me}_4\text{bpz})_2\}_2\{\mu\text{-SiF}_6\}\{\text{NCS}\}_2] \rightarrow [\text{M}(\text{Me}_4\text{bpz})_2\{\mu\text{-SiF}_6\}]$ , as will be demonstrated with the example of compounds **1**–**5** (Table 2).

The first representative of the series, the framework of lower connectivity of four is supported by  $\text{Me}_4\text{bpz}$  links only. It occurs in  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_3^2\text{CH}_2\text{Cl}_2$  (**1**), which possesses a 3D NbO-like structure and is isotypical with  $[\text{Fe}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_3^2\text{CH}_3\text{CN}$ , reported by Ganesan and Kepert.<sup>9c</sup> Two identical nets (related by a single translation vector) are interpenetrated (class Ia interpenetration,  $Z = 2$ ),<sup>17</sup> with the double-helical strand generated by a specific NH···S (N···S = 3.41; 3.58  $\text{\AA}$ ) hydrogen bonding between two present frameworks (Fig. 1).

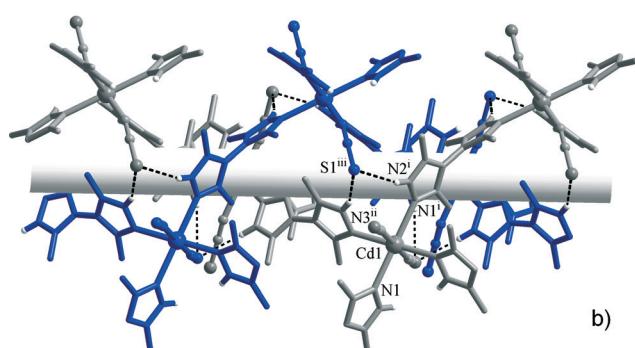
Additional topological link for the framework in  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot6\text{CHCl}_3$  (**2**) and  $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot2\text{CH}_2\text{Cl}_2$  (**3**) arises under partial elimination of terminal NCS<sup>-</sup> groups and their substitution for  $\text{SiF}_6^{2-}$  groups linking pairs of the adjacent Cd ions. The control over the

**Table 2** Main features of coordination geometries in **1–5** ( $\text{\AA}$ ,  $^\circ$ )

|                                 | <b>1</b>           | <b>2</b>              | <b>3</b>              | <b>4</b>            | <b>5</b>               |
|---------------------------------|--------------------|-----------------------|-----------------------|---------------------|------------------------|
| Cd–N(pz)                        | 2.386(2), 2.500(2) | 2.333(4)–2.376(4)     | 2.294(6)–2.422(6)     | 2.288(3), 2.336(3)  | 2.3183(18), 2.3204(18) |
| Cd–N(NCS)                       | 2.257(2)           | 2.223(4)              | 2.178(8)–2.234(7)     | —                   | —                      |
| Cd–F                            | —                  | 2.395(2)              | 2.420(4)–2.489(3)     | 2.340(2)            | 2.3156(12)             |
| N(pz)–Cd–N(pz) ( <i>cis</i> )   | 82.28(7), 97.72(7) | 87.24(13)–90.09(13)   | 81.5(2)–102.9(3)      | 82.68(15)–94.83(16) | 84.31(7), 95.69(7)     |
| N(pz)–Cd–N(pz) ( <i>trans</i> ) | 180                | 161.34(13)–163.60(13) | 153.15(18)–155.77(19) | 173.82(10)          | 180                    |
| N(pz)–Cd–N(NCS)                 | 82.42(7)–97.58(7)  | 98.05(15)–99.95(15)   | 97.6(2)–106.9(3)      | —                   | —                      |
| N(pz)–Cd–F                      | —                  | 80.15(11)–82.67(11)   | 76.52(17)–80.70(15)   | 84.67(9)–94.59(9)   | 79.41(6)–100.59(6)     |
| N(NCS)–Cd–F                     | —                  | 179.27(14)            | 171.5(3)–176.4(3)     | —                   | —                      |
| F–Cd–F                          | —                  | —                     | —                     | 177.84(10)          | 180                    |



a)

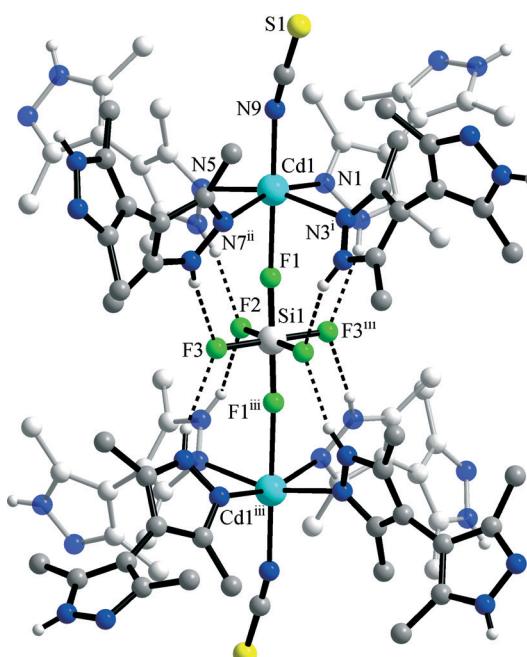
**Fig. 1** (a) Two-fold interpenetration of NbO-type frameworks in **1**; (b) Double-helical strand supported by  $\text{NH}\cdots\text{S}$  hydrogen bonds, which link together two independent interpenetrated frameworks.

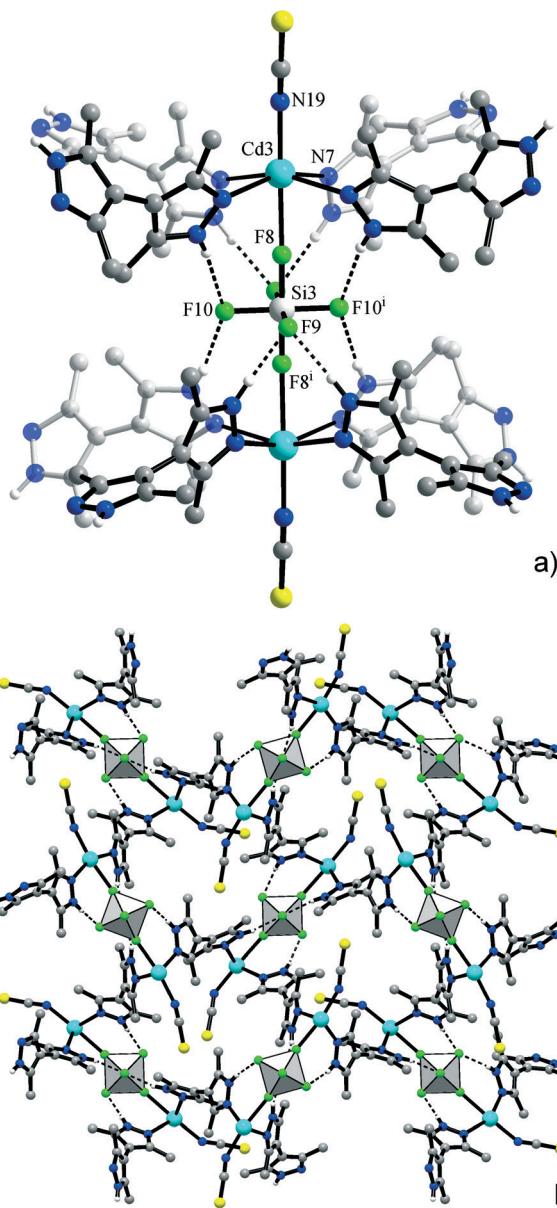
stabilization of 5-coordinated nodes is offered by extensive  $\text{NH}\cdots\text{F}$  bonding (Scheme 1). This complements formation of the coordination bonds and totals in the most efficient trapping of  $\text{SiF}_6^{2-}$  octahedra between pairs of parallel  $\text{Cd}(\text{Me}_4\text{bpz})_4^{2+}$  fragments. All eight NH-donors are positioned towards  $\text{SiF}_6^{2-}$  and establish short and directional bonds (Table 3). The mode of such bonding is variable: in **2**, the equatorial fluorides uniformly accept two bonds from both  $\text{Cd}(\text{Me}_4\text{bpz})_4^{2+}$  fragments (Fig. 2), while **3** exhibits a slightly different environment involving double  $\text{NH}\cdots\text{F}$  bonding with *cis*-positioned pyrazoles (Fig. 3). Supramolecular isomerism of the hydrogen bonding patterns adopted by pyrazole and anionic co-ligands is known also for simpler

**Table 3** Geometry of  $\text{SiF}_6^{2-}$ /pyrazole hydrogen bonding in **2–5**<sup>a</sup>

|   | Number | Bond                      | $\text{H}\cdots\text{F}/\text{\AA}$ | $\text{N}\cdots\text{F}/\text{\AA}$ | $\angle\text{NH}\cdots\text{F}/^\circ$ |
|---|--------|---------------------------|-------------------------------------|-------------------------------------|--|
| 2 | 8      | N2–H2…F3 <sup>iii</sup>   | 2.29                                | 3.083(4)                            | 152                                    |
|   |        | N4–H4…F2 <sup>iv</sup>    | 2.29                                | 3.056(5)                            | 147                                    |
|   |        | N6–H6…F2                  | 2.13                                | 2.974(4)                            | 165                                    |
|   |        | N8–H8…F3 <sup>v</sup>     | 2.14                                | 2.973(5)                            | 161                                    |
| 3 | Si1: 8 | N2–H2…F3 <sup>iii</sup>   | 2.01                                | 2.873(7)                            | 170                                    |
|   |        | N12–H12…F2 <sup>v</sup>   | 2.08                                | 2.926(6)                            | 163                                    |
|   | Si2: 8 | N4–H4…F7                  | 2.07                                | 2.928(5)                            | 168                                    |
|   |        | N6–H6…F5                  | 2.17                                | 3.025(6)                            | 169                                    |
|   |        | N10–H10…F6 <sup>iv</sup>  | 2.12                                | 2.909(7)                            | 150                                    |
|   |        | N14–H14…F6                | 2.07                                | 2.914(7)                            | 163                                    |
|   | Si3: 8 | N8–F8…F9                  | 1.99                                | 2.863(7)                            | 177                                    |
|   |        | N16–H16…F10 <sup>vi</sup> | 2.11                                | 2.947(5)                            | 163                                    |
| 4 | 4      | N2–H2…F2                  | 1.96                                | 2.800(4)                            | 162                                    |
|   |        | N4–H2…F3 <sup>v</sup>     | 1.99                                | 2.857(4)                            | 172                                    |
| 5 | 4      | N2–H2…F3 <sup>iv</sup>    | 2.13                                | 2.9632(18)                          | 160                                    |
|   |        | N4–H2…F2 <sup>v</sup>     | 1.89                                | 2.732(2)                            | 162                                    |

<sup>a</sup> Symmetry codes for **2**: (iii)  $-x, -y, 1 - z$ ; (iv)  $-0.5 - x, -y, -0.5 + z$ ; (v)  $0.5 + x, 0.5 - y, 1 - z$ ; for **3**: (iii)  $1 - x, 1 - y, z$ ; (iv)  $1 - x, 2 - y, z$ ; (v)  $y, 1 - x, 0.5 - z$ ; (vi)  $1 - y, 1 + x, -0.5 + z$ ; for **4**: (v)  $0.5 - x, 0.5 + y, 1.5 - z$ ; for **5**: (iv)  $-x, 1 - y, -z$ ; (v)  $0.5 - x, 1.5 - y, 0.5 - z$ .

**Fig. 2** Hexafluorosilicate link between the adjacent  $[\text{Cd}(\text{Me}_4\text{bpz})_2]_n$  layers, as it occurs in **2**. Note the perfectly complementary donor and acceptor functionalities resulting in an eight-fold  $\text{NH}\cdots\text{F}$  bonding.



**Fig. 3** (a) Hydrogen bonding pattern adopted by  $\text{SiF}_6^{2-}$  anion in **3**, with double  $\text{NH}\cdots\text{F}$  bonds to *cis*-pyrazole groups; (b) fragment of framework in **3** showing  $\text{SiF}_6^{2-}$  links embedded into the metal-organic net.

molecular species, for example  $[\text{Ni}(\text{Hpz})_4\{\text{CH}_3\text{CO}_2\}_2]$  and  $[\text{Ni}(\text{Hpz})_4\{\text{CH}_3\text{CO}_2\}_2]\cdot\text{H}_2\text{O}$  ( $\text{Hpz}$  is pyrazole).<sup>18</sup>

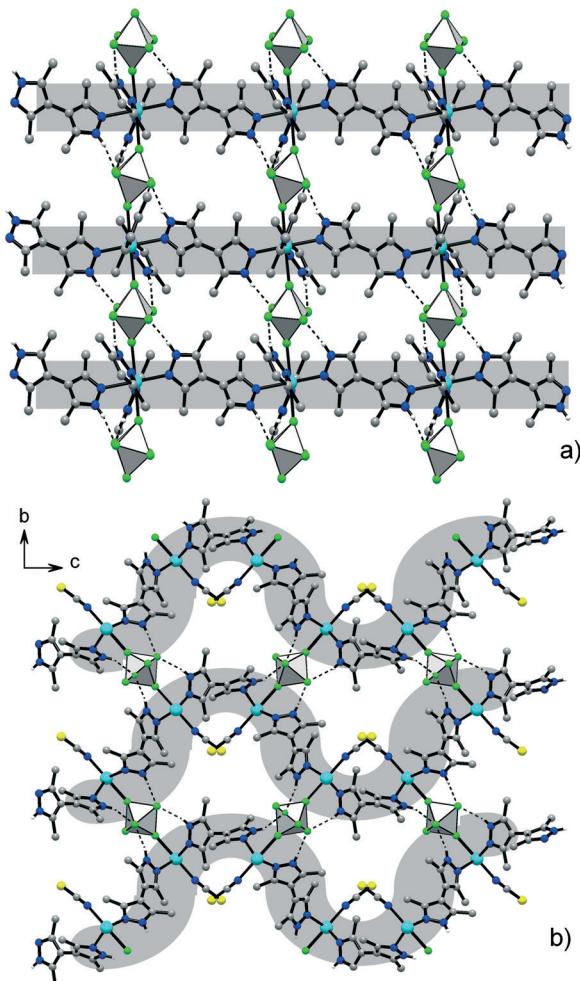
Interestingly, the  $[\{\text{Cd}(\text{Me}_4\text{bpz})_2\}_2\{\mu\text{-SiF}_6\}\{\text{NCS}\}_2]$  synthon strictly dominates a close parallel alignment of the  $\text{Cd}(\text{Me}_4\text{bpz})_2^{2+}$  planes with  $\text{Cd}\cdots\text{Cd} = 8.16\text{--}8.35 \text{ \AA}$  (which is inaccessible for the parent four-connected  $\text{NbO}$ -like net seen in **1**) and therefore the introducing of a fifth topological link requires reorganization of the  $[\text{Cd}(\text{Me}_4\text{bpz})_2^{2+}]$  subtopology itself. Such  $\text{SiF}_6^{2-}$ -promoted isomerization could be particularly facile for the  $\text{Me}_4\text{bpz}$  structures, since the twisted conformation of the tecton predetermines angular orientation of two  $\text{M-N}$  vectors.<sup>9e,12a</sup> The latter excludes limitations imposed by the octahedral coordination geometry of the metal ions and therefore many peculiar topological archetypes (**kgm**, **lvt**, **pts**) are possible for  $\text{Me}_4\text{bpz}$  systems (Table 4), unlike the common rod-like connectors (*cf.* 4,4'-bipyridine).<sup>19</sup>

In **2**, the metal-organic linkage exists in the form of corrugated square grid layers ( $4^4$ ), which are cross-linked by  $\mu\text{-SiF}_6$  (Fig. 4) giving rise a rarely encountered uninodal 5-coordinated net with a point Schläfli symbol  $\{4^4.6^6\}$  (three-letter notation **noz**).<sup>9f,20</sup> At the same time, four-connected  $[\text{Cd}(\text{Me}_4\text{bpz})_2^{2+}]$  linkage in **3** exhibits binodal 3D cooperite topology ( $\{4^2.8^4\}$ , three-letter notation **pts**), which is new for  $[\text{M}(\text{Me}_4\text{bpz})_2^{2+}]_n$  species further expanding a number of observed supramolecular isomers (Fig. 3). The inorganic anions are embedded into the framework providing additional links between the nodes and generation of a new binodal 5,5-coordinated net with a point symbol  $\{4^2.5^5.6^2.7\}\{4^2.5^6.6^2\}$  (Table 5).

A further step for increase of the framework connectivity, up to six, is best illustrated by  $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}]\cdot n\text{Solv}$  (**4**:  $\text{Solv} = \text{H}_2\text{O}$ ,  $n = 6$ ; **5**:  $\text{Solv} = \text{CH}_2\text{Cl}_2$ ,  $n = 1.5$ ), adopting very similar 3D framework structures in the form of six-connected primitive cubic nets, **pcu** ( $\alpha\text{-Po}$ ) (Table 5). The latter are constituted by the above 2D square grid  $[\text{Cd}(\text{Me}_4\text{bpz})_2]_n$  subtopologies, which are cross-linked in a third direction by  $\text{SiF}_6^{2-}$  "pillars" ( $\text{Cd-F} = 2.32\text{--}2.34 \text{ \AA}$ , Table 2). Such morphology is identical to the  $[\text{M}(bipy)_2\{\text{SiF}_6\}]$  ( $\text{M} = \text{Zn}, \text{Cu}$ ) prototype.<sup>3</sup> The 1D inorganic chains of  $[\text{Cd}\{\text{SiF}_6\}]_n$  effectively accommodate pyrazole groups by a concerted action of coordination and

**Table 4** Library of four-connected nets adopted by  $[\text{M}(\text{Me}_4\text{bpz})_2^{2+}]_n$  ( $\text{M}^{2+}$  = octahedral metal ion)

| D  | Type       | Symbol        | Occurrence   | Morphology  | Ref.      |
|----|------------|---------------|--|---|-----------|
| 2D | <b>sql</b> | $\{4^4\}$     | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NO}_3\}_2]$  | Flat neutral network  | 9d        |
|    |            |               | $[\text{Cu}(\text{Me}_4\text{bpz})_2(\text{H}_2\text{O})][\text{BF}_4]_2\cdot 0.5\text{PhBr}$  | Corrugated cationic network   | 9d        |
|    |            |               | $[\text{M}_2(\text{Me}_4\text{bpz})_4\{\text{SO}_4\}_2(\text{H}_2\text{O})_2]\text{X}_2\cdot \text{H}_2\text{O}$ ,<br>$[\text{M}_2(\text{Me}_4\text{bpz})_2\{\text{SO}_4\}_2\{\text{NCS}\}_2]\cdot n\text{Solv}$ | 3D: $\{\text{SO}_4\}$ -linked flat networks ( $\text{M} = \text{Co}, \text{Ni}; \text{X} = \text{NO}_3, \text{ClO}_4$ ) | 9f        |
|    |            |               | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot 6\text{CHCl}_3$   | 3D: $\{\text{SO}_4\}$ -linked corrugated networks ( $\text{Solv} = \text{CHCl}_3, \text{MeOH}$ )                        | 9f        |
|    |            |               | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}]_n$   | 3D: $\{\text{SiF}_6\}$ -linked corrugated network   | This work |
|    |            |               | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{SiF}_6\}]_n\text{Solv}$  | 3D: $\{\text{SiF}_6\}$ -pillared flat square networks ( $\text{Solv} = \text{H}_2\text{O}, \text{CH}_2\text{Cl}_2$ )    | This work |
| 2D | <b>kgm</b> | $\{3.6\}^2$   | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NO}_3\}_2]\cdot 2\text{CH}_3\text{OH}$   | Flat neutral Kagomé net   | 9g        |
|    |            |               | $[\text{Co}(\text{Me}_4\text{bpz})_2(2\text{-Furoate})_2]\cdot n\text{PhBr}$   | Flat neutral Kagomé net   | 21        |
|    |            |               | $[\text{Co}(\text{Me}_4\text{bpz})_2(\text{H}_2\text{O})_2]\{\text{NO}_3\}_2$  | Flat cationic Kagomé net  | 22        |
| 3D | <b>nbo</b> | $\{6^4.8^2\}$ | $[\text{M}(\text{Me}_4\text{bpz})_2\{\text{S}_2\text{O}_6\}_2]\cdot n\text{H}_2\text{O}$   | $\{\text{S}_2\text{O}_6\}$ -pillared flat Kagomé networks; ( $\text{M} = \text{Co}, \text{Zn}, \text{Cd}$ )             | 10        |
|    |            |               | $[\text{Fe}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_2\cdot \text{CH}_3\text{CN}$   | Two-fold interpenetrated frameworks   | 9c        |
| 3D | <b>lvt</b> | $\{4^2.8^4\}$ | $[\text{Cd}(\text{Me}_4\text{bpz})_2\{\text{NCS}\}_2]_2\cdot \text{CH}_3\text{OH}$   | Two-fold interpenetrated frameworks   | This work |
|    |            |               | $[\text{Co}(\text{Me}_4\text{bpz})_2\{\text{C}_6\text{H}_5\text{CO}_2\}_2]_2\cdot 2\text{C}_6\text{H}_5\text{Br}$  | 3D porous framework   | 9e        |
| 3D | <b>pts</b> | $\{4^2.8^3\}$ | $[\text{Cd}_2(\text{Me}_4\text{bpz})_4\{\text{SiF}_6\}\{\text{NCS}\}_2]\cdot 2\text{CH}_2\text{Cl}_2$  | Cooperite framework with $\{\text{SiF}_6\}$ -cross-links  | This work |



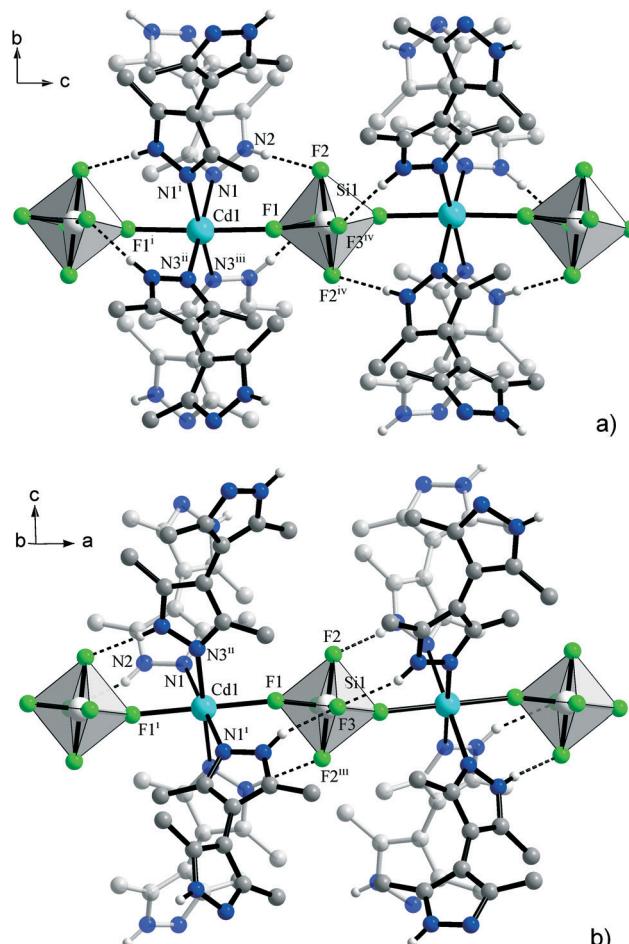
**Fig. 4** Inorganic links between  $4^4$  coordination layers  $[\text{Cd}(\text{Me}_4\text{bpz})_2]^{2+}_n$  of different shape (indicated with a grey strip): (a)  $\text{SiF}_6^{2-}$ -pillared flat networks in **4** and (b)  $\text{SiF}_6^{2-}$ -connected corrugated layers in **2**.

NH···F bonds (Fig. 5) and produce a special pattern, which is similar to 1D structures of  $\text{CuSiF}_6$  complexes with pyrazole<sup>8b</sup> and 5-phenylpyrazole.<sup>8a</sup> Thus a doubled functionality of the  $\text{Me}_4\text{bpz}$  tecton serves for the extension of this array into the 3D framework. At the same time, NH···F bonding with the octahedral  $\text{SiF}_6^{2-}$  is particularly important for the control over orientation of the adjacent coordinated pyrazole groups and

**Table 5** Topology of new MOFs **1–5** and the role of  $\text{SiF}_6^{2-}$  for the generation of additional topological links and increase of the structure dimensionality

| D                    | Topology of $[\text{Cd}(\text{Me}_4\text{bpz})_2]_n$ | Connect. of the nodes | Symbol (notation) for the entire net |
|----------------------|--|-----------------------|--------------------------------------|
| 1 3D                 | $\{6^4.8^2\}$ (nbo)                                  | 4                     | $\{6^4.8^2\}$ (nbo)                  |
| 2 2D→3D <sup>a</sup> | $\{4^4\}$ (sql)                                      | $4 \rightarrow 5^b$   | $\{4^4.6^6\}$ (noz)                  |
| 3 3D                 | $\{4^2.8^4\}$ (pts)                                  | $4 \rightarrow 5$     | $\{4^2.5^2.6^2.7\}\{4^2.5^6.6^2\}^c$ |
| 4 2D→3D              | $\{4^4\}$ (sql)                                      | $4 \rightarrow 6$     | $\{4^{12}.6^3\}$ (peu)               |
| 5 2D→3D              | $\{4^4\}$ (sql)                                      | $4 \rightarrow 6$     | $\{4^{12}.6^3\}$ (peu)               |

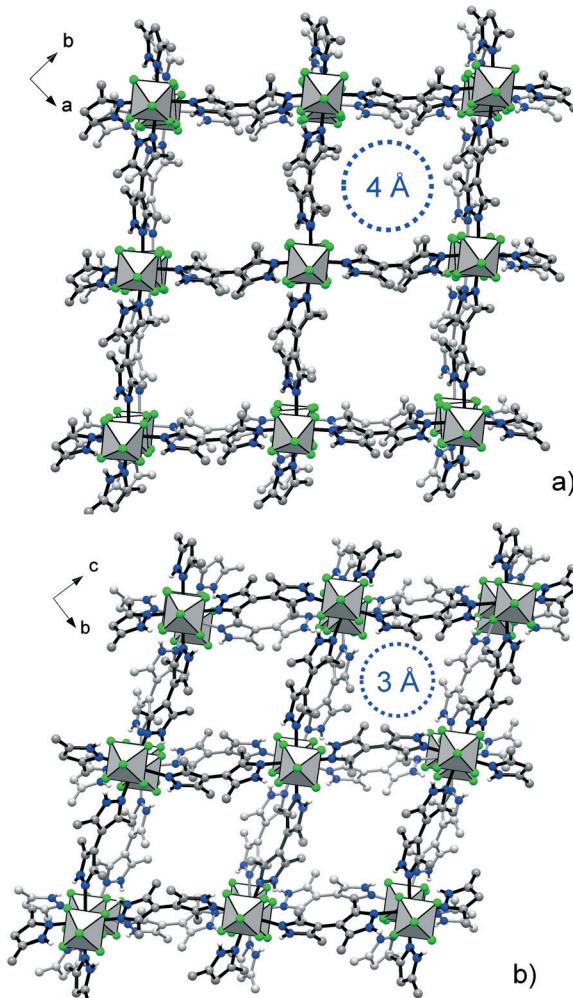
<sup>a</sup> Dimensionality of the  $[\text{Cd}(\text{Me}_4\text{bpz})_2]_n$  subtopology and the entire dimensionality of the  $\text{SiF}_6^{2-}$ -linked framework. <sup>b</sup> Connectedness for the  $[\text{Cd}(\text{Me}_4\text{bpz})_2]_n$  subtopology and for the entire framework. <sup>c</sup> New and as yet unnamed topology.



**Fig. 5** Function of  $\text{SiF}_6^{2-}$  anions as inorganic links between the coordination layers in **4** (a) and **5** (b). Note the mode of the  $\text{NH}\cdots\text{F}$  bonding, which is individual in each case.

generation of flat  $4^4$  subtopologies. This may be compared with a series of  $\text{S}_2\text{O}_6^{2-}$  pillared frameworks  $[\text{M}(\text{Me}_4\text{bpz})_2 \{\text{S}_2\text{O}_6\}] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Co}$ ),<sup>10</sup> based upon flat Kagomé layers. Facile interconversion of **kgm** and **sql** layers is a special feature of  $[\text{M}(\text{Me}_4\text{bpz})_2]^{2+}$  systems exhibiting supramolecular isomerism within two dimensions.<sup>9g</sup>

It is worth noting that *trans*-bridging  $\text{SiF}_6^{2-}$  groups uniformly accept pairs of  $\text{NH}\cdots\text{F}$  bonds from each of the successive layers (Table 3), in effect maximizing the interlayer interactions ( $\text{Cd}\cdots\text{Cd} = 7.95 \text{ \AA}$ ). However, the mode of such H-bonding is variable, similarly to the above five-connected structures: in **4**, four equatorial F atoms are functionally equivalent and each of them accepts a single strong  $\text{NH}\cdots\text{F}$  bond ( $\text{N}\cdots\text{F} = 2.800(4), 2.857(4) \text{ \AA}$ ). Structure of **5** demonstrates only two such interactions  $\text{NH}\cdots\text{F}2$  together with a double  $\text{NH}\cdots\text{F}3\cdots\text{HN}$  bridge (Fig. 5), while the fourth fluoride atom (F4) does not participate in the hydrogen bonding. Such differentiation results in a progressive elongation of equatorial Si–F bonds depending on a number of H-bonded pyrazoles ( $\text{Si}1\text{--F}4 1.647(2), \text{Si}1\text{--F}2 1.6762(13)$  and  $\text{Si}1\text{--F}3 1.693(2) \text{ \AA}$ ). Interestingly, the frameworks of **4** and **5**, being topologically equivalent, are different in view of the metrics. In the first case,



**Fig. 6** View of 3D pcu frameworks in **4** (a) and **5** (b) along *a* direction of inorganic  $[\text{Cd}(\text{SiF}_6)]_n$  chains, which demonstrates variations in the size of the channels, orientation of the organic tectons and the shape of the frameworks.

the solvent accessible area is as large as 31.1%,<sup>23</sup> while in **5** the framework is contracted leaving 27.2% space for accommodation of  $\text{CH}_2\text{Cl}_2$  guests. Moreover, orientation of the  $\text{Me}_4\text{bpz}$  linkers leads to shielding of the  $[\text{Cd}(\text{SiF}_6)]_n$  inorganic chains (Fig. 6). Such effects as well as the variable bonding modes of  $\text{SiF}_6^{2-}$  blocks suggest the possibility for fine-tuning of their steric environment and generation of accessible underbonded sites, which are relevant to selective host–guest interactions and selective sorption.<sup>4,5,7</sup>

## Conclusions

Our study suggests significant potential of pyrazole species and  $\text{SiF}_6^{2-}$  as co-ligands for the synthesis of framework coordination polymers based upon 1D  $[\text{M}(\text{pzH})_4\{\text{SiF}_6\}]_n$  and discrete cage-like  $[\{\text{M}(\text{pzH})_4\}_2\{\text{SiF}_6\}]$  supramolecular synthons, which can be anticipated for a diversity of octahedral transition metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , etc.) and polyfunctional pyrazole ligands. The cationic  $[\text{M}(\text{Me}_4\text{bpz})_2]^{2+}$  subtopology and  $\text{SiF}_6^{2-}$  linkers may be regarded as a perfectly fitted self-

complementary system, in view of either charge compensation or generation of multiple specific interactions involving coordination bonds and conventional strong hydrogen bonding. The cage-like local coordination motif of **2** and **3** is interesting also as a prototype for a selective multi-center molecular receptor of  $\text{SiF}_6^{2-}$ . Developing of protocols for selective complexation of fluorosilicates has a significance in view of their wide applications for fluoridation of potable water<sup>24</sup> and considering their hazardous properties and potential for health damage.<sup>25</sup>

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